GLASS-CERAMICS: THEIR PRODUCTION FROM WASTES

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ABSTRACT

GLASS-CERAMICS: THEIR PRODUCTION FROM WASTES. Glass-ceramics are fine, polycrystalline materials that are produced by the controlled crystallization (devitrification) of a glass. The fundamental principles of the crystallization are presented briefly and the various processing methods for glass-ceramics described in light of these fundamental principles. Two examples of the production of glass-ceramics from wastes are discussed in detail; the wastes are slag from steel production and fly ash from incineration.

Key words : glass, ceramics, devitrification, slag, fly ash

ABSTRAK

PEMBUATAN KERAMIK GELAS DARI LIMBAH. Keramik gelas adalah bahan polikristal berbutiran halus yang diperoleh melalui proses kristalisasi gelas (devitrifikasi). Dalam makalah ini, prinsip dasar proses tersebut diuraikan secara singkat berikut beberapa teknik proses pembuatan. Dari contoh proses produksi (*ceramic*) gelas diuraikan secara detail; bahan limbah berasal dari industri baja dan abu hasil produksi insenerasi.

Kata kunci : Gelas, keramik, devitrifikasi, *slag*, *fly ash*.

INTRODUCTION

Glasses are metastable, non-crystalline materials and the precursor for glass-ceramics. 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. 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.

Glasses may be based on various species, for example there are silicate, phosphate and oxynitride glasses, and depending on the presence of other additions all have been shown to suitable for glass-ceramic production. Usually a glass-ceramic is not fully crystalline; typically the microstructure is 50vol% to 95vol% 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. But in addition the glass-ceramic may exhibit other beneficial properties 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 employed for thermal shock resistant applications such as ovenware, cooker tops and heat resistant windows.

CRYSTALLISATION

The crystallisation, or devitrification, of glass to form a glass-ceramic is a heterogeneous transformation. A heterogeneous transformation:

i. results in drastic atomic rearrangements on a local scale,
ii. produces a well-defined interface between the parent phase (glass in this case) and the product (crystalline) phase(s),
iii. consists of two stages, namely a nucleation stage and a growth stage.

It is appropriate to consider (iii) in more detail. In the nucleation stage small, stable volumes of the product (crystalline) phase are formed, usually at preferred sites

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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 [1]. 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 Figure 1(a).

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 Figure 1(a).

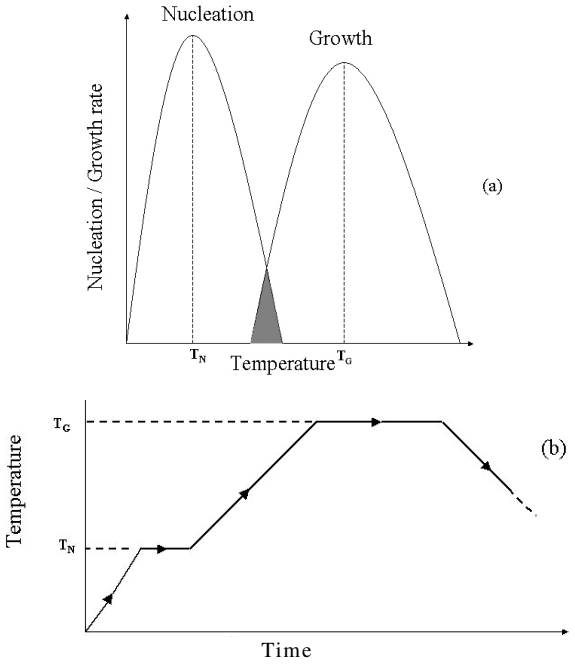

Figure 1. Crystallization of glass to form a glass-ceramic. (a) temperature dependence of the nucleation and growth rates with negligible overlap (b) two-stage heat treatment.

PROCESSING ROUTES

Conventional Method (Two-Stage)

The conventional method for producing a glass-ceramic is to devitrify a glass by a two-stage heat treatment (Fig 1(b)). The first stage is a low temperature heat treatment at a temperature that gives a high nucleation rate (around T_N in Fig.1) 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. However, glass production and the heat treatments are energy intensive and therefore expensive.

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. 1(a)). 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 case, possible to obtain the necessary overlap. By judicious choice of nucleating agents this was first achieved for the glass-ceramic system known as Silceram as will be discussed later.

Petrurgic Method

It was found with Silceram that it made little difference whether the glass was heated up to T_{NG} from room temperature or the molten glass was cooled to T_{NG} . 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 literature as the petrurgic method [2], nucleation and growth of the crystals take place during the cooling. Both the modified conventional (single-stage) and the petrurgic methods are more economical that the conventional method (two-stage).

Powder Methods

The shaping by cold compacting a powder followed by a high temperature heat treatment to sinter

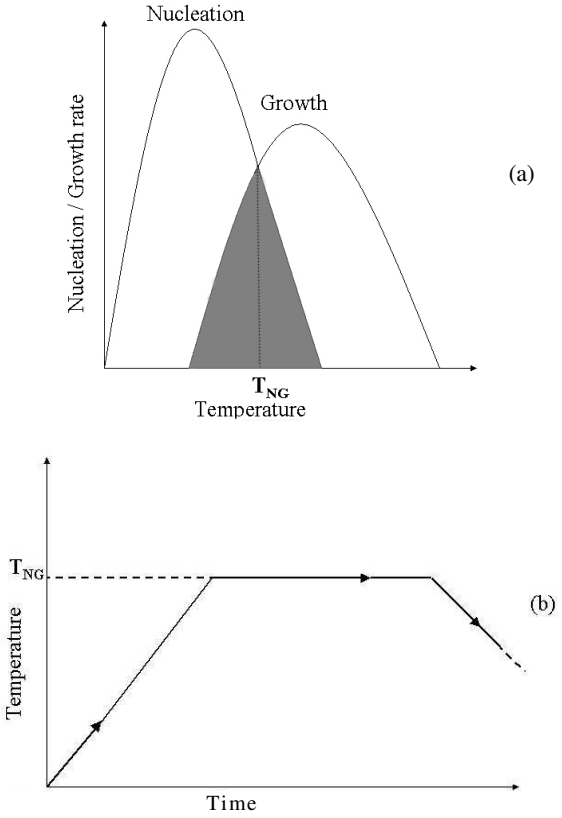

Figure 2. Crystallization of glass to form a glass-ceramic by a single-stage heat treatment (a) temperature dependence of the nucleation and growth rates with significant overlap (b) single-stage heat treatment.

the compact is a common route for the fabrication of ceramics and has also been employed for glass-ceramic production. As there are limitations on the size and shape of component that may be cold compacted, and as there is 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. In contrast it is more attractive to sinter a parent glass powder since lower temperature are involved. It is important to have appropriate rates for the processes of sintering and crystallization. If crystallization is too rapid the resulting high degree of crystallinity will hinder the low temperature sintering leading to an unacceptable amount of porosity. On the other hand, if the sintering is fully complete before any crystallization then the final product is unlikely to differ significantly from those fabricated by other methods. Optimisation of composition and sintering temperature can lead to different microstructures, and even different crystalline phases, compared to those from other method, and hence different properties for the product. Often an additional heat treatment is required after the sintering stage in order to complete devitrification. Other powder methods such as hot pressing and HIPping have been successfully applied but although these give improved products they are more expensive than cold pressing and sintering.

Powder technology facilitates the production of glass-ceramic matrix composites. Particulate and whisker reinforcement involve intimately mixing the powdered parent glass with the reinforcement in the required proportions. The mixture is then shaped and crystallized. Hard reinforcement particles hinder the sintering process, therefore hot pressing is often employed in order to reduce the amount of porosity in the product.

The production of continuous fibre reinforced glass-ceramics is more complex and requires dedicated apparatus (Figure 3). As for particulate reinforcement, intimate mixing of the constituents is essential and this is achieved by drawing the bundles of fibres, known as tows, through a slurry of the powdered parent glass, which is usually water based with a water soluble resin binder. The tows, impregnated with the slurry, are wound onto a mandrel with flat faces to give a tape. The tape is allowed to dry then cut into plies which are stacked into the required stacking sequence, e.g., unidirectional, cross-ply, angle-ply. The final stages are burnout of the binder, hot pressing to consolidate and, often, a heat treatment to complete crystallization.

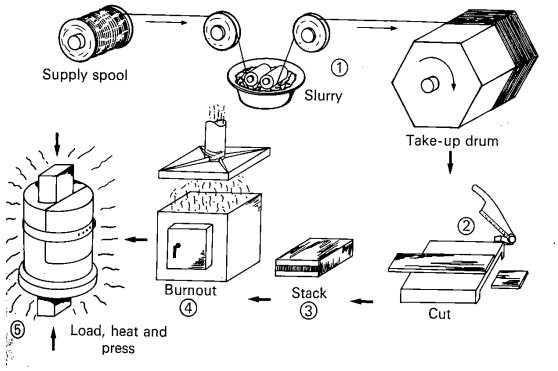

Figure 3. Production of glass-ceramic matrix composites reinforced with continuous fibres[3].

Sol-Gel Precursor Glass

In the discussion so far the glass has been produced from the molten state but in the last decade there has been considerable interest in using sol-gel techniques to obtain the precursor glass. Sol-gels techniques, usually employing colloidal or alkoxide solutions, can produce precursor glass in either bulk or powder forms. Thus all the methods for glass-ceramic production discussed previously may be used with glass produced by this route.

There are some benefits of sol-gel processing such as good control over purity and homogeneity.

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Furthermore it is relatively easy to introduce additional species such as nucleating agents. Indeed it is sometimes possible to obtain compositions by low temperature sol-gel technology that are difficult to achieve via melting because of complications such as loss of volatile species at the high temperatures and phase separation, or even uncontrolled crystallisation, during cooling. Nevertheless, there are some disadvantages, namely the high cost of the solutions, the large shrinkage during processing and the long processing times. The long processing times associated with the production of bulk glass samples are exemplified by recent work on a glass-ceramic with $KTiOPO_4$ as the crystalline phase [4]. The sol was cast into a mould and left at room temperature for several days to form a gel. To avoid cracking the gel was dried for two months, again at room temperature, and finally heated at a slow heating rate of 1°C/min to 660°C and held for five hours.

The temperatures required to crystallize a sol-gel produced glass, whether bulk or powder, are usually lower than those needed for melt-derived glass. In the case of powders this may, in part, be a consequence of the fact that sol-gel powders are often finer than those produced by grinding a melt-derived glass. However generally, as first proposed to account for the rapid crystallisation of sol-gel celsian glass [5], the fast kinetics are probably attributable to the high hydroxyl content. A high OH content lowers the glass transition temperature and increases material transport at a given heat treatment temperature thereby enhancing the rate of crystallisation.

GLASS-CERAMICS FROM WASTES

A wide range of glass-ceramics with tailored properties, eg, bioactive, low dielectric constant, machineable, magnetic, have been developed however this paper will only consider the production of glass-ceramics from wastes.

It has to be accepted that there cannot be zero waste from any manufacturing process (and here power generation is considered as a manufacturing process). 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. An example of recycling is the use of waste glass, know 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. This section is concerned with reuse of waste materials to produce glass-ceramics [6]. Many wastes have been used as raw materials for glass-ceramics, e.g., coal ash [7-9], and mud from zinc hydrometallurgy [10] but only slag from steel production and ash from incinerators will be discussed here.

Slag From Steel Production

Blast-furnace slag was the first 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 constituent, 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. This glass-ceramic was known as Slagceram and was produced by the conventional, two-stage, heat treatment method [11, 12] A similar material, Slagsitall, was being developed in the USSR at about the same time [13,14]. A more recent work investigated the effect of adding titania as a nucleating agent to slag; glass-ceramics with acceptable properties were produced using a two-stage heat treatment [15].

Silceram was developed with the objective of reducing the production costs by simplifying the heat treatments required for crystallisation. The composition was adjusted by mixing the blast-furnace slag with up to 30% colliery shale (another waste product) and small amounts of pure oxide components; a typical composition (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 are Cr_2O_3 and Fe_2O_3 as these are 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 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°C to 1150°C with a maximum at 950°C as illustrated in Figure 4 (a). 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). Nucleation in a single stage heat treatment at 950°C is dominated by the secondary nuclei whose density is about three orders of magnitude greater that that of the primary nuclei.

Figure 4 also 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 Figure 4(b) [16, 17]. 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 savings could also be made in the energy

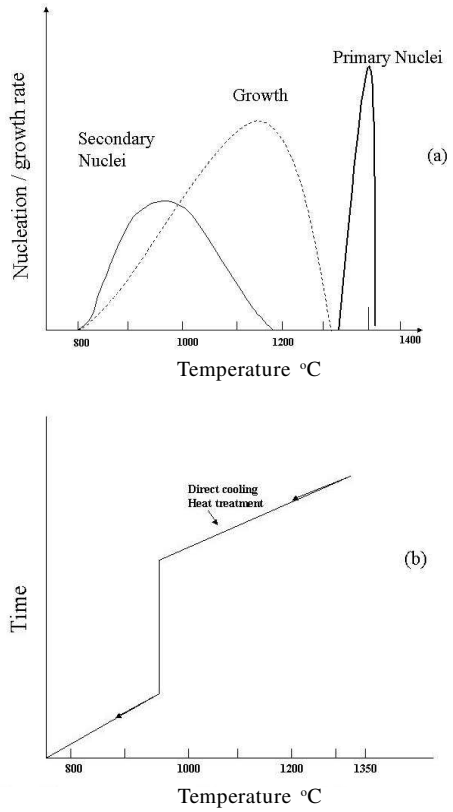

Figure 4. Production of glass-based Silceram glass-ceramic by direct cooling and a single-stage heat treatment (a) temperature dependence of the nucleation and growth rates with significant overlap (b) direct cooling/ heat treatment [adapted from 16,17]

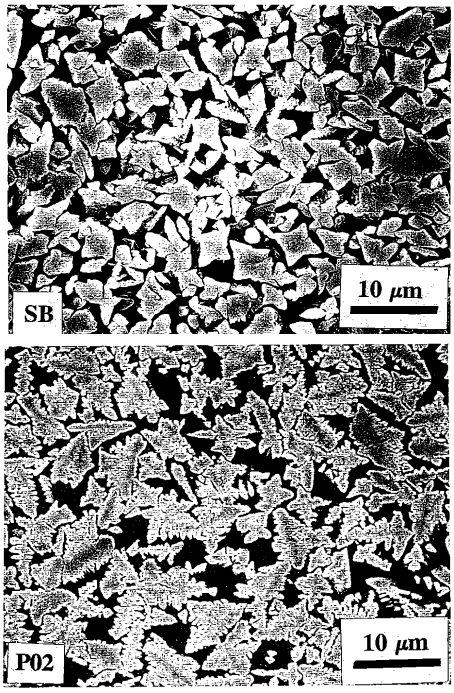

Figure 5. Microstructure of (a) slag-based and (b) pure constituents-based Silceram glass-ceramics[26]

requirements if the production plant was situated at a steel works so that hot slag was used as a raw material [18].

The main crystalline phase in Silceram is a pyroxene of composition close to diopside ($CaMgSi_2O_6$) although small quantities of anorthite are found after excessively long heat treatments [19,20]. Depending on the exact composition and processing parameters 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 (Fig. 5). However, the difference in properties between slag-based and pure constituents-based Silcerams is not significant and data from both types of Silceram are used in the following discussion for illustrative purposes.

The mechanical properties of Silceram glass-ceramics have been extensively studied but it is the more complex properties of ballistic impact resistance and erosion/wear resistance that will be presented briefly. The impact resistance of Silceram has been investigated at velocities up to nearly 300m/s using a gas gun in the laboratory and its performance found to be comparable to alumina and a glass-ceramic, LZ16, developed for ballistic applications. In view of these encouraging results Silceram was tested for the front face of a composite armour system. A composite armour consists of front face of a hard, brittle material bonded to a soft, deformable backing of a fibre-reinforced polymer laminate. The function of the front face is to dissipate the energy of the projectile by fracturing and to distribute the load over a larger area of the backing plate. The back-up plate absorbs the remaining energy by bending and/or delaminating [Fig.6]. The ballistic resistance is determined by measuring the residual velocity of the projectile as it leaves the composite armour as a function of the initial impact velocity of the projectile. Extrapolation of the curve of residual velocity (or residual momentum) again initial velocity to zero residual velocity (or residual momentum) yields the critical velocity below which the armour system is not defeated. Results for a non-optimised Silceram composite armour system of total areal density of 22.4kg/m^2 show that the critical velocity is about 660m/s (Fig.7). This performance is only slightly inferior to the well-established aluminar-Kevlar reinforced laminate backing composite armour system. It is considered that reducing the thickness of the Silceram front face and increasing the thickness of the laminate backing would improve the Silceram composite armour's performance [21,22].

As for most brittle materials the erosion resistance of Silceram is a function of the angle of impact with the maximum erosion rate at an impact angle of 90°. Preliminary erosion studies demonstrated that Silceram had superior erosion resistance to many rival erosion resistant materials such as cast basalt, Slagsitall and

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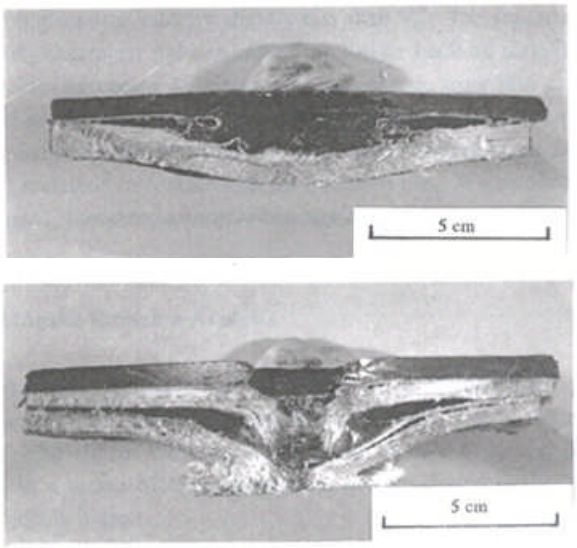

Figure 6. Cross-section of a ballistically impacted Silceram-Kevlar armour system of areal density 22.4kg/ m2 after impact with 7.62mm ball round at (a) 619 m/s and (b) 830m/s (the Siceram front face is on the top in these photographs) [22]

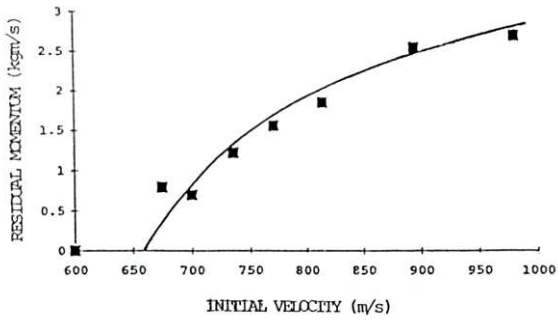

Figure 7. Graph of residual momentum plotted against the initial impact velocity of the projectile for Silceram-Kevlar armour system of areal density 22.4kg/m^2 [21]

alumina (75% purity) although inferior to the more expensive 97.5% purity alumina [23,24]. A more detailed study showed that the 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 [25]. Abrasion resistance was found to be even less microstructure sensitive as it was crystal size independent [26]. This insensitivity to microstructure is encouraging as it means that any microstructural variations that may occur during production on an industrial scale are unlikely to affect performance.

Although bulk nucleation is clearly effective, studies have also been made on producing Silceram by the powder route in which surface nucleation plays a more important role [27,28]. The micrograph of Figure 8 shows a continuous crystalline layer that was nucleated at the particle surface and also individual crystals in the

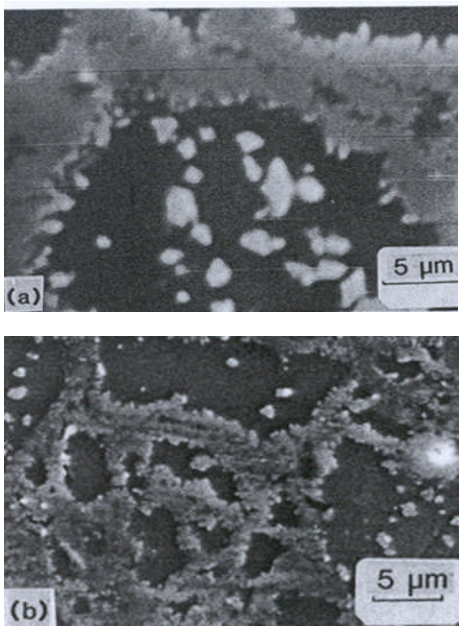

Figure 8. Scanning electron micrograph showing surface and bulk crystallization in sintered Silceram glass-ceramics

interior that were bulk nucleated. Both cold compacting followed by a single sintering/ crystallization treatment and hot pressing without a post pressing crystallization treatment were employed. The main crystalline phase was diopside, as found in the glass-ceramics produced by conventional methods, but there was a marked increase in the propensity for the formation of anorthite. The mechanical properties of the hot pressed glass-ceramic were superior to the properties of the materials manufactured by the conventional methods and cold compacting (Table 1). However, the main benefit of this research was that it provided the prerequisite knowledge for the fabrication of Silceram matrix composites.

Fibre-reinforced and particle-reinforced composites have been investigated with the emphasis on the latter in order to minimise the cost of materials. The usual physical and mechanical properties of the composites have been reported [29,30] but only thermal shock and erosion resistance will be discussed here. The coefficient of thermal expansion of Silceram is too

Table 1. Comparison of the mechanical properties of Silceram glass-ceramics produced by various methods (HP and CP are hot pressed and cold pressed & heat treated respectively)

Method	K_{1C} ($MNm^{-3/2}$)	Bend Strength (MPa)
Modified conventional	2.1	174
HP (940ºC, 90 min)	3.0	186
HP (900ºC, 120min)	2.2	262
CP	1.4	90

high (7.5 x 10 $^{-6}K^{-1}$) and the thermal conductivity too low ($1.76Wm^{-1}K^{-1}$) 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 for monolithic material manufactured by the modified conventional method and SiC particulate-reinforced Silceram are presented in Figure 9. It can be seen 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. A similar trend has also been observed when TiC is used for reinforcement and it maybe that the improved thermal shock resistance is a fortuitous consequence of the sintering flaws present in the composites [30,31].

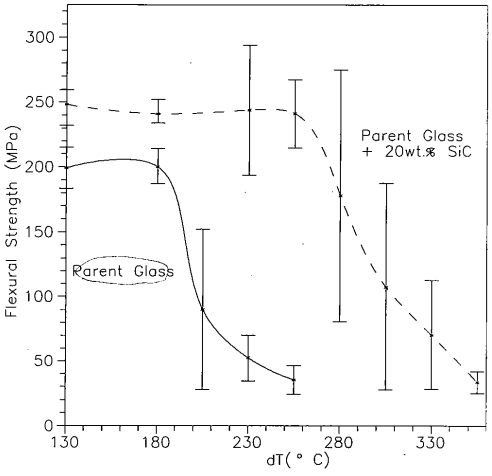

Figure 9. Residual strength data showing the superior thermal shock resistance of particulate-reinforced Silceram glass-ceramics in comparison to monolithic material [31]

Silceram was developed as a wear/erosion resistant materials and these properties are well documented as discussed earlier. 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 [32]. The erosion occurred by lateral crack formation and small TiC particles were less effective in enhancing erosion resistance as they were readily removed with the glass-ceramic matrix debris (Fig.10(a) and (b)). Reinforcement particles of size greater than the lateral crack depth were more effective and stood proud of the eroded surface (Fig.10(c)). Irrespective of particle size the higher the volume fraction of reinforcement, the lower the erosion rate (Fig. 11).

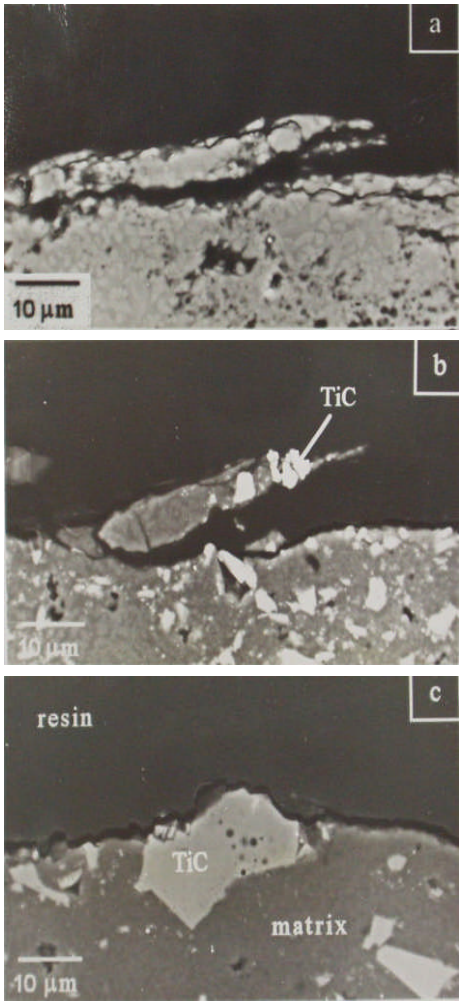

Figure 10. Cross-section of eroded surface of hot pressed Silceram and Silceram reinforced with particulat TiC (a) Monolithic Silceram (b) small (<20 µm) TiC particles (c) large (20-38 µm) TiC particles [32]

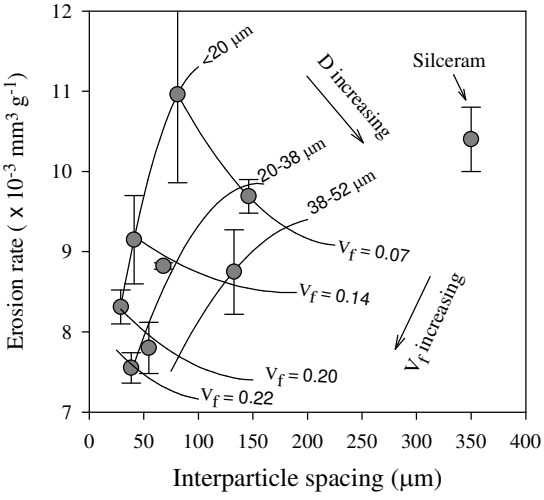

Figure 11. Effect of volume fraction (Vf) and particle size (diameter D) of TiC reinforcement on the erosion performance of Silceram composites [32]

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Ash from urban incinerators

A major and growing problem is the disposal of the large quantity of domiciliary waste (DSW) that is generated. 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. Unfortunately the incineration process itself also results in waste. 10 to 25wt% of DSW remains as solid residues, such as bottom ash, fly ash and slag, after incineration. The size 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/ year and (b) the estimated total fly ash rate for Taiwan for 2003 is 2,000,000 tonnes/year. In view of these figures it is not surprising that assessing the feasibility of developing fly ash based glass-ceramics has been an active area of research over the last decade.

Fly ash is a fine powder, typically with particles in the range 0.5μm -700μm, with the main components being CaO (19-29wt%), SiO_2 (11-35wt%) and Al_2O_3 (5-19wt%) with varying amounts of other oxides such as Fe_2O_3, TiO_2 and P_2O_5 which are capable of acting as nucleating agents (Table 2). It has been established that a glass may be obtained from some fly ashes and bulk samples devitrified by a two-stage heat treatment without the necessity of the addition of further nucleating agents [e.g., 33, 34].

Table 2. Chemical analysis of fly ash from urban incinerators

	RG (F)	BKS (F)	Tyseley (F)	RRRB	CUCC
CaO	19.2	21.1	23.4	29.34	19.19
SiO_2	34.2	38.0	27.1	11.47	18.18
Al_2O_3	18.8	17.5	11.1	5.75	9.34
MgO	2.9	2.4	2.0	3.02	2.74
Na_2O	3.5	3.5	2.8	8.70	8.51
K_2O	4.5	1.8	3.1	7.02	7.36
P_2O_5	2.8	1.6	1.5	1.69	np
TiO_2	np	1.7	2.3	0.85	1.87
ZnO	np	3.5	1.6	np	3.25
LOl	np	np	8.8	9.2	np
Total	89.2	99.1	86.1	78.3	72.3

LOI is loss on ignition
np is not reported.

Glasses formed from fly ashes with a relatively low concentration of nucleating agents (see RRRB and CUCC in Table 2) 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 Cheng et al [35] and Romero et al [36]. Both research groups heated the cold compacted parent glass to a temperature in the range 800°C-1000°C at which both sintering and crystallization occurred. The crystalline phases identified by Romero et al were diopside and both monoclinic and triclinic wollastonite ($CaSiO_3$) and Time-Temperature-Transformation (TTT) diagrams for these phases were determined (Fig.12). In contrast, the major phase detected by Cheng et al was the melilite group mineral, gehlenite ($Ca_2Al_2SiO_7$), this difference presumably reflecting differences in the composition of the precursor fly ashes. The gehlenite-containing glass-ceramic demonstrated good corrosion resistance in a various liquids with the noticeable exception of HCl (Table 3). It was suggested that the poor chemical resistance to HCl maybe attributable to gelatinisation of the gehlenite.

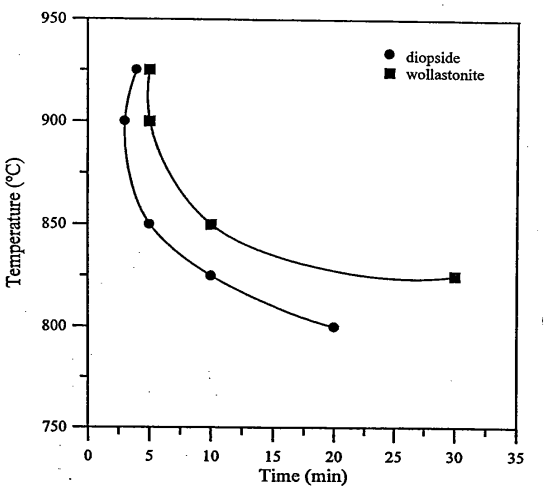

Figure 12. Time-Temperature-Transformation (TTT) diagram for diopside and wollastonite phases crystallizing during the sintering of fly ash compacts [36]

Table 3. Chemical resistance in various liquids of a fly ash based glass-ceramic as a function of sintering/heat treatment temperature [35]

Liquid	Loss (wt%)				
	850°C	900°C	950°C	1000°C	1050°C
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

Sometimes fly ash is mixed with the residue from a gas purification reactor; this residue is formed from an excess of $Ca(OH)_2$ and calcium salts in the purification of acid gases. The viscosity of the melt at 1500°C formed from this mixture is too high and an addition of waste glass is required to produce a melt of acceptable viscosity and which does not crystallise on cooling; 35wt% addition of waste glass was found to be the optimum

[37]. Thus this is another interesting example of a mixture of wastes being employed to fabricate a glass-ceramic (the previous example being a mixture of slag and colliery shale used to produce Silceram).

Most studies have concentrated on using fly ash but about an order of magnitude more by weight of bottom ash is produced than fly ash [38]. The composition of the bottom ash is similar to that of fly ash but it is more variable in morphology. Before use it 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 [38,39].

CONCLUSIONS

The investigations discussed in this paper have demonstrated the potential of turning wastes into a useful product. The process is one of vitrification of a waste, or a mixture of wastes, followed by crystallization to form a glass-ceramic. Pilot plants have been successfully operated for the manufacture of these glass-ceramics, but unlike the situation with technical glass-ceramics produced from high purity raw materials for specific applications, the author is not aware of a readily available industrially produced glass-ceramic from waste. Although there are obvious environmental benefits for recycling wastes it appears that some well defined, high tonnage applications need to be identified in order to encourage industrial manufacture.

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