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Glass-ceramics: Their production from wastes—A Review

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Glass-ceramics are polycrystalline materials of fine microstructure that are produced by the controlled crystallisation (devitrification) of a glass. Numerous silicate based wastes, such as coal combustion ash, slag from steel production, fly ash and filter dusts from waste incinerators, mud from metal hydrometallurgy, different types of sludge as well as glass cullet or mixtures of them have been considered for the production of glass-ceramics. Developments of glass-ceramics from waste using different processing methods are described comprehensively in this review, covering R&D work carried out worldwide in the last 40 years. Properties and applications of the different glass-ceramics produced are discussed. The review reveals that considerable knowledge and expertise has been accumulated on the process of transformation of silicate waste into useful glass-ceramic products. These glass-ceramics are attractive as building materials for usage as construction and architectural components or for other specialised technical applications requiring a combination of suitable thermo-mechanical properties. Previous attempts to commercialise glass-ceramics from waste and to scale-up production for industrial exploitation are also discussed.

1. Introduction

Glass-ceramics are fine-grained polycrystalline materials formed when glasses of suitable compositions are heat treated and thus undergo controlled crystallisation to the lower energy, crystalline state [1, 2]. It is important to emphasise a number of points in this statement on glass-ceramics. Firstly, only specific glass compositions are suitable precursors for glass-ceramics; some glasses are too stable and difficult to crystallise, such as ordinary window glass, whereas others crystallise too readily in an uncontrollable manner resulting in undesirable microstructures. Secondly, the heat treatment is critical to the attainment of an acceptable and reproducible product. As will be discussed later, a range of generic heat treatments procedures are used each of which has to be carefully developed and modified for a specific glass composition [1–3].

Usually a glass-ceramic is not fully crystalline; typically the microstructure is 50–95 vol% crystalline with the remainder being residual glass. One or more crystalline phases may form during heat treatment and as their composition is normally different from the precursor (parent) glass, it follows that the composition of the residual glass is also different to the parent glass.

The mechanical properties of glass-ceramics are superior to those of the parent glass. In addition, glass-ceramics may exhibit other distinct properties which are beneficial for particular applications, as exemplified by the extremely small coefficient of thermal expansion of certain compositions in the Li_2O-Al_2O_3-SiO_2 system which consequently are suitable for thermal shock resistant applications [2–4]. A wide range of glass-ceramics with tailored properties have been developed and several comprehensive review articles and dedicated books on their production, properties and applications, have been published [1–7].

There has been considerable research on the production of glass-ceramics from silicate waste in the last few decades. However, to the authors' knowledge, there is no previous review article on this topic. This review is intended to cover this gap in literature; it will consider the production of glass-ceramics from a variety of silicate

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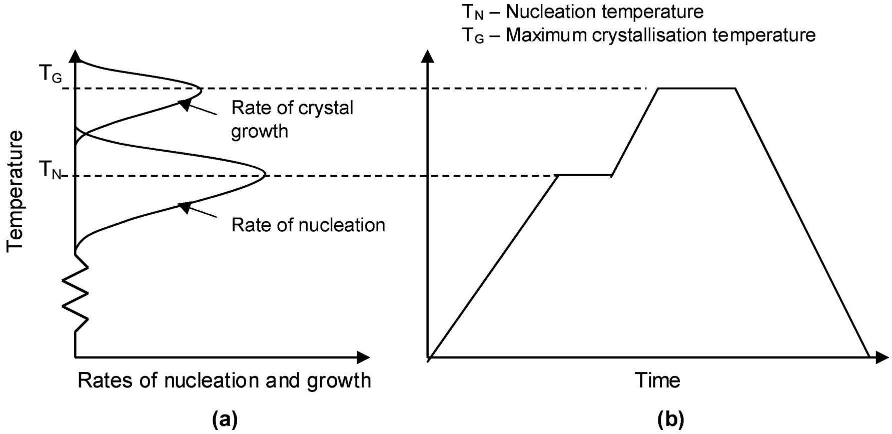

Figure 1 Crystallisation of a glass to form a glass-ceramic. (a) Temperature dependence of the nucleation and growth rates with negligible overlap and (b) two-stage heat treatment.

wastes and will include discussion of processing methods, properties achieved and potential applications of the products.

2. The glass crystallisation process

The crystallisation, or devitrification, of glass to form a glass-ceramic is a heterogeneous transformation and as such consists of two stages, namely a nucleation stage and a growth stage. In the nucleation stage small, stable volumes of the product (crystalline) phase are formed, usually at preferred sites in the parent glass. The preferred sites are interfaces within the parent glass or the free surface. The latter is usually undesirable as the resulting glass-ceramic microstructure often consists of large oriented crystals that are detrimental to mechanical properties. However, in a few instances an oriented structure is beneficial, e.g., glass-ceramics for piezoelectric and pyroelectric devices [8] and machinable glass-ceramics [9]. In most cases internal nucleation, also known as bulk nucleation, is required and the parent glass composition is chosen to contain species that enhance this form of nucleation. These species are termed nucleating agents and may be metallic (e.g., Au, Ag, Pt, and Pd) or non-metallic (e.g., TiO_2, P_2O_5 and fluorides). The rate of nucleation is very temperature dependent as illustrated in Fig. 1a.

Once a stable nucleus has been formed the crystal growth stage commences. Growth involves the movement of atoms/molecules from the glass, across the glass-crystal interface, and into the crystal. The driving force for this process is the difference in volume or chemical free energy, ΔG_v, between the glass and crystalline states. The transport of atom/molecules across the interface is thermally activated with an associated activation energy ΔG_a. Models, involving the terms ΔG_v and ΔG_a, have been developed for the temperature dependence of the growth rate and the form of the resulting curve is given in Fig. 1a. Further in-depth treatment of the glass crystallisation process can be found in the previous cited works [1, 3].

3. Processing routes for glass-ceramic production

3.1. Conventional method (two-stage)

The conventional method for producing a glass-ceramic is to devitrify a glass by a two-stage heat treatment (Fig. 1b). The first stage is a low temperature heat treatment at a temperature that gives a high nucleation rate (around T_N in Fig. 1a) thus forming a high density of nuclei throughout the interior of the glass. A high density of nuclei is important as it leads to a desirable microstructure consisting of a large number of small crystals. The second stage is a higher temperature heat treatment at around temperature T_G to produce growth of the nuclei at a reasonable rate.

The parent glass may be shaped prior to crystallisation employing any of the well-established, traditional glass shaping methods such as casting and forming [1–4] or more special methods such as extrusion [10–12]. Glass production and the subsequent heat treatments are in general energy intensive and therefore expensive.

3.2. Modified conventional method (single-stage)

The reason for the two-stage heat treatment of the glass is a consequence of the limited overlap between the nucleation and growth rate curves (Fig. 1a). If there is extensive overlap of the rate curves then nucleation and growth can take place during a single-stage heat treatment at temperature T_{NG} as indicated in Fig. 2. The rate curves, particularly the nucleation rate curve, is sensitive to composition and hence by optimising the glass composition it is, in some cases, possible to obtain the necessary overlap. By judicious choice of nucleating agents, this was first achieved for the glass-ceramic system known as "Silceram" [13], as will be discussed later.

3.3. Petrurgic method

It was found with "Silceram" that it made little difference whether the glass was heated up to T_{NG} from room

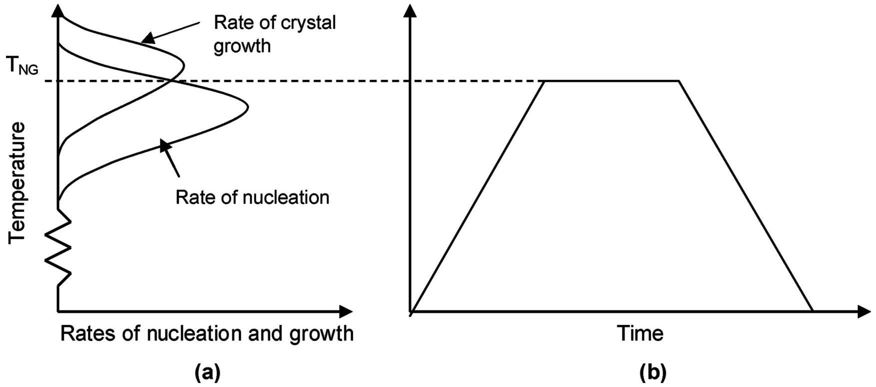

Figure 2 Crystallisation of a glass to form a glass-ceramic by a single-stage heat treatment. (a) Temperature dependence of the nucleation and growth rates with significant overlap and (b) single-stage heat treatment.

temperature or the molten glass was cooled to T_{NG} [13]. This led to the development of the production of certain glass-ceramics by a controlled, usually very slow, cooling of the parent glass from the molten state without a hold at an intermediate temperature. With this method, referred to in the recent literature as the petrurgic method [14, 15], both nucleation and crystal growth can take place during the cooling. Both the modified conventional (single-stage) and the petrurgic methods are more economical that the conventional method (two-stage).

3.4. Powder methods

The shaping by cold-compacting a powder followed by a high temperature heat treatment to sinter the compact is a common route for the fabrication of ceramics and it has been also employed for glass-ceramic production [16–20]. As there are limitations on the size and shape of components that may be cold compacted, and also a cost in producing a powder, this method is only used if an obvious benefit is identified. In most cases there is little advantage in compacting and sintering a glass-ceramic powder because a high sintering temperature is required and the properties of the final product do not differ significantly from those of glass-ceramics produced by the other routes. It is more attractive to sinter a parent glass powder, which sinters by a viscous flow mechanism at lower temperatures [21]. It is important to consider the rates of viscous flow sintering and crystallisation and the interaction of these processes. If crystallisation is too rapid the resulting high degree of crystallinity will hinder the low temperature sintering leading to an unacceptable amount of porosity [22, 23]. On the other hand, if sintering is fully completed before crystallisation, then the final product is unlikely to differ significantly from those fabricated by other methods. With appropriate rates it is possible in some cases to fabricate dense glass-ceramics by a sintering process in which both densification and crystallisation take place simultaneously at the same temperature. The technological significance of this process as well as the theoretical complexities of its kinetics have been discussed in the literature [24–26].

Optimisation of composition and sintering temperature can lead to different microstructures, and even different crystalline phases, compared to those from the conventional method, and hence different properties of the product. Pressure assisted densification methods such as hot pressing and HIPping have also been successfully applied for production of glass-ceramics from powders. Although these methods give improved products exhibiting near full densification, they are more expensive than cold pressing and sintering and thus unlikely to be employed for processing wastes into monolithic glass-ceramics.

Powder technology facilitates the production of dispersion reinforced glass-ceramic matrix composites [27]. Fabrication of these particle-reinforced composites involves intimately mixing the powdered parent glass with the reinforcement in the required proportions. The mixture is then shaped, sintered and crystallised. Hard and rigid inclusions used as reinforcement hinder the sintering process. The production of continuous fibre reinforced glass-ceramics is more complex and requires dedicated apparatus [28]. For both particulate- and fibre-reinforced glass-ceramics the densification is usually carried out by hot pressing and a final heat treatment is required to achieve crystallisation of the glass matrix.

3.5. Sol-gel precursor glass

So far only glasses produced from the molten state have been considered but in the last decades there has been considerable interest in using sol-gel and colloidal techniques to obtain the precursor glass in either powder or bulk form [29]. Thus all the methods for glass-ceramic production discussed previously may be used with glass produced by this route. However, the sol-gel method will not be discussed further in this review as it is not applicable for the production of glass-ceramics from waste materials.

4. Dense glass-ceramics from wastes

4.1. Background

It has to be accepted that there cannot be zero waste from any manufacturing, industrial or energy conversion process including power generation. It follows that for efficient use of the world's resources recycling and reuse of waste is necessary. Recycling is the selection, classification and reemployment of waste as a raw material to produce the same, or very similar product, to the parent material, e.g. the use of waste glass, known as cullet, in glass production. Reuse is the processing of waste to produce a useful product that is not similar to the material whose manufacture produced the waste. The present review is concerned with reuse of waste materials to produce glass-ceramics. The versatility of the glass-ceramic production process is manifested by the many wastes that have been used as raw materials for glass-ceramics, which include coal fly ash [30–33], mud from zinc hydrometallurgy [34–37], slag from steel production [13, 38–43], ash and slag from waste incinerators [44–57], red mud from alumina production [58], waste glass from lamp and other glass products [59] as well as electric-arc furnace dust and foundry sands [60]. Much work has been carried out on the immobilisation of nuclear waste in glass and ceramic matrices and recently there has been some interest in the use of glass-ceramic matrices for this purpose [61, 62]. However, although a waste material is involved it is not the major component of the glass-ceramic and neither is the product for recycling or reuse but just for storage of the radioactive waste. This area of glass-ceramics will therefore not be covered in this review.

To produce an appropriate parent glass for crystallisation, additions to the wastes are often required. It must be pointed out, however, that there is always a trade-off between the amount of waste recycled and the optimisation of properties of the new products. In general, since the main objective is to reutilise the waste material, the quantity of pure materials or non-waste additions introduced for improving performance must be kept as low as possible.

There is a recent good review paper on the vitrification of waste materials and production of glass-based products from wastes [63], however, unlike the present review, it is not comprehensive or detailed enough on the subject of production of glass-ceramics from wastes and their mechanical, chemical, and physical properties. A wide variety of industrial wastes have been used in the production of glass-ceramics. The differing composition and morphology of these wastes necessitate the employment of specific processing routes and conditions and result in glass-ceramics with a range of microstructures and properties. For these reasons, and for ease of reference and clarity, we have subdivided the contents of this review according to the types of waste employed.

4.2. Slag from metallurgical processes (iron and steel production)

4.2.1. Melting and subsequent heat treatment—conventional two-stage method

Blast-furnace slag was the first silicate waste to be thoroughly investigated as a source material for glass-ceramics. These slags consist of CaO, SiO_2 and MgO in decreasing amounts as the main constituents, together with minor constituents such as MnO, Fe_2O_3 and S. The first attempt to commercialise a glass-ceramic from slag was by the British Iron and Steel Research Association in the late 1960s [64]. This glass-ceramic was known as "Slagceram" and it was produced by the conventional, two-stage, heat treatment method [64, 65]. A similar material, "Slagsitall", was developed in the former Soviet Union at about the same time [66, 67]. More recent works have investigated the effect of adding nucleating agents to the slag; in particular glass-ceramics with acceptable properties were produced using a two-stage heat treatment and addition of titania [68]. It is interesting to review in more detail the effect of TiO_2 as nucleating agent in glass-ceramics from slags.

A low titania content is usually present in metallurgical slag, but Ovecoglu [68] looked at the effect of adding TiO_2 as a nucleating agent in concentration of 2, 3, and 5 wt% of the overall mixture. As in many studies thermal analysis was used to assist in the selection of heat treatment schedule. For samples with no additional TiO_2, the shallow exothermic peaks indicated that surface crystallisation was the predominant mechanism of glass-ceramic formation [68]. With extra TiO_2, the exothermic peaks were much better defined suggesting that bulk crystallisation takes over as the main mechanism. This led to grain refinement of the crystallites. A nucleation temperature of 725°C was employed and crystallisation temperatures in the range 950–1100°C investigated. At the low crystallisation temperature of 950°C, crystallisation was not complete and only small amounts of gehlenite ($Ca_2Al_2SiO_7$) and merwinite ($Ca_3Mg(SiO_4)_2$) were formed. The optimised crystallisation temperature was found to be 1100°C, and the main crystalline phase of the slag-based glass-ceramic with TiO_2 as an additive was a melilite solid solution, containing gehlenite and akermanite ($Ca_2MgSi_2O_7$). The subsequent mechanical testing results showed the effect of the crystallisation temperature and TiO_2 content. The Knoop hardness (1040 kg/mm^2), fracture toughness (5.2 $MPa{\cdot}m^{1/2}$), and bending strength (340 MPa) for the 5 wt%TiO_2 containing glass-ceramic produced by a 1100°C heat treatment were better than the values for samples with 3 wt%TiO_2 crystallised at 1100°C and with 5 wt%TiO_2 crystallised at 950°C [68]. It was also observed that as the amount of nucleating agent increases, the wear rate of the glass-ceramic material appeared to be decreasing.

Another example of TiO_2 nucleated slag-based glass-ceramics comes from the study of Gomes *et al*. [69]. A combination of steelwork slag, limestone, sand, bauxite, and ilmenite was used to produce glass-ceramics via the conventional melting followed by heat treatments. The authors did not disclose the exact quantity of each component used in the raw mixture, but the slag was claimed to be the majority component. Sand was used to increase the SiO_2 content, CaO and Al_2O_3 contents were enriched by the inclusion of limestone and bauxite, respectively and ilmenite was used to introduce TiO_2 as the nucleating agent. Through microstructural and thermal analysis, the authors selected 720 and 883°C for the nucleation temperature and the crystallisation stage respectively and claimed that this heat treatment resulted in bulk crystallisation. The main crystalline phases were diopside ($CaMgSi_2O_6$) and augite ($(Ca,Na)(Mg,Fe,Al)(Al,Si)_2O_6$), which are part of a solid solution of the pyroxene group, and these phases were homogeneously distributed in the residual glass matrix. Ferreira *et al.* [70] experimented with another type of slag, basic-oxygen-furnace (BOF) slag, and produced glasses and glass-ceramics with good physical and mechanical properties and attractive aesthetics. Glasses from mixtures of BOF slag, sand, and Na_2O in different proportion were produced by melting at 1400 to 1450°C for 1 h in Al_2O_3/ZrO_2 crucibles. The best mixture (in wt%, 60 BOF slag, 35 sand, and 5 Na_2O), i.e. with a relatively good glass-forming ability, gave the most intense exothermic peak and exhibit bulk crystallisation [70]. Samples of this composition were nucleated at 660°C followed by an isothermal crystallisation heat treatment at 775°C. It was found that augite was the main crystalline phase after 5 min but a second crystalline phase (wollastonite, $CaSiO_3$) was observed after 50 min at 775°C. The bending strength of glass-ceramic samples (~136 MPa) was higher than that of typical marble (~5 MPa) and of soda-lime glass (~50 MPa), indicating the feasibility of use as floor tiles and other building applications.

Fredericci *et al*. [71] have produced a glass from blast furnace slag and investigated its ability to crystallise upon heating via both surface and bulk crystallisation mechanisms. The internal crystallisation was only possible through the presence of Pt_3Fe, a compound formed during the melting stage of the slag through reaction with the platinum crucible. However, either Pt_3Fe is a poor nucleating agent or there was an insufficient amount present as differential scanning calorimetry (DSC) curves for glass powders of different particle sizes showed the crystallisation peaks to shift to higher temperatures with increasing particle size; this suggests that bulk crystallisation was not significant and that surface crystallisation was dominant [71].

As far as other glass-ceramic systems are concerned, El-Alaily [72] recently investigated some basic physical and chemical properties of lithium silicate glass and glass-ceramics derived from blast furnace slag with additions. The study was based around a 20 wt%Li_2O-80 wt%SiO_2 glass mixed with slag up to a concentration of 35 wt%. It is well documented that an addition of 30%Li_2O to SiO_2 reduces the liquidus temperature significantly from 1713 to 1030°C [72]. Thus El-Alaily [72] was able to melt slag-containing mixtures at 1350°C, which is 100°C or more lower than in the previously discussed systems. Heat treatment involved 1 h hold at 500°C and then another 1 h hold at 850°C to complete crystallisation. Surprisingly the hardness of the glass-ceramics was less than that of their parent glasses. This was attributed to microcracking associated with the crystals, although from the text it was not clear whether the microcracking was thought to occur at, or when cooling from, the crystallisation temperature.

4.2.2. Melting and subsequent heat-treatment—modified one-stage method

Developments at Imperial College London (UK) in the 1980s were aimed at reducing the production costs of glass-ceramics from slags by simplifying the heat treatments required for crystallisation [13, 74, 75]. The material produced was called "Silceram", which has been extensively studied and will be considered in detail in this section. The composition of the starting batch was adjusted by mixing the blast-furnace slag with up to 30 wt% colliery shale (another waste product) and small amounts of pure oxide components. A typical composition of "Silceram" parent glass (in wt%) is: SiO_2, 48.3; TiO_2, 0.6; Al_2O_3, 13.3; Cr_2O_3, 0.8; Fe_2O_3, 4.0; MnO, 0.4; MgO, 5.7; CaO, 24.7, Na_2O, 1.2; K_2O, 1.1. Of particular significance is the Cr_2O_3 and Fe_2O_3 content, as these oxides act as the nucleating agents. Either oxide alone is capable of initiating nucleation but there is a synergistic effect if they are both present. These oxides promote the formation of small crystals of spinel, which in turn act as nucleation sites for the main crystal phase, a pyroxene.

When Cr_2O_3 is used on its own, the spinel ($MgCr_2O_4$) nuclei, termed primary nuclei, are formed over a narrow, high temperature range centred at around 1350°C. The primary nuclei are also formed when Cr_2O_3 and Fe_2O_3 are both present but, in addition, secondary nuclei are created. The secondary nucleation occurs over the temperature range 850–1150°C with a maximum at 950°C as illustrated schematically in Fig. 3a. The important feature of this figure is that the growth rate curve overlaps the secondary nucleation rate curve thereby permitting successful crystallisation at a single temperature by the modified conventional method (single stage). The main crystalline phase is a pyroxene of composition close to diopside although small quantities of anorthite ($CaAl_2Si_2O_8$) are found after excessively long heat treatments [76, 77]. Depending on the exact composition and processing pa-

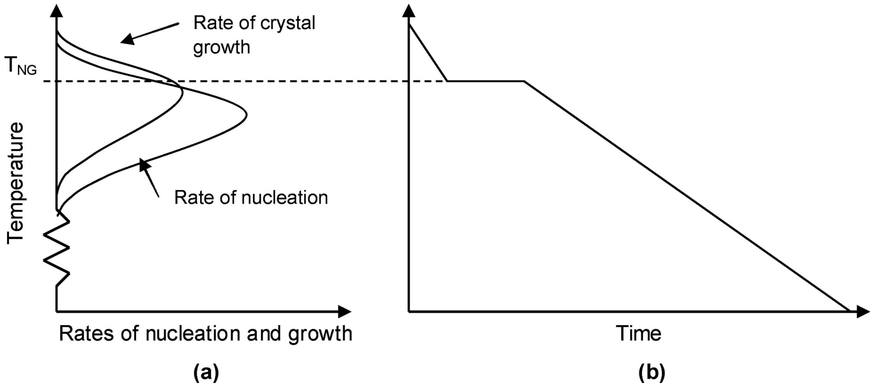

Figure 3 Production of slag-based "Silceram" glass-ceramic by direct cooling and a single-stage heat treatment (a) temperature dependence of the nucleation and growth rates with significant overlap of the secondary nuclei rate and the growth rate curves and (b) direct cooling/heat treatment.

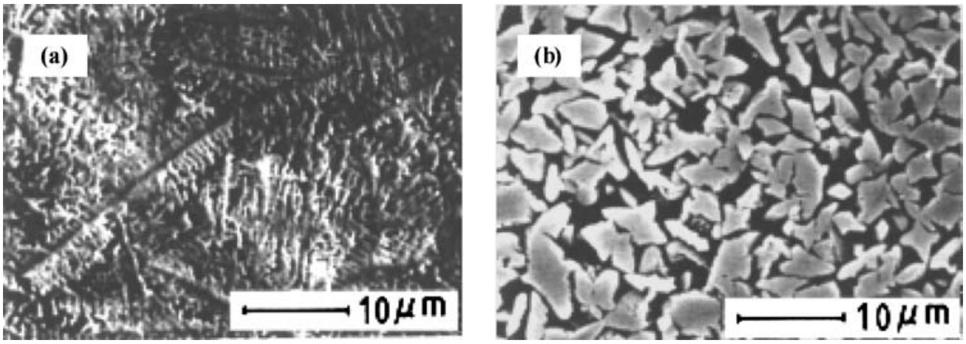

Figure 4 Microstructure of (a) pure constituents-based and (b) slag-based "Silceram" glass-ceramics [77].

rameters the crystals exhibited varying degrees of dendritic morphology, for example some "Silcerams" produced from pure constituents have a more marked dendritic structure than those of slag-based "Silceram", as depicted in Fig. 4. However, the difference in properties between slag-based and pure constituents-based "Silceram" is not significant and data from both types have been obtained, focussing on potential applications of the materials in structural applications, including thermal shock, erosion, impact and abrasion resistant components [13, 76–82].

Preliminary erosion studies demonstrated that "Silceram" had superior erosion resistance to many rival erosion resistant materials such as cast basalt, "Slagsitall" and alumina (75% purity) although inferior to the more expensive 97.5% purity alumina [79]. It was found that erosion resistance decreased with increasing diopside crystal size but that neither the volume fraction of diopside nor the presence of a second crystalline phase played a major role in determining resistance. Abrasion resistance was found to be even less microstructure sensitive as it was also crystal size independent [79]. This insensitivity to microstructure is encouraging as it means that any microstructural variations that may occur during production from wastes on an industrial scale are unlikely to affect performance.

The ballistic resistance of Silceram has been investigated at velocities up to nearly 300 m/s using a gas gun and its performance found to be comparable to that of alumina and a glass-ceramic, LZ16, developed for ballistic applications [80]. In view of these encouraging results composite armour with Silceram as the front face was tested in field trials with 5.56 mm ball rounds over a velocity range 600–1000 m/s. The critical velocity below which the armour was not defeated was 660 m/s which is only slightly inferior to the well-established alumina-Kevlar armour system. The armour system used for the field trials was not optimised and it was considered that reducing the thickness of the Silceram front face and increasing the thickness of the laminate backing would further improve the armour's performance.

Recent work on slag glass-ceramics using the single-stage heat-treatment method was reported by Francis [83]. The heat-treatment temperature range of 900–1100°C was derived from DTA data, which showed a well-defined exothermic peak at about 1010°C and another less well-defined at temperatures just around 900°C. The temperatures of these peaks were not sensitive to particle size indicating bulk crystallisation. The phases in the glass-ceramics were gehlenite, diopside and $BaAl_2Si_2O_8$; the morphology of the gehlenite and $BaAl_2Si_2O_8$ tended to be acicular or rod-like whereas the diopside was dendritic.

The erosion resistance of the glass-ceramic in slurry was reported but no data from the parent glass or other materials were presented for comparison purposes. The glass-ceramic showed good chemical resistance in a 10% NaOH solution but not in 10% HCl solution [83].

4.2.3. Petrurgic method

Fig. 3a indicates that rather than reheating the parent glass to 950°C it would be feasible to cool it (after shaping) from a high temperature to the heat treatment temperature. This heating schedule is given in Fig. 3b and this particular method has been analysed for production of "Silceram" [74]. It has been estimated that controlled cooling with a hold at 950°C would result in an energy saving of about 60% when compared to the conventional two-stage heat treatment. Significant additional energy savings could also be made if the production plant was situated at a steel works so that hot slag was used as a raw material [75].

4.2.4. Powder technology and sintering

Although it has been established that bulk nucleation may be achieved in parent glasses with a slag component, studies have also been carried out on fabrication of glass-ceramics by the powder route in which surface nucleation usually plays a more important role [81, 82]. For example, the micrograph of Fig. 5 shows a continuous crystalline layer that was nucleated at the particle surface and also individual crystals in the interior that were bulk nucleated in "Silceram" material [81]. Both cold compacting followed by a single sintering/crystallisation treatment and hot pressing without a post pressing crystallisation treatment have been employed in the case of Silceram glass-ceramics [13, 81]. The main crystalline phase was diopside, as found in the glass-ceramics produced by conventional methods, but there was also a marked increase in the propensity for the formation of anorthite.

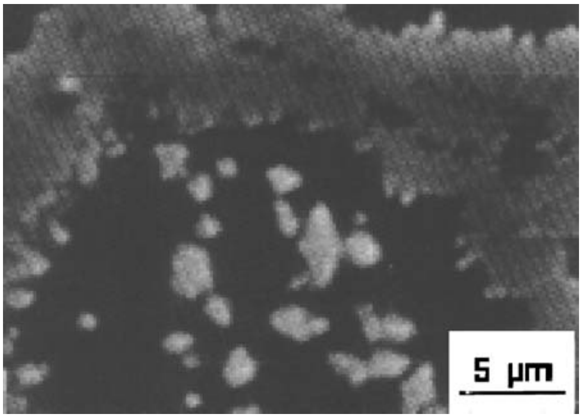

Figure 5 Scanning electron microscopy (SEM) micrograph showing surface and bulk crystallisation in sintered "Silceram" glass-ceramic [81].

There are a few recent studies that involved using the sintering route to produce slag-based glass-ceramics. Cimdins *et al*. [84] used mixtures of metallurgical slag as the main component, peat ash and clay as sources of silica and other glass formers. The addition of clay lowered the sintering temperature while maintaining the final density of the glass-ceramic at about 3 g/cm^3. The appropriate sintering temperature was found to be around 1100 to 1180°C, depending on the starting composition. The best properties were obtained from a specimen with high contents of SiO_2 (60.6 wt%) and Al_2O_3 (17.9 wt%) produced from 15 wt% peat ash; 55 wt% metallurgical slag and 30 wt% clay mixture. The bending strength achieved was 96 MPa, and the material also exhibited the least shrinkage during sintering. The chemical durability of this glass-ceramic in 0.1 N HCl solution was superior to the one without clay. Dana *et al*. [85] sintered two combinations of clay, feldspar, and a limited amount of slag (20 and 30 wt%) from steel plants to produce ceramic floor tiles with superior mechanical properties and similar thermal expansion coefficients to those of commercial products. Compacts were subjected to a single stage firing at a temperature between 1060 and 1180°C for 30 min with the denser samples being obtained at the higher end of this temperature range. Sintering at 1180°C produced the highest Young's modulus and best resistance to water absorption, similar to that specified for commercial floor tiles, whereas an 1160°C treatment resulted in a slightly better flexural strength. In general, the mechanical properties become poorer when the content of slag increases, suggesting there is a trade-off between cost and strength when the more expensive feldspar is replaced by the slag.

As mentioned earlier, hot-pressing may be used to fabricate dense glass-ceramics from slags. In general, the mechanical properties of hot pressed glass-ceramic are superior to the properties of the materials manufactured by the conventional methods and cold compacting, as shown in Table I for "Silceram" materials. However, the main benefit of research on hot-press glass-ceramics is that it provides the prerequisite knowledge for the fabrication of glass-ceramic matrix composites [28].

TABLE I Comparison of the mechanical properties of "Silceram" glass-ceramics produced by various methods (HP and CP are hot pressed and cold pressed and heat treated respectively)

Method	K_{1C} (MPa·m$^{-1/2}$)	Bend strength (MPa)
Modified conventional	2.1	174
HP (940°C, 90 min)	3.0	186
HP (900°C, 120 min)	2.2	262
CP	1.4	90

4.2.5. Slag-based glass-ceramic matrix composites

Fibre-reinforced and particle-reinforced composites where the matrix is a "Silceram" glass-ceramic have been investigated with the emphasis on the latter in order to minimise the cost of materials [86–88]. Particulate reinforcement was found to increase strength but to have a negligible effect on toughness. The thermal shock and erosion resistance of different "Silceram" matrix composites have been also investigated [87–89]. The coefficient of thermal expansion of "Silceram" is too high (7.5×10^{-6} K^{-1}) and the thermal conductivity too low (1.76W m^{-1} K^{-1}) for it to be considered as thermal shock resistant material. Nevertheless during fabrication and service materials may be subjected to rapid temperature changes and hence the thermal shock performance has to be considered. The standard method for determining thermal shock resistance is to hold samples at a known elevated temperature, quench rapidly into water and then to measure the residual strength. Data acquired this way, shown in Fig. 6, demonstrate that the fall in residual strength of the composite occurs over a temperature range that is almost 100°C higher than that for the monolithic glass-ceramic manufactured by the modified one-stage method [87].

"Silceram" was developed as a wear and erosion resistant material and these properties are well documented as discussed above [79, 81]. It was of interest to determine whether particulate-reinforcement affected the erosion resistance. Three sizes of TiC particles were incorporated into "Silceram" to varying volume fractions in the range 0.1 to 0.3 and the erosion resistance compared with that of monolithic "Silceram" prepared by an identical hot pressing route [89]. The erosion occurred by lateral crack formation and small TiC particles were not effective as they were readily removed with the glass-ceramic matrix debris. Reinforcement particles of size greater than the lateral crack depth were more effective and stood proud of the eroded surface. Irrespective of particle size of TiC inclusions, the higher the volume fraction of reinforcement, the lower the erosion rate [89].

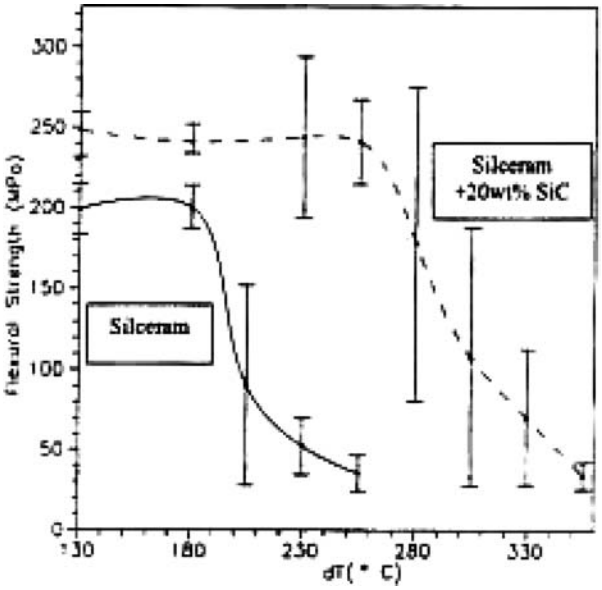

Figure 6 Residual strength data showing the superior thermal shock resistance of particulate-reinforced "Silceram" glass-ceramic in comparison to hot pressed monolithic material [87].

The only other work on slag-based composites known to authors is the recent development of alumina platelet reinforced glass-ceramics made from a combination of steel slag and fly ash of Latvian origin [90]. The authors used uniaxial pressing and pressureless sintering at 1065°C to fabricate glass-ceramic composites with densities of more than 90% of the theoretical density and with reasonable fracture strength (97 MPa) but low hardness (4.7 GPa). As found in platelet-reinforced glasses [91], the addition of 30 vol% alumina platelets provided a significant improvement of the fracture toughness (1.92 MPa·$m^{1/2}$) over that of the un-reinforced silicate matrix (0.77 MPa·$m^{1/2}$). Hence, given that the composite material possesses an acceptable combination of hardness and fracture toughness, the investigators suggested potential applications as building and construction materials as well as high-performance tiles and machine tools. Table II presents a summary of mechanical properties of glass-ceramics made from metallurgical slag, summarising the studies described in the proceeding sections and other results in the literature.

4.3. Coal ash from power stations

There are two kinds of coal ash generated from combustion of coal in thermal power stations: fly ash and bottom ash. Fly ash, which accounts for about 80% of the total ash generated, is trapped and recovered from gas flow. The remaining 20% is called bottom ash as it is collected at the bottom of the furnace. Mixtures of these wastes are sometimes stored and weathered in water ponds to give what is known as pond ash. Significant amounts of fly ash (e.g. in the order of 15 million tonnes per annum in an industrialised country such as Germany [31]) are produced continuously as a by-product of coal combustion in power stations. However, only a small percentage of the fly ash is utilised, mainly in the cement industry or in road construction [92, 93]. Glass-ceramic production is an alternative for the reuse of coal fly ash, as documented by numerous reports in the literature, which will be discussed in this section. From the study of Benavidez *et al.* [94] and others it is clear that the principal difference between fly and bottom ashes is that the former has (i) a lower residual coal carbon content (ii) a much higher proportion of spherical particles and (iii) finer particles and a narrower particle size distribution. Typical compositions

TABLE II Summary of properties of glass-ceramics and composites made from metallurgical slag by different routes

			Material properties					
Starting material	Method	Main crystalline phase	Density (g cm^{-3})	Thermal expansion coefficient ($\times 10^{6}$°C^{-1})	Bending strength (MPa)	Young's modulus (GPa)	Microhardness	Reference
Blast furnace slag + 5 wt%TiO_2	Conventional	Solid solution of melilite, i.e. gehlenite and akermanite	2.877 (as-cast glass)	9.1 [250–800°C]	340	n/r	1020 kg mm^{-2}	Ovecoglu [68]
60 wt% BOF slag + 35 wt% sand + 5 wt%Na_2O	”	Augite/wollastonite	3.3	n/r	136 ± 14	n/r	7.8±0.2 GPa	Ferreira *et al.* [70]
Blast furnace slag only	”	Melilite and larnite (Ca_2SiO_4)	n/r	n/r	69 ± 9	n/r	5.5±0.1 GPa	Fredericci *et al.* [71]
(80 wt%SiO_2 + 20 wt%Li_2O) + 20 wt% blast furnace slag	”	Lithium disilicate ($Li_2O.2SiO_2$), lithium aluminium silicate ($Li_2AlSi_3O_8$), and wollastonite	3.408	n/r	n/r	n/r	590 kg mm^{-2}	El-Alaily [72]
Silceram, iron blast-furnace slag based glass-ceramic (SCR25-76)	Conventional/Powder technology/ Sintering	Diopside	2.9	7.5	180	122	7 GPa	Carter *et al.* [77]
15 wt% peat ash + 55 wt% steel plant slag + 30 wt% clay	Powder technology/ Sintering	n/r	3.04	n/r	96	n/r	n/r	Cimdins *et al.* [84]
45 wt% clay + 35 wt% feldspar + 20 wt% metallurgical slag	Powder technology/ Sintering	Quartz and feldspar	∼2.3	7.08 [up to 1000°C]	56.6	31.2	7 (Mohs' scale)	Dana *et al.* [85]
Steel plant flyash (10–30 wt%) + peat ash (90–70 wt%) with 20 wt% Al_2O_3 platelets	Powder technology/ Sintering	Glass matrix (quartz, diopside, and augite), franklinite ($ZnFe_2O_4$) and alumina platelets[a]	2.92	n/r	97	116–120	4.7 GPa	Rozenstrauha *et al.* [90]

n/r: not reported.

[a] Glass-ceramic matrix composite.

of coal fly ash reported from different countries are given in Table III. Although there are exceptions, as a general rule, coal fly ash contains more silica but less calcia than slags.

4.3.1. Melting and subsequent heat treatment

Glass-ceramics from coal fly ash were produced using the melt quenching/heat treatment method as early as in the 1980s by DeGuire and Risbud [95]. The fly ash was melted at 1500°C without any additives and then cast into graphite moulds. An unusual two stage nucleation treatment was used: 2 h at 650 or 700°C followed by 5 or 10 h at a temperature in the range 800–950°C, prior to a crystallisation treatment at 1000 or 1150°C. It was claimed that the extent of crystallisation was not significantly affected by the different nucleation treatments prior to the crystallisation stage, hence, a single-stage nucleation heat treatment may be feasible. However, as the authors noted, the percentage crystallisation was low (less than 25%) which was attributed to the limited amount of TiO_2 present to act as a nucleating agent [95].

Cumpston *et al.* [96] used $CaCO_3$ (20 wt%) and TiO_2 additions to fly ash to achieve 40 vol% crystallinity with anorthite as the main crystalline phase. The addition of $CaCO_3$ lowered the melting temperature and the viscosity of the melt allowing a homogeneous amorphous glass to be obtained with a melting temperature 100°C less than used in the previous study [95]. The small percentage of TiO_2 added made little difference to the final degree of crystallinity and the main crystalline phase remained anorthite. However the crystal morphology and distribution must have been affected as the hardness of the TiO_2-containing glass-ceramic was higher than that of the glass-ceramic without that additive. A decrease in crystallinity was observed with increasing crystallisation temperature, and this can be explained by the fact that the heat-treatment temperature was above the maximum of the crystal growth rate curve. However, since no new crystalline phase was observed, the authors concluded that this occurrence was due to the formation of a metastable amorphous phase with increasing heat-treatment temperature. The glass-ceramic was heat treated for 48 h at 1000°C, which highlights the energy intensiveness of such a processing method. Technical applications such as high-temperature crucibles or refractory materials were suggested for this glass-ceramic [96].

Similar but more recent studies using two Turkish fly ashes (Table III) and the conventional two-stage method have been carried out by Erol and co-workers [97, 98]. The fly ash powders were melted, crushed and remelted at 1550°C without any additives or nucleating agents. Based on the DTA analysis, nucleation temperature of 680°C and crystallisation temperature of 924°C were employed for the Cayirhan ash [98] whereas the corresponding temperatures for the Seyitőmer ash were 728 and 980°C, respectively [97]. The main crystalline phase in the glass-ceramics so produced was diopside-alumina ($Ca(Mg,Al)(Si,Al)_2O_6$). An interesting feature of the investigation was the correlation found between heat treatment and microstructure, hardness and wear resistance. Surprisingly, increasing the nucleation time for the Cayirhan ash glass-ceramic, whilst holding the crystallisation time and temperature constant, led to an increase in crystal size. This in turn resulted in a decrease in hardness and wear resistance with increasing nucleation time. For the Seyitőmer ash glass-ceramics increasing the crystallisation time was found, as expected, to increase both crystal size and degree of crystallinity. As a consequence the hardness and wear resistance increased with increasing crystallisation time. The Portuguese ashes investigated by Leroy *et al.* [99] gave melts that were too viscous to pour at 1520°C and hence 10 wt%Na_2O and 10 wt%CaO (by adding pure Na_2CO_3 and $CaCO_3$) were added to the ash to lower the viscosity. Pourable melts were obtained which were successfully transformed into glass-ceramics with esseneite ($CaFeAlSiO_6$) as the main crystalline phase formed and nepheline ($NaAlSiO_4$), as secondary phase [99, 100]. The microstructures were notable for their fineness; the crystals being about 0.1 and 0.2 μm after crystallisation treatments at 800 and 870°C, respectively. The authors mentioned the pleasing aesthetic quality of the glass-ceramics, comparable to that of dark marble and malachite, and concluded that, taken together with the acceptable mechanical properties, thermal expansion coefficient and chemical stability, potential applications for these materials are related to the structural and building industries, such as kitchen and laboratory benches, and wall, roof, and floor tiles. More recently, a group of Chinese researchers [101, 102] produced interesting yet unusual glass-ceramics with nano-sized spherical crystals ($<$300 nm) from both low ($\sim$15 wt%) and high ($\sim$30 wt%) alumina containing fly ashes. The crystals were reported to be wollastonite, but the authors made no attempt to explain their fineness and morphology. The optimised glass-ceramics based on the high alumina fly ash had slightly better mechanical properties (Hv: 7.1 GPa; 4-point bending strength: 103 MPa) than those of the low alumina fly ash based glass-ceramic and the glass-ceramics reported by Ferro *et al.* [100].

Barbieri and co-workers have published a series of papers [103–105] on glass-ceramics produced from fly ash mixed with other waste materials. The other wastes were mainly float dolomite ($CaMg(CO_3)_2$) from mineral extraction operations, which was used to increase CaO and MgO content, and glass cullet to increase the amount of SiO_2, Na_2O and CaO present in the parent glass. In this way the authors were able to study the crystallisation of parent glasses of a wide range of compositions. Particularly noteworthy was their use of constitutional diagrams to predict suitable parent glasses and the phases resulting

TABLE III Typical coal fly ash compositions (wt%) from various sources

Oxides	Poland [92]	Illinois, USA [95]	Utah, USA [96]	Seyitömer, Turkey [97]	Çayırhan, Turkey [98]	Portugal [99]	China [101]	China [102]	Rete, Italy [103]*	Meirama, Spain [103]	Teruel, Spain [103]	Egypt [115]	India [117]
SiO_2	61.96	47.6	65.37	44.58	42.82	66.15	58.30	55.30	15.17	58.88	51.56	31.0	57.00
Al_2O_3	19.68	29.6	22.14	22.54	13.36	21.63	15.36	29.36	7.14	25.50	29.13	11.4	29.3
Fe_2O_3	8.52	15.8	3.61	9.85	7.01	7.20	11.58	5.84	3.76	6.58	4.78	43.5	6.5
CaO	2.55	4.2	4.66	6.76	16.38	0.36	6.84	4.58	23.71	5.64	4.21	4	3.9
MgO	2.32	0.6	1.53	8.98	5.85	0.85	0.35	0.33	1.35	1.12	1.62	1.3	1.1
Na_2O	0.65	0.5	0.62	0.22	5.06	0.40	0.15	0.46	0.90	0.28	0.26	–	0.2
TiO_2	1.01	–	0.96	–	–	0.97	1.25	1.22	0.31	1.24	1.66	2.3	0.13
K_2O	2.72	1.7	1.10	0.60	1.83	2.14	1.23	1.13	0.44	0.49	0.80	–	0.3
MnO	0.27	–	–	–	–	0.05	–	–	–	–	–	–	–
ZnO	0.06	–	–	–	–	–	–	–	–	–	–	1.4	–
P_2O_5	0.12	–	–	–	–	0.18	0.56	0.25	–	–	–	–	–
Cr_2O_3	–	–	–	–	–	–	–	–	–	–	–	0.9	–
PbO	0.05	–	–	–	–	–	–	–	–	–	–	–	–
SO_3	0.08	–	–	–	6.47	–	0.95	0.82	–	–	–	–	–
Total	99.99	100	99.99	93.53	98.78	99.93	96.57	99.29	52.78*	99.73	94.02	95.8	98.43

*Loss on ignition = 41 wt%.

from devitrification. The diagrams employed were that due to Ginsberg [106], which indicate the composition of suitable glasses for crystallisation, and those proposed by Raschin-Tschetveritkov [107] and Lebedeva [106], both of which aid in predicting the phase formed on devitrification. By judicious selection of the mixtures of wastes, and hence compositions of parent glasses, and of heat treatment schedules, Barbieri and co-workers were able to produce a series of glass-ceramics containing different phases [103–105]. For example glass-ceramics from fly ash with only glass cullet as an additive had acicular wollastonite as the crystalline phase whereas, with the further addition of dolomite, this phase was only found after heat treatment in a narrow temperature range around 1000°C and most heat treatments resulted in a microstructure with dendritic pyroxene (diopside) and a small amount of acicular feldspar (anorthite).

These reports are summarised in Table IV which presents the properties of different glass-ceramics produced from coal fly ash using the conventional method with and without additives.

Unlike fly ash, coal bottom ash has been subjected to limited number of investigations as a viable waste material for producing glass-ceramics. This is simply due to the inhomogeneous nature of bottom ash, containing much coarser particles and residues of unburnt coal, unfavourable for glass-ceramic production. Nonetheless, Kniess *et al.* [108] produced glass-ceramics in the Li_2O-Al_2O_3-SiO_2 system using the conventional method. The bottom ash used in the study was submitted to magnetic field separation with the goal of reducing the iron content as the authors had found difficulties with controlling the crystallisation of glasses with high iron content [108]. The magnetic separation reduced the amount of magnetic crystalline phases, which were mainly magnetite and hematite, from 9.96 to 5.36 wt% Fe_2O_3. After the reduction, the bottom ash was mixed with 2 wt% TiO_2 (rutile) and 5 wt% Al_2O_3. 85 wt% of this mixture and 15 wt% Li_2CO_3 was then calcined at 800°C. The addition of Li_2O to aluminosilicate glasses helped to reduce the melt viscosity and to form stable glass [109]. The calcined charge was melted and the viscosity at 1550°C was such that the flow of the melt was satisfactory and a dark glass was readily obtained. Samples of the bulk glass were heat treated at 730°C for 15 min for the nucleating stage and at 866°C for up to 20 min for the crystallisation stage. As expected the longer the crystallisation treatment the greater the degree of crystallinity but surprisingly the authors' claimed that the grain size decreased. The crystalline phases produced after the heat treatments were lithium aluminosilicate ($Li_xAl_xSi_{1-x}O_2$) and virgilite ($Li_xAl_xSi_{3-x}O_6$), as predicted from the ternary phase diagram, and resulted in low values for the coefficient of thermal expansion (-23.4×10^{-7}°C^{-1} and 2.2×10^{-7}°C^{-1} over the temperature ranges 25–325 and 25–700°C respectively). Given the low thermal expansion coefficient of this glass-ceramics based on the SiO_2-Al_2O_3-Li_2O system, the commercial application is likely to be mainly kitchen hot plates with relatively low production costs [108]. However, glass-ceramics from this system could find applications also in photolithographic processes, since the thermal expansion coefficient of the glass and of the used metal are compatible [110], and for substrates for telescopes [111].

4.3.2. *Powder technology: Monolithic material and composites*

Mixtures of coal ash and waste glass have been used in early technological approaches to the fabrication of glass-ceramics and glass matrix composites by powder technology and sintering [31, 112, 113]. However, it is only recently that fundamental studies have appeared focussing specifically on the production of sintered glass-ceramics from coal ash.

For example, powder technology and sintering have been used recently to obtain novel glass-ceramics with magnetic properties from mixtures of coal ash with high iron content and borosilicate glass [114]. Samples containing ash and glass in a 50/50 wt proportion and sintered at 1500°C for 5 h showed the best results in terms of densification, microstructure and magnetic properties. A typical microstructure of the material is shown in Fig. 7; the large dark grey grains were identified as being cristobalite, while the small bright particles were found to be enriched in metals, especially iron and titanium, and consequently were assumed to be the ferrite-type phase that was detected by XRD. It is the latter which is responsible for the soft magnetic characteristics of the glass-ceramic. The saturation magnetisation increased with sintering/crystallisation time which was attributed to a concomitant increase in the proportion of the ferrite phase. Comparison of the magnetisation saturation values for an iron-containing ferrite and the glass-ceramic (6 emu/g) indicated that about 10% of the ferrite-type phase was present in the latter, which was consistent with the microstructural observations. This work demonstrated a convenient way of dealing with high iron-content ash by transforming it into useful magnetic glass-ceramic products, via a simple and cost-effective powder technology and sintering route [114].

Francis *et al.* [115, 116] also explored the combination of coal fly ash and soda-lime glass using the powder route. In this case parent glasses were produced which were ground and then given a sintering/crystallisation treatment. The microstructural development varied with both the quantity of cullet used and the heat treatment schedule. For the particular treatment at 1000°C for 15 h, it was deduced that increasing the proportion of glass leads to a decrease in both crystalline phases of SiO_2 (i.e. quartz and cristobalite) and hematite. On the other hand, the propensity for the formation of pyroxenes (diopside

TABLE IV Properties of glass-ceramic materials made from coal ash with and without additive and using various processing methods

		Material properties					
Starting material	Main crystalline phase	Density (g cm^{-3})	Thermal expansion coefficient ($\times10^{6}$°C^{-1})	Bending strength (MPa)	Fracture toughness (MPa·m$^{-1/2}$)	Microhardness	Reference
Coal fly ash (Two-stage)	Ferroaugite [(Ca, Fe^{2+})(Al, Fe^{3+})$_2$SiO$_6$] and potassium melilite [KCaAlSi$_2$O$_7$]	2.73	5.63 ± 0.70 (100–600°C)	n/r	n/r	458.6±45.8 kg mm^{-2}	DeGuire *et al.* [95]
Coal fly ash + 20 wt%CaCO$_3$ + 1 wt%TiO$_2$ (Two-stage)	Anorthite	1.69	n/r	n/r	n/r	627.2 kg mm^{-2}	Cumpston *et al.* [96]
Coal fly ash (Two-stage)	Diopside-alumina [Ca(Mg, Al)(Si, Al)$_2$O$_6$]	3.29	7.31 (100–850°C)	n/r	n/r	2899±135 kg mm^{-2}	Erol *et al.* [97]
Coal fly ash + 10 wt%Na$_2$CO$_3$ + 10 wt%CaCO$_3$ (Single-stage)	Esseneite and nepheline	2.73	10.1 (20–400°C)	67.02 ± 13.3	1.46±0.2	7.18±0.5 GPa	Leroy *et al.* [99], Ferro *et al.* [100]
Coal fly ash +8 wt%Na$_2$O and 9.2 wt%CaO	Wollastonite	2.57–2.67	8.8–9.7	63–79	n/r	5.4–6.9	Peng *et al.* [101]
Coal fly ash +9 wt%BaO and 9.1 wt%CaO							
Coal fly ash +5.7 wt%Na$_2$O, 8.6 wt%CaO, and 5 wt%B$_2$O$_3$	Wollastonite and anorthite	2.58–2.72	8.9–9.9	48–103	n/r	5.2–7.1	Peng *et al.* [102]
Coal fly ash +6 wt%Na$_2$O and 9 wt%CaO							
40 wt% coal fly ash + 30 wt% glass cullet + 30 wt% dolomite (Single-stage)	Diopside/augite + anorthite/albite + iron spinels (magnetite Fe$_3$O$_4$, magnesioferrite MgFe$_2$O$_4$, and maghemite Fe$_2$O$_3$)	n/r	n/r	n/r	3.0	7.3 GPa	Barbieri *et al.* [103]
50wt% coal fly ash + 50wt% waste glass cullet	Pyroxene (diopside, augite and hedenbergite)	n/r	n/r	90	n/r	4.4	Boccaccini *et al.* [112]
Coal fly ash + 10wt%CaO (from ark shell) + 7wt%TiO$_2$ (Petrurgic)	Identified as (Ca$_{0\cdot05}$)AlSi$_{0.75}$P$_{0.5}$O$_{4.5}$ by EDS	2.77–2.81	5.49–6.49	98–176	1.121–3.100	91–100 GPa	Kim *et al.* [119]

n/r: not reported.

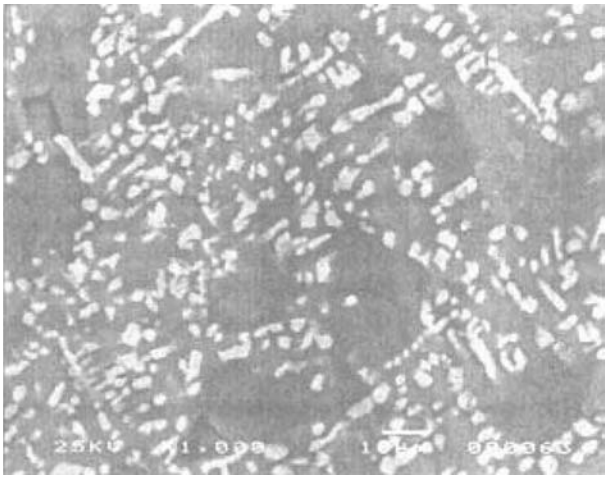

Figure 7 SEM micrograph of a sample made of a 1/1 mixture of Fe-containing coal ash and showing crystalline microstructure consisting of cristobalite (dark grains) and titanium bearing ferrite (bright phase), embedded in a glassy phase [114].

and augite) and anorthite increased with glass content. At the higher heat treatment temperature of 1050°C, due to the complete reaction of SiO_2 with other components present in the mixture, another phase ν-Fe_2O_3, known as maghemite, was detected in the sample containing 50 wt% soda-lime glass. Most work, e.g. thermal analysis to determine (i) heat treatment schedules, (ii) activation energy for crystallisation and (iii) Avrami exponent, was carried out on a parent glass containing 40 wt% coal ash as this exhibited a good combination of ease of melting, good fluidity and controllable sintering/crystallisation. For this composition pyroxene dominated at low heat treatment temperature but was displaced by plagioclase at higher temperatures (950°C). In another study where the powder route was investigated, Benavidez *et al.* [94] looked at the effect of processing parameters on the densification of mixtures of fly ash and bottom ash with the objective of making dense ceramic materials. Although in this study the authors made no attempt to produce glass-ceramics, the information on calcining and sintering is relevant. Different calcination temperatures were investigated, and the results confirmed the removal of most of residual carbon and volatiles in the ashes when calcined at 600°C for 2 h. Calcining also affected the particle size distribution with the fraction of particles in the range 75–150 μm increasing for both ashes. The final density of the sintered compacts increased with prior calcining as a consequence of the reduction in residual carbon. The highest final density was obtained using calcined fly ash only; this was attributed to the narrower particle size distribution, with more spherical particles, of the fly ash [94].

In the previous section the production of low coefficient expansion glass-ceramics with lithium aluminosilicate and virgilite phases was discussed. Low coefficient glass-ceramics have also been formed via sintering although in this case the main phase is indialite, which is a hexagonal form of cordierite ($2MgO\cdot2Al_2O_3\cdot5SiO_2$) [117]. Mixtures of fly ash, talc and alumina powder were sintered at 1370°C to produce a cordierite-based glass-ceramic with a density of 2.4 g/cm^3, Young's modulus of 100 GPa, flexural strength of 78.4MPa, and a low thermal expansion coefficient (about 1–2 × 10^{-6}/°C in the 250–650°C range).

In the studies discussed so far in this review, conventional furnaces were used, however it has been shown that coal fly ash can be immobilised into a glass-ceramic material in a much shorter time by microwave processing while improving the physical and mechanical properties compared to those achieved via conventional heating [118].

The authors are not aware of any recent literature on glass-ceramic composites produced from coal fly and bottom ashes. However there is a report on the sintering of fly ash, waste glass and alumina platelets to give an alumina-reinforced glass [112]. Rigid inclusions have a detrimental effect on sintering and in this work 20 wt% fly ash and 20 vol% alumina were found to be the maximum quantities if good sintered densities, and hence acceptable mechanical properties, were to be achieved. The same workers have also melted mixtures of coal fly ash and waste and ground the resulting glass. The glass powder was pressed and sintered with the objective of producing dense sintered glasses at low sintering temperatures rather than to form glass-ceramics [31, 113]. However certain compositions showed a tendency to crystallise indicating the potential for the formation of glass-ceramics.

4.3.3. Petrurgic method

Magnetic glass-ceramics have been obtained from mixtures of coal ash and 20–60 wt% soda-lime glass by the petrurgic method (see Section 3) [15]. The mixtures were melted at 1500°C for 5 h and then cooled in the furnace at 10°C/min or 1°C/min. At a cooling rate of 1°C/min, there was a greater propensity for the formation of plagioclase with increasing soda-lime glass content as the added glass supplied the Na and Ca required for this crystalline phase. The authors also reported that the glass-ceramics with 20 and 40 wt% glass addition had good aesthetic qualities because of their black shiny surfaces [15]. Samples that were cooled at 10°C/min had limited time of residence at temperature to crystallise fully, and therefore, there was an absence of augite and plagioclase phases. However, a dendritic magnetite crystalline phase was formed instead, as shown in Fig. 8, conferring to the glass-ceramic material interesting magnetic properties.

Kim *et al.* [119] recently published their work on a coal fly ash based glass-ceramic produced via an economic single-stage heat treatment method. This method has the same principle as the "Silceram" method described

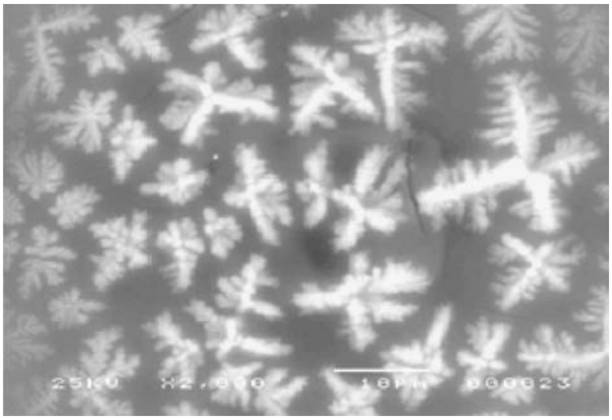

Figure 8 Dendritic microstructure of magnetic glass-ceramic produced using the petrurgic method from Fe-containing coal ash [15].

in Section 4.2.2. Ark shell was added to the coal ash as a source of CaO to reduce the melting temperature of the overall mixture, and TiO_2 was used as the nucleating agent. The molten mixture was cast into a preheated (750°C) mould before being transferred to a furnace for crystallisation. The interruption during cooling makes this process slightly different from the described petrurgic method. The glasses crystallised successfully to produce a new phase, $(Ca_{0.05})AlSi_{0.75}P_{0.5}O_{4.5}$, which has a monoclinic crystal structure. This phase has a rod-like morphology of which the aspect ratio increased with crystallisation time and temperature up to 1000°C. Promising mechanical properties were obtained from this coal fly ash based glass-ceramic, particularly the maximum fracture toughness value of 3.1 $MPa{\cdot}m^{1/2}$ which is associated with the presence of high aspect ratio crystals (Table IV).

4.4. Residues from urban incinerators

A major and growing problem is the disposal of the large quantity of domiciliary solid waste (DSW) being generated, especially in large cities in developed countries. It is feasible to recycle about 50% of DSW which leaves the issue of the disposal of the remaining 50%. The growing option for the disposal of the non-recyclable fraction is incineration with energy recovery [120]. Unfortunately the incineration process itself also results in waste. About 10 to 25 wt% of DSW remain as solid residues, such as bottom ash, electrofilter fly ash and slag, after incineration [120, 121]. The magnitude of the problem is illustrated by the following facts: (a) a single large European urban incinerator may produce fly ash at the rate of 10,000 to 60,000 tonnes per year [122] and (b) the estimated total incinerator fly ash rate for a country like Taiwan for 2003 was 2,000,000 tonnes per year [123]. Filter ashes (fly ash), collected in the air pollution control systems of incinerators, are particularly problematic because they contain significant concentrations of undesirable elements and heavy metals (e.g. As, Pb, Sb, Sn, Sr) as well as trace amounts of organic pollutants (e.g. polychlordibenzo-dioxins and -furanes). Due to increasingly stringent environmental regulations, these residues are regarded as hazardous in most countries [124–126].

Thermal treatment of problematic wastes by vitrification has been well-documented regarding its effectiveness in immobilising the toxic contents in inert glass-matrices [127]. Vitrification technologies used around the world for treatment of incinerator residues vary from the conventional electric furnaces to the more recent plasma arc technology [127–136]. The end product in all cases is a glassy slag, which encapsulates the toxic elements and heavy metal residues present in the incinerated ash. Often the vitrified product has adequate and satisfactory technical properties to compete against conventional materials for some building applications. However, an end-product with better physical, mechanical, and, perhaps, aesthetic properties may be needed to overcome the perception of it being inferior because of the waste origin. Hence, investigations are being carried out aiming at producing glass-ceramic materials with superior properties to glassy slag from incinerator wastes. In particular, the feasibility of developing novel glass-ceramics from incinerator fly ash has been an active area of research over the last few years, with first developments reported in Germany in 1994 [44, 46]. Table V gives some typical compositions of electrofilter fly ash used to fabricate glass-ceramics, and a summary of systems investigated is given in Table VI. It is important to note that concurrent with the studies into producing glass-ceramics to reuse incinerator wastes, other ceramic-based end applications have been under investigation with reasonable success, for example, fabrication of construction bricks [137, 138] and porcelainised stoneware tiles [139, 140].

TABLE V Typical electrofilter ash compositions from incinerators in different countries (wt%)

	BKS germany [46]	Tyseley UK [122]	RRRB Spain [141]	CUCC Taiwan [123]
CaO	21.1	23.4	29.34	19.19
SiO_2	38.0	27.1	11.47	18.18
Al_2O_3	17.5	11.1	5.75	9.34
MgO	2.4	2.0	3.02	2.74
Na_2O	3.5	2.8	8.70	8.51
K_2O	1.8	3.1	7.02	7.36
P_2O_5	1.6	1.5	1.69	NR
TiO_2	1.7	2.3	0.85	1.87
ZnO	3.5	1.6	NR	3.25
LOl	NR	8.8	9.2	NR
Total	99.1	86.1	78.3	72.3

LOI: loss on ignition.
NR: not reported.

TABLE VI Typical physical and mechanical properties of glass-ceramics made from municipal incinerator residues (n/r not reported)

		Material properties						
Starting material (processing route)	Main crystalline phase	Density (g cm^{-3})	Thermal expansion coefficient ($\times 10^{6}$°C^{-1})	Bending strength (MPa)	Compressive strength (MPa)	Young's modulus (GPa)	Hardness (GPa)	Reference
100% vitrified filter dust from waste incinerators (two-stage)	Diopside	2.89	6.5 (20–700°C)	n/r	n/r	124	7.9	Boccaccini *et al.* [44, 46]
Vitrified glass of incinerator fly ash (two-stage)	Akermanite	3.02±0.01	8.7±0.5	n/r	n/r	115.2±0.5	6.6±0.2	Romero *et al.* [122]
65 wt% incinerator fly ash + 35 wt% glass cullet (two-stage)	Clinoestatite and Akermanite	2.95	9	n/r	n/r	134.4	5.9	Romero *et al.* [141]
Vitrified mixture of 75 wt% MSW incinerator fly ash + 20 wt%SiO_2, 5 wt%MgO, and 2 wt%TiO_2 (two-stage)	Diopside	2.78	8.95	127	n/r	n/r	6.73	Park *et al.* [142]
10 wt% steel dust + 90 wt% incinerator fly ash (single-stage)	Augite, Akermanite, Donathite	3.2	n/r	25.2	1.2 GPa	n/r	8.5	Cheng [144]
100% vitrified incinerator fly ash (powder route)	Gehlenite	2.07	8.61 (25–450°C)	22.57	56.29	n/r	n/r	Cheng *et al.* [123]
100% vitrified incinerator fly ash (single-stage)	Gehlenite	2.7–2.8	n/r	47-50	150	n/r	8–9	Cheng *et al.* [143]
(powder route)		2.5		40–42	80–85		2–3	
Vitrified glass frits containing 60 parts of incinerator fly ash, 25 parts of glass cullet, 25 parts of quartz, and 4 parts of H_3BO_3 (powder route, Small/Intermediate/Large particle size range)	Ferrobustamite	2.61/2.65/2.65	6.81/7.9/8.81	69/58/48	220/300/360	85/84/85.5	5.57/5.88/5.67	Karamanov *et al.* [147]
Bottom ash − Bergamo, Italy + waste from kaolin ore extraction (powder route)	Feldspars (anorthite & albite), and pyroxenes (diopside & augite)	2.2	6.4 (80–280°C)	61	n/r	53	2	Appendino *et al.* [158]

4.4.1. Melting and subsequent heat treatment—conventional two-stage method

Electrofilter fly ash (or Air Pollution Control (APC) residues) from waste incinerators is a fine powder, typically with particles in the range 0.5–700 μm, with the main components being CaO (19–29 wt%), SiO_2 (11–35 wt%) and Al_2O_3 (5–19 wt%) and varying amounts of other oxides such as Fe_2O_3, TiO_2 and P_2O_5, which are capable of acting as nucleating agents. It has been established that a glass may be obtained from some fly ashes without any additions and bulk samples devitrified by a two-stage heat treatment without the necessity of the addition of further nucleating agents [46, 121]. The traditional route involves melting the as-received ash at temperatures $\geq$1400°C, quenching in air to room temperature and subsequent two-stage heat-treatment at temperatures typically in the range 550–1050°C to induce nucleation and crystal growth. The microstructure of glass-ceramics produced in this way usually consists mainly of nanosized crystals of the pyroxene group (e.g. diopside) embedded in a glassy matrix [46], as shown in Fig. 9, but Romero *et al*. [122] found akermanite to be the major phase produced using a fly ash with a higher CaO and lower SiO_2 content.

In other cases additions have been made to the waste. Park *et al*. [130, 142] mixed 20 wt% SiO_2 and 5 wt% MgO with fly ash to improve glass formation and to obtain the desired crystalline phase, diopside; 2 wt% TiO_2 was also added as the nucleating agent. The authors reported that apart from the good mechanical properties, this material also met the toxicity regulation standard after leaching-tested according to the TCLP (Toxicity Characteristic Leaching Procedure of the US Environmental Protection Agency), which is an important achievement for products made of this type of waste from an environmental and safety point of view [142].

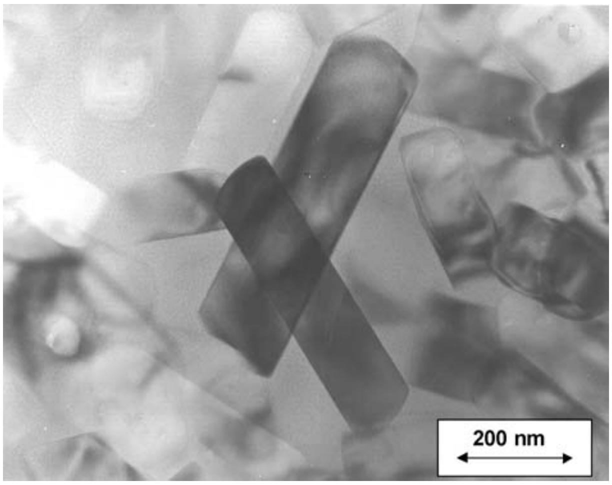

Figure 9 TEM micrograph showing the microsctructure of a diopside-containing glass-ceramic fabricated from vitrified incinerator filter ash, consisting mainly of crystals of the pyroxene group (e.g. diopside) embedded in a glassy matrix [46].

Often the waste from an incinerator is supplied as a mixture of fly ash and a residue of $Ca(OH)_2$ and calcium salts from the purification of acid gases. Glass additions are required to this waste to obtain a stable glass with acceptable flow characteristics [45, 122]. Differential thermal analysis curves from such glasses have two distinct peaks from which activations energies and Avrami exponents can be determined [45]. In the material investigated by Romero *et al*. [45], the activation energy and the exponent for the lower temperature peak were 379 kJ/mol and 1.1, respectively, and this peak was attributed to surface crystallisation. The corresponding values for the second peak, which was considered to be associated with bulk crystallisation, were 319 kJ/mol and 3.1. Values of the same order have been reported for the devitrification of glasses formed from 100% fly ash (388 kJ/mol and 1.8 [122]) and fly ash with oxide additions (499 kJ/mol and 1.09 [142]).

4.4.2. Melting and subsequent heat treatment—modified single-stage method

Cheng *et al*. have conducted single-step heat treatment of glasses obtained from vitrified incinerator fly ash [143] and of a mixture of electric arc furnace (EAF) dust and fly ash in the ratio of 1:9 [144]. The glass was moulded at 1500°C, annealed at 600°C and then heated up to crystallisation temperatures in the range 800–1100°C. Gehlenite was the major phase in the 100% fly ash based glass-ceramic whereas, as a consequence of the high iron content of the EAF addition, the iron-containing phases augite ($Ca(Fe,Mg)Si_2O_6$) and donathite ($(Fe,Mg)(Cr,Fe)_2O_4$) were the major crystalline phases together with akermanite. The presence of akermanite became more significant with increasing temperature.

4.4.3. Powder technology and sintering

Fly ash (APC residues): Glasses formed from incinerator fly ashes with a relatively low concentration of nucleating agents (see RRRB and CUCC in Table V) do not exhibit bulk nucleation but can undergo crystallisation via surface nucleation. In such circumstances the powder route is a viable production method as reported by many groups [123, 141, 145–148]. These research groups heated powder compacts of glass made from vitrified fly ash, in some cases with additions [146, 147] to temperatures in the range 800–1050°C at which both sintering and crystallisation occurred. The crystalline phases identified by Boccaccini *et al*. [148] and Romero *et al*. [141] were diopside and both monoclinic and tri-

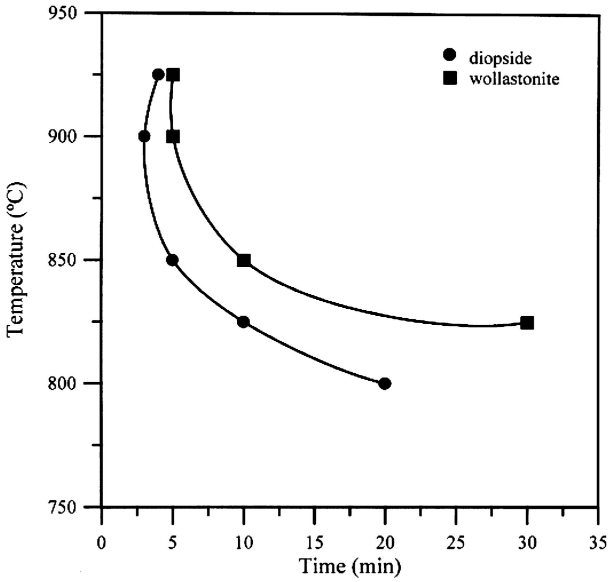

Figure 10 Time-Temperature-Transformation (TTT) diagram for diopside and wollastonite phases crystallising during the sintering of municipal incinerator fly ash compacts [141].

clinic wollastonite. The major phase in a glass-ceramic produced from a mixture of fly ash, sand and glass-cullet was ferrobustamite ($CaO_{1-x}FeO_xSiO_2$) which has a structure very similar to triclinic wollastonite [147]. In contrast, the major phase detected by Cheng *et al.* [123, 145] and Karamanov *et al.* [146] was the melilite group mineral, gehlenite. In some cases, the Time-Temperature-Transformation (TTT) diagrams for these phases were determined, an example is shown in Fig. 10 [141].

As incinerator fly ash is considered hazardous it is important that any product from the reuse of fly ash is not harmful. For this reason the chemical durability and toxicity of some fly ash based glass-ceramics have been measured. In an early attempt to increase the acceptability of the products, toxic potential of the glass-ceramics made from incinerator fly ash was assessed by cell culture tests by Boccaccini *et al.* [47]. By measuring the cell activity after contact with extracts from different samples, it was shown that the toxic potential of the glass-ceramic material was slightly higher than that of the as-quenched glass. This would indicate that the release of substances that inhibit cell activity, for example heavy metals, may have been more pronounced in crystallised samples. Assuming that most heavy metals are concentrated in the crystalline phases, as SEM/EDX analyses had revealed [145], the increase of toxicity of the glass-ceramic could be simply explained on the basis of a poorer leaching resistance of these crystalline phases in comparison to that of the parent glass matrix [47].

The gehlenite-containing glass-ceramic exhibited good corrosion resistance in various liquids with the noticeable exception of HCl, as reported in Table VII [123, 143, 144]. It was suggested that the poor chemical resistance to HCl maybe attributable to gelatinisation of the gehlenite phase [123]. It can also be seen from the data that the gehlenite-containing glass-ceramics produced by the conventional melting and subsequent heat treatment route perform slightly better than their sintered counterparts. Table VII also includes similar data from the same research group [144] for glass-ceramics produced by the conventional route and having augite, akermanite and donathite as the major crystalline phases and these data demonstrate that, with an optimised heat treatment, slightly better chemical resistance was achieved but HCl attack remained a problem. Finally it has been shown that the ferrobustamite-containing glass-ceramics have a su-

TABLE VII Chemical resistance in various liquids of a municipal incinerator fly ash based glass-ceramic as a function of sintering/heat treatment temperature

		Weight loss after 1 h (wt%)				
Methods	Chemical (20 wt%)	850°C	900°C	950°C	1000°C	1050°C
(Gehlenite) powder sintering process [123]	CH_3COOH	3.41	4.23	3.65	3.02	4.26
	HCl	15.12	11.57	11.06	10.29	11.72
	H_2SO_4	0.15	0.77	0.99	1.17	1.57
	NaOH	0.74	1.92	0.55	0.55	5.19
(Gehlenite) powder sintering process [143]	CH_3COOH	6.6	6.3	7.5	9.7	10.3
	HCl	19.0	17.1	18.3	25.9	30.9
	H_2SO_4	2.1	1.9	1.6	0.3	0.4
	NaOH	<0.1	0.6	0.8	0.2	1.1
(Gehlenite) conventional melt process [143]	CH_3COOH	6.4	5.8	4.0	4.0	6.1
	HCl	16.9	26.1	16.1	24.1	19.6
	H_2SO_4	1.4	1.4	0.5	1.1	1.3
	NaOH	0.2	<0.1	<0.1	0.1	<0.1
(Augite, Akermanite, Donathite) Conventional melt process [144]	CH_3COOH	–	3.4	–	2.7	–
	HCl	–	9.9	–	12.8	–
	H_2SO_4	–	0.5	–	0.6	–
	NaOH	–	0.1	–	0.1	–

perior chemical resistance to HCl and NaOH than marble and granite [147]. It is apparent that further microstructure and chemical analyses utilising measurement techniques of high resolution are required in order to obtain a clearer view of the relationship between crystallisation and chemical durability in these glass-ceramics. In particular, the distribution and relative concentration of the elements such as Cl and of the heavy metals in the different phases must be assessed. The potential hazardous effect of these materials should be analysed by conducting standard chemical durability tests (e.g. Soxhlet, "Swiss" [149], German DEV-S4 tests [150], TCLP of the US Environmental Protection Agency or ASTM C1285 test methods), in addition to cell toxicity tests such as those used in reference [47].

A comparison of the mechanical and physical properties of gehlenite-containing glass-ceramics produced by the conventional and sintering processing routes has been reported by Cheng *et al*. [143]. In general, the samples produced by the single-stage heat-treatment of bulk glass had less porosity and, therefore, better mechanical and physical properties than the ones prepared via powder sintering route. Moreover, the best physical and mechanical properties were obtained by heat-treatments or sintering at 900–950°C. Higher sintering and heat-treatment temperatures have led to poorer properties, possible due to the crystal growth that occurred at temperatures above 1000°C.

Bottom ash: Most studies have concentrated on using incinerator electrofilter fly ash but about an order of magnitude more quantity by weight of bottom ash is produced than fly ash in municipal waste incinerators [151]. The composition of the bottom ash is very similar to that of the fly ash, but containing a burnt-out mixture of slag, ferrous and non-ferrous metals, ceramics, glass, other non-combustibles and residual organics. Bottom ash is also more variable in morphology [e.g. 152, 153]. Moreover bottom ash does not contain heavy metals and therefore the problem of chemical durability and toxicity does not arise. Before use, bottom ash has to be oven dried and ground in order to improve homogeneity. It has been established that it is possible to manufacture glass-ceramics from bottom ash and from bottom ash mixed with other wastes, namely glass cullet and steel fly ash [151, 154–158], and this will be considered in more detail here.

Cheeseman and co-workers [155, 156] have concentrated on producing glass-ceramics from bottom ash, having quartz, calcite, gehlenite and hematite as the main crystalline phases, without the use of any additives. The bottom ash was subjected to a thorough homogenisation process involving wet ball milling, filtering, drying, grinding and finally sieving through 150 μm sieve; this process resulted in a fine homogeneous powder, suitable for cold pressing, from 6 representative samples of bottom ash collected over a 10 week period. The effect of various processing parameters including compaction pressure (4–64 MPa) and sintering temperature (1020–1120°C) were investigated. Increasing the compaction pressure increased the green density but had a minimal effect on sintered density; it therefore follows that less shrinkage was observed at the higher compaction pressures. Insufficient sintering occurred at the lowest sintering temperature and at the higher sintering temperatures porosity, attributed to decomposition of sulphates, was found. A maximum density of 2.6 g/cm^3 was obtained at the optimum sintering temperature. The main crystalline phase(s) were reported to be diopside [155] and diopside and wollastonite [156].

The sintered glass-ceramics as well as the as-received ash were subjected to the acid neutralisation capacity (ANC) test and leachate analysis [156]. The results clearly showed a significant reduction in ANC and leaching of Ca, Mg, K, Zn, Pb, Al, and Cu, at all pH but especially at alkali pH levels. The only exception was Na leaching which was only reduced at alkali pH levels. This is further support for the concept of encapsulation and incorporation of problematic (e.g. toxic) elements present in wastes into the glassy and crystalline phases of glass-ceramics.

Barbieri *et al*. [154] sintered powder mixtures made up of incinerator bottom ash and glass cullet, which were vitrified at 1500°C before milling. As well as varying ash content (10 to 100% ash) the effect of using water and polyvinyl alcohol (PVA) as binders was investigated. In all cases it was found that nucleation begins from the surface of the particles and sintering occurs ahead of crystallisation, thus powder compacts are easily sintered into dense glass-ceramics at a relatively low temperature of 850°C. However, the 100% ash based material was considered the most suitable for sintering as low ash content samples softened around 1000°C and samples containing 50% ash swelled at >950°C. This is encouraging as the aim is to reuse as much waste as possible. Furthermore it was established that there was no advantage in using expensive PVA binder to improve the handling of the pressed pellets.

Two Italian bottom ashes have been vitrified and powdered and in one case mixed with a corundum-based waste and in the other with kaolin [158]. Both powder mixtures were successfully sintered. For the former, XRD showed corundum to still be present in the final product which perhaps should therefore be considered as a glass-ceramic matrix composite. The main crystalline phases in kaolin, namely kaolinite ($Al_2Si_2O_5(OH)_4$) and zinnwaldite ($KLiFeAl(AlSi_3)O_{10}(F,OH)_2$) were not found in the glass-ceramic sintered from the kaolin containing mixture.

A comparison of incinerator bottom and fly ashes as raw materials for glass-ceramic production has been reported [157]. Both ashes were mixed with 30 wt% feldspar and glass powders produced in the normal way by melting, casting and grinding and sieving. Three particles size ranges were investigated and it was found that the densification of fly ash based material was not strongly dependent on particle size. In contrast the best densification for the bottom ash based material was obtained with a small particle size ($<45\ \mu$m) which was more expensive to produce. These differences in densification were reflected in water absorption results.

The results summarised in Table VI support the feasibility of reusing incinerator fly ash for the production, by a variety of routes, of glass-ceramics with a range of properties.

4.5. Other silicate wastes

Apart from the extensive research effort made on the three main silicate waste streams considered above, namely metallurgical slag, coal ash and municipal incinerator wastes, there is growing interest in recycling other types of silicate wastes for production of glass-ceramic materials. Table VIII presents a summary of wastes and systems investigated, and details of selected glass-ceramics produced are given in the following paragraphs.

4.5.1. Other slag-type wastes

Fabrication of glass-ceramics using slag-type wastes from non-ferrous metal production has been reported, these include copper slag [159, 160] and phosphorus slag [161]. Up to 40wt% of copper slag was incorporated into a base glass composition to produce tiles via the powder sintering method [159]. The corresponding glass-ceramic possessed the best properties after sintering at 1025°C for 1 h and phases were hematite, maghemite, and amorphous silica. The tiles have a bending strength of 57 MPa, 2 wt% water absorption, and a microhardness of $750\mathrm{VH}_{(200)}$. The material also showed excellent resistance to mineral acids. These properties make the material suitable for production of chemical resistant floor tiles.

Phosphorus slag is generated during the refining of elemental phosphorus. The refinement involves separation of elemental phosphorus from the phosphate-bearing rock in an electric arc furnace. Silica and carbon are added as flux materials to remove impurities during the slagging process. Phosphorus slag is the residual waste after the removal of the elemental phosphorus and ferrophosphorus. Murat *et al.* [161] demonstrated that devitrification of the phosphorous slag in the $CaO\text{-}SiO_2\text{-}CaF_2$ system at temperatures between 700 and 830°C led to nucleation and crystallisation of cuspidine ($3CaO\cdot2SiO_2\cdot CaF_2$) as well as α- (metastable) and β-wollastonite. The study also highlighted that it was not necessary to heat-treat the glass via the conventional two-step heat-treatment, but the adoption of a single heating step up to 1000°C was sufficient to obtain glass-ceramics with optimised mechanical strength.

4.5.2. Slag from gasification processes

IGCC (Induction Gasification Combined Cycle) slag comes from a process for obtaining electrical energy from burning coal and coke from petroleum refining. IGCC slag is produced in large quantities (typically 10^5 ton/year from a single plant), and is not related to slag obtained from other conventional thermal power plants being vitreous and of unique composition. Acosta *et al.* [162] have reported the excellent potential of such waste material to be recycled in the production of glass-ceramic. This potential results from the vitreous nature of the slag, which is economically favourable since the requirement of initial melting (vitrification) of the waste is removed and the ease of crystallisation during a controlled heat-treatment to hematite, anorthite, cristobalite and spinel in varying proportions depending on the heat treatment temperature.

4.5.3. Electric Arc Furnace dust (steel fly ash)

Electric Arc Furnace (EAF) dust (or steel fly ash) is a waste by-product of the steel-making process. About 650–700 kilotons per year of EAF dust are produced in the USA and 1 million tons per year in Europe. It was reported that the world production of furnace dust will reach about 5 million tons per year in 2005 [163]. The dust contains elements such as Pb, Cr, Zn, Cd, and Cu, whose solubility in leaching media exceeds the environmental regulatory limits in EU and USA. Hence, vitrification and subsequent heat-treatment to devitrify the glass have been investigated as a process to immobilise the hazardous elements in the waste [60, 164].

EAF dusts from two sources (carbon steel making and stainless steel making process) were mixed with glass cullet and sand in varying proportions and examined after vitrification and heat-treatment [164]. The results showed that it is important to have a high Si/O ratio to ensure stable glass network and thus impart chemical resistance to the glass. It was found that a mixture containing stainless steel EAF dust and 50 wt% glass cullet had poor chemical resistance but showed the highest tendency to crystallise and therefore the formation of a glass-ceramic from this composition was studied. The main crystalline phases were chromite-magnetite spinels and pyroxene. In commercial glass-ceramics, the stable crystal phases formed from crystallisation usually improves the chemical durability compared to their parent glasses [2, 3]. The glass-ceramic made from 50% EAF dust, however, exhibited a poorer chemical durability than its parent glass. Similar results were obtained from the carbon steel EAF dust, where a glass-ceramic was produced from 45 wt% dust, 35 wt% glass cullet, and 20 wt% sand. The poor leaching characteristics of the glass-ceramics were attributed to spinel and pyroxene phases being more prone to leaching than the parent glass coupled with no improvement in the performance of the residual glass as its SiO_2 content

TABLE VIII Summary of properties of glass-ceramics obtained from a variety of silicate wastes

Starting material	Main crystalline phase	Material properties						Reference
		Density (g cm^{-3})	Thermal expansion coefficient ($\times 10^{6}$°C^{-1})	Bending strength (MPa)	Compressive strength (MPa)	Young's modulus (GPa)	Hardness (GPa)	
Feldspar with combinations of limestone dust, Na_2CO_3, Fe_2O_3, Cr_2O_3, phosphorus slurry, alumina, metallurgy slag, and/or CaF_2	Diopside or diopside-hedenbergite solid solution	2.63–2.76	9.6–12.8	n/r	n/r	n/r	3.53–4.94	Gorokhovsky *et al*. [166]
100 wt% sewage sludge incinerated ash + 15 wt% CaO	Anorthite and wollastonite	n/r	6.7	n/r	164	n/r	n/r	Endo *et al*. [168]
100 wt% sewage sludge incinerated ash + 50 wt% limestone	Anorthite, diopside, and forsterite	3.0	6.7	n/r	n/r	n/r	6 for Mohs' hardness	Suzuki *et al*. [169]
90 wt% sewage sludge incinerated ash + 10 wt% CaO	Diopside	2.87	8.3	92	n/r	n/r	6.23	Park *et al*. [170]
37.2 wt% calcined goethite + 23.0 wt% granite + 37.8 wt% glass cullet + 2.0 wt% TiO_2	Titanomagenetite, franklinite (zinc ferrite) and diopside pyroxenes	3.104 (zero porosity, and 75% crystallinity)	7.7	n/r	n/r	145	9.5	Marabini *et al*. [174]
60 wt% goethite + 10 wt% dolomite + 30 wt% glass cullet	Magnetite and franklinite	3.41*	9.0*	n/r	n/r	171*	6.85*	Romero *et al*. [14, 175]

n/r: not reported.
*Properties of the parent glass.

had not significantly increased with respect to that of the parent glass.

4.5.4. Cement dust

In some countries where cement dust is not re-introduced back into the cement production cycle, the dust can be a serious health hazard due to its fine nature. Morsi *et al.* [165] prepared glass specimens by melting mixtures of magnesite, feldspar, quartz sand, kaolin and cement dust with dust content in the range 25–37 wt%. The glasses were subsequently heat-treated in two stages consisting of a nucleation treatment at 850°C and growth treatment at 1000 or 1100°C. The microstructures were characterised by dendritic diopside, acicular anorthite and fine crystals of microcline in proportions that depended on both crystallisation temperature and composition, e.g. with increasing SiO_2/CaO ratio the amounts of anorthite and monocline increased at the expense of diopside. Results indicate that it is possible to use up to 37 wt% cement dust in the mixture to produce glass-ceramics but unfortunately mechanical and physical properties were not reported.

4.5.5. Ore-refining quartz-feldspar waste

Gorokhovsky *et al.* [166] produced diopside-based glass ceramics based on a combination of a wide range of wastes (quartz-feldspar waste, limestone dust, phosphorus slurry, metallurgical slag) and selected commercially available chemicals, such as Cr_2O_3, as a nucleating agent. The main component of the starting mixture was quartz-feldspar waste from ore refining, which was used in the range 37.5 to 52 wt%. Various nucleating agents were used, and thus the colour of each glass-ceramic material was different. These glass-ceramics were produced using the conventional two-stage heat treatment method (720 and 950°C) after their parent glasses were made by melting at 1380–1400°C for 60–90 min. It was shown that the introduction of P_2O_5 from phosphorus slurry instead of Cr_2O_3 increased chemical resistance but decreased hardness. This was attributed to the formation of leucite and orthoclase. High hardness values were obtained when fine crystals of diopside-hedenbergite solid solutions were homogeneously dispersed in the residual glass matrix. In general, these samples had a higher Fe_2O_3 content (i.e. with addition of Fe_2O_3 or metallurgical slag), which may have led to more nucleation sites during the first stage of heat treatment, and thus achieving a very fine homogeneous microstructure.

4.5.6. Fluorescent glass waste

Yun *et al.* [167] prepared glass-ceramics from a mixture of fluorescent glass and waste shell in a weight ratio of 4:1. The starting materials were washed before mixing to remove organic residues from the shell and Hg from the cullet. The route selected was sintering of parent glass powder at temperatures of 800, 900, and 1000°C. The main crystalline phases detected from samples fired at 800 and 900°C were a mixture of β-wollastonite, gehlenite and sodium calcium silicate ($Na_2Ca_3Si_6O_{16}$) whereas at 1000°C, the glass-ceramic was highly crystallised with whisker-shaped β-wollastonite. Chemical stability of the latter in 1 N H_2SO_4 was poor.

4.5.7. Sewage sludge

Fly ash from the incineration of sewage sludge has been studied by Endo *et al.* [168], Suzuki *et al.* [169] and Park *et al.* [170] regarding the production of glass and glass-ceramics to reduce the environmental impact of such waste. Endo *et al.* [168] focused mainly on the feasibility of crystallising the glass obtained from melting of the fly ash. The work was considered successful, where the slag was crystallised into 80% anorthite with properties meeting the requirement for construction and civil works materials. Suzuki *et al.* [169] and Park *et al.* [170] added CaO (the former workers as limestone) to lower the melting point of the parent glass and to obtain anorthite or diopside as the crystalline phases. Anorthite-based glass-ceramics were produced by both research groups using a conventional two-stage heat-treatment of the molten glass. The results at only one crystallisation temperature (1100°C) were reported by Suzuki *et al.* [169] whereas Park *et al.* [170] investigated crystallisation over the temperature range 1050 to 1200°C and found that diopside dominated at lower temperature and anorthite at the higher temperature. Suzuki *et al.* [169] only obtained bulk crystallisation in a reducing atmosphere which they claimed was a consequence of nucleation in the parent glass being due to iron sulphide which oxidises and vaporises in an oxidising atmosphere. Both groups pointed out that some of the relevant properties of these glass-ceramics were superior to construction materials, such as granite and marble.

4.5.8. Anodising plant industrial waste

Companies that are dedicated to metallic coating, using Al, Zn, Ni and Cr (e.g. galvanising and anodising) generate an inorganic solid residue, which contain sulphates and chlorides. Diaz *et al.* [171] recently reported that it is possible to produce cordierite glass-ceramics from inorganic wastes of anodising plants. The process involved vitrification of the waste to obtain the starting parent glass material, which is then subjected to a single-stage heat treatment at 900°C. No mechanical properties or potential applications have been reported or suggested. However these wastes are disposed in special landfill sites, creating undesirable environmental hazards, and the primary aim of this research was based around the encapsulation of the waste to reduce the need for specialised landfill sites.

4.5.9. Zinc-hydrometallurgy wastes

Reusing jarosite and goethite from hydrometallurgical processes to obtain glass and glass-ceramic materials has been reported in several papers [172–178]. Jarosite ($KFe_3(SO_4)_2(OH)_6$) red mud comes from electrolytic zinc hydrometallurgy. Goethite (α-FeOOH) is the other type of zinc hydrometallurgy waste produced depending on the type of treatment used to remove the iron content.

Rincon and co-workers have studied the formation of glass [175] and glass-ceramics [172, 173] from goethite. Because of the high iron oxide and zinc oxide content in goethite, additives such as glass cullet, dolomite, and granite have been added to adjust the glass composition. A range of glasses, some of which contained some crystalline phases in the as-cast condition, were produced but although the kinetics of crystallisation were studied no attempt was made to make glass-ceramics in the study by Rincon and Romero [175]. In the other study the starting mixture, which consisted of 37.2 wt% calcined goethite, 23.0 wt% granite, 37.8 wt% glass cullet and 2.0 wt%TiO_2, gave a glass of chemical composition of (wt%): 44.6SiO_2, 3.3Al_2O_3, 25.5Fe_2O_3, 1.6MgO, 4.5CaO, 5.9Na_2O, 3.1PbO, 6.5ZnO, 1.0K_2O, 2.0TiO_2, and 2 wt% of other elements in trace amounts. A conventional melting/two-stage heat treatment (670 and 860°C) method was employed to give a high crystalline volume fraction of 0.80–0.85 [172]. The main crystalline phase was pyroxene, which occurred on the magnetite crystals nucleated at the first heat treatment step. Minor phases were residual magnetite crystals and zinc ferrite. It has been suggested that the zinc ferrite ($ZnFe_{2.5}O_4$, franklinite) was nucleated on the magnetite by the incorporation of zinc oxide in the glass matrix associated with the magnetite phase [173, 176]. There is also one interesting observation in that longer nucleation times produced an adverse effect on the crystalline volume fraction. This is thought to be caused by the coalescence of the magnetite with time thereby leaving fewer nucleation sites. However, as normal a longer crystallisation time increased the volume fraction of the crystalline phase. The fracture toughness was found to be dependent on the volume fraction of crystalline phase, as the extended network of dendritic pyroxene matrix and magnetite microcrystals improve the crack propagation resistance.

The production of sintered glass-ceramics from jarosite has been reported by Karamanov *et al.* [36] who melted a mixture of jarosite, granite, quartz sand, limestone, and Na_2CO_3, with subsequent water quenching to produce glass frits. From the thermal analysis of powder and bulk samples, it was found that formation of hematite occurs on the surface, whereas magnetite is formed via bulk crystallisation. A complex three stage heat treatment was developed consisting of a nucleation step at 700°C for the formation of hematite, a crystallisation step at 1029°C and finally another crystallisation stage at 750–800°C to give pyroxene in the bulk of the material. The study also showed that crystallisation can be achieved by slow controlled cooling, i.e. petrurgic method.

Pelino [177] also reported the reuse of zinc-hydrometallurgy wastes, i.e. jarosite and goethite, for glass and glass-ceramic materials including industrial scale-up. It was demonstrated that pyroxene glass-ceramics can be made from jarosite, granite mud and glass cullet via different processing routes, namely conventional melting and heat treatment, petrurgic method and sintering. Glass-ceramics tiles made from a two-stage heat treatment (630–650°C and 750–800°C) had a crystal volume fraction of 0.40–0.55 of fine magnetite-pyroxene crystals. The glass-ceramic tiles showed good fracture toughness (as high as 2.0 $\text{MPa}\cdot\text{m}^{1/2}$) and relatively low thermal expansion coefficient for both the parent glass and the glass-ceramic ($5.21 \times 10^{-6}{}^{\circ}\text{C}^{-1}$ and $6.08 \times 10^{-6}{}^{\circ}\text{C}^{-1}$, respectively). The main reason for not aiming for a higher degree of crystallisation was to avoid a too high concentration of heavy metal, such as Pb in the glass matrix, leading to a possible high leaching rate of this element.

The outcome of the project led by Pelino [177] has indicated that vitrification improves the chemical durability and reduces the volume of waste that has to be disposed. The scale-up was tested using the custom-made pilot plant shown in Fig. 11. It showed flexibility as various combinations of waste streams were processed, including jarosite, goethite, granite mud, and lead foundry slag, along with additives such as sand, limestone, and Na_2CO_3. Problems of scaling up laboratory based experiments were identified and tackled. For example, dusts and gaseous products, such as SO_2, SO_3, zinc and lead vapours, generated during vitrification, were trapped and collected via filters and condensers, respectively. These streams can be recovered or recycled back into the process. Based on results from pilot runs, this plant is capable of continuously processing and producing 1 ton of glass frits per day, or discontinuously making 250–300 kg of frits per batch.

In another study by the same Italian group [178], the chemical durability of pyroxene-magnetite based glass-ceramics from jarosite wastes were investigated. The parent glass samples were heat treated in a single step at 720°C for 1.5 h. Glass cullet and sand were added to compensate for the lack of silica, thus improving the melt viscosity and glass formation. In the composition containing 40 wt% of jarosite, pyroxene solid solution was the main crystalline phase, while magnetite and franklinite spinel were the main crystalline phases in the composition containing 50 wt% jarosite. The pyroxene based glass-ceramic exhibited higher chemical resistance than its parent glass, indicating that pyroxene is a chemi-

Figure 11 Photo of the pilot plant for production of glass-ceramic tiles from industrial wastes, situated in Iglesias, Italy [177]. (Photo courtesy Prof. M. Pelino, University of L'Aquila, Italy).

cally stable crystal phase. On the other hand, leaching test showed the franklinite was soluble in HCl and thus the magnetite-based glass-ceramic was less chemically durable. Nevertheless, the jarosite derived glass-ceramics showed potential for advanced applications for example in chemical plants, as their chemical durability is comparable to commercial soda-lime glasses, basaltic glasses and glass-ceramics [178].

4.5.10. Clay-refining waste (Kira)

Only the fine fraction of the mined kaolin clay is used for porcelain production. The coarse fraction that remains after the refining process is normally reburied as a waste product. Given its composition, consisting mainly of quartz, kaolinite, feldspar and mica, it is a suitable raw material for glass-ceramics. Toya *et al.* [179] produced two types of glass-ceramics in the $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ system, one was rich in diopside and the other rich in anorthite, by sintering glass powders originated from mixtures of Kira and dolomite (in mass ratios, 65/35 and 75/25, respectively). The authors highlighted one of the key benefits of Kira as being low in Fe_2O_3 and TiO_2, which normally provide the dark colouring to the end product. From the mechanical properties of two glass-ceramics sintered at 1000°C for 1 h (130 MPa for diopside-rich and 73 MPa for anorthite-rich glass-ceramic) as well as work done by Park *et al.* [170], it can be deduced that diopside is the more favourable crystalline phase for enhancing mechanical strength than anorthite. Nevertheless, given the non-hazardous nature of the mixture, i.e. kaolin clay, one must justify the costs associated in producing glass-ceramics via energy-intensive melting and grinding processes to produce the glass powder instead of using as-received powdered materials directly.

5. Foamed glass-ceramics from wastes

Foam glass (e.g. [180, 181]) was developed as one of the innovative glass based materials for recycling waste glasses. In contrast, to the authors' knowledge, there has been limited study of the feasibility of producing foamed glass-ceramics from silicate wastes. Nevertheless, the ease of manufacturing foamed glass-ceramics was demonstrated through the sintering of different types of silicate wastes, namely cathode ray tube (CRT) glasses [182] and oil shale ash [183], with 5 wt% $CaCO_3$ and 5 wt% limestone, respectively, as foaming agent. The foaming process used in these two studies was based on the conventional powder sintering process for producing dense materials as described in Section 3.4, except for the incorporation of a foaming agent and the relatively shorter heat-treatment step. Fig. 12 [183] illustrates that regardless of the amount of foaming agent used, there is little increase in porosity after 10 min at the optimum sintering temperature of 900°C. As a rule of thumb, the foaming process, i.e. the decomposition or reaction of the foaming agent, should occur close to the glass softening temperature to maintain the gas bubbles, thus pores, during sintering.

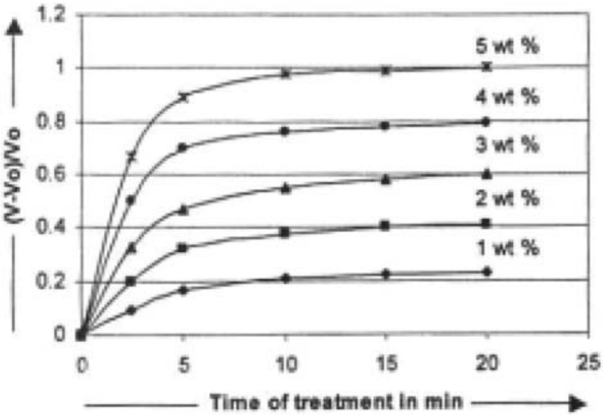

Figure 12 Kinetics of foaming for the different admixtures of limestone at 900°C in glass-ceramic mixtures based on oil shale by-products [183].

The foaming behaviour of both limestone and pure $CaCO_3$ are based on decomposition of the carbonate into lime and CO_2 at temperatures between 700–950°C. In CRT glasses, foaming was achieved at a relatively low temperature of 725°C, resulting in an open porous structure with pores about 100 μm in diameter and some isolated pores of about 10 μm [183]. The foamed material is mainly amorphous with a low concentration of wollastonite as the crystalline phase. The compressive strength was found to vary between 0.7 to 4.5 MPa depending on relative density. In the case of recycling oil shale ash [184], the best mixture (80 wt% oil shale ash, 16 wt% soda ash, and 4 wt% sand) was foamed at 900°C for 10 min, and a porosity of about 85% was achieved. The pore sizes were similar to the study on CRT glasses [182] (open pores of 50–120 μm in diameter and closed pores of 5–20 μm in diameter). Following the foaming stage the porous material was crystallised to different pyroxenes and gehlenite with traces of albite and andradite by an additional hour-long heat treatment at 800°C. This can also be applied to the foamed CRT glasses in order to increase the crystallinity of the glass-ceramic foam. The foamed glass-ceramic was shown to have a thermal conductivity of 0.10–0.13 W/(m K), which makes it useful for thermal insulation purposes, and a reasonable bending strength of 3 MPa. The material is therefore comparable and superior, to certain extent, to commercial foamed glass according to Russian Standard GOST 24748-81, in which the thermal conductivity is 0.07–0.10 W/(m K) and the flexural strength is only 0.3–0.8 MPa [183]. It was also demonstrated by Gorokhovsky [183] that excessive limestone as the foaming agent (>5 wt%) is detrimental to the mechanical properties of the foamed glass-ceramic.

Another method for producing glass-ceramic foam from silicate wastes was demonstrated by Fidancevska *et al.* [39]. In this study, polyurethane foam and bundles of carbon fibres were the two types of pore creator investigated. They were soaked with a slurry formulated with the starting parent glass mixture, and the preforms were subjected to different heat-treatments for drying the slurry, burning-off of the perform, and sintering and crystallisation. This method is known as the replication process [39]. Bearing in mind the original structures of the polymer preform, it was not surprising that foams of uniform open pore structure was obtained; the porosity was 65% with pore diameters ranging from 600 to 800 μm. The glass-ceramic foam based on the bundles of carbon fibres had a much more anisotropic, cylindrical porous structure. The porosity was lower (55%) and thus slightly better mechanical strengths were achieved.

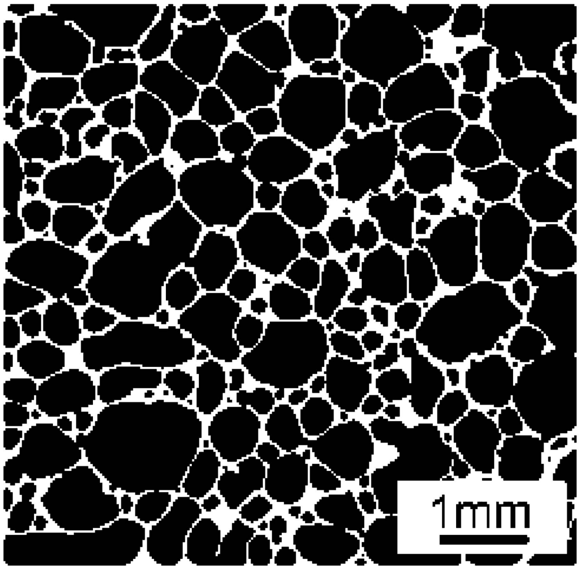

Figure 13 A 2D X-ray microtomographical image showing the cross-section of a glass-ceramic foam with 2 wt%SiC as foaming agent, sintered at 1000°C for 5 min [184].

The authors [184] have also recently produced foamed glass-ceramics from a mixture of coal pond ash and waste bottle glass cullet that incorporated less than 5 wt% of fine SiC powder (5–25 μm) as foaming agent. A short single-stage sintering/crystallisation treatment, that also promoted the reaction of SiC with oxygen, thus generating CO_2 as pore forming gas, was employed. Fig. 13, which is a 2D X-ray microtomographical image, illustrates the porous structure of the coal ash—waste glass based glass-ceramic foam sintered at 1000°C for 5 min. Wollastonite was found as the main crystalline phase, and the porosity ranged between 70–90% with increasing pore size (0.2–1.5 mm) with increasing sintering temperature.

Scaling up may present problems for both of these processes: (1) sintering with foaming agent and (2) replication process. The challenge with scaling-up the process when using foaming agents is to retain the shape of the product while foaming. Even though the replication process may have the advantage of producing near-net shaped product, the infiltration of the slurry into the polymeric or carbonaceous preform may prove difficult at larger scales.

Both of these problems need to be overcome in order to ensure uniformity of the porous structure. Nevertheless, reusing silicate wastes as a source material for producing glass-ceramic foams is an interesting and feasible alternative option to the reuse of industrial wastes in useful products.

6. Conclusions

The investigations discussed in this paper demonstrate the potential of turning silicate wastes into useful glass-ceramic products. The general process involves the vitrification of a silicate waste, or a mixture of wastes, followed by crystallisation to form a glass-ceramic. Pilot plants have been successfully operated for the manufacture of these glass-ceramics [78, 177, 185], but unlike the situation with technical glass-ceramics produced from high purity raw materials for specific applications, industrially produced glass-ceramics from waste are not yet widely commercially available. Although there are obvious environmental benefits to be gained from the recycling of wastes, it appears that some well defined, high tonnage applications need to be targeted more specifically in order to encourage industrial manufacture and assure commercial success. Moreover, in particular in the case of toxic residues such as incinerator electrofilter fly ash, more pressure from the law makers may lead to increased interest (requirement) for their thermal treatment with the aim of inertisation, which will automatically shift interest to the production of useful products such as glass-ceramics from the vitrified residue. Indeed, if a wide application and commercial exploitation of the products is to be expected, concerns related to the toxic potential of products made from industrial wastes will have to be fully addressed and clarified, in order to ensure their acceptance by the public. The present review should supply a complete and reliable source of information to those involved, both in academia and industry, in searching for new ways of reusing silicate waste, whereby the production of glass-ceramics will become a viable and sound technical alternative.

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