Journal of the European Ceramic Society 23 (2003) 827–832

www.elsevier.com/locate/jeurceramsoc

Sintered glass-ceramics from Municipal Solid Waste-incinerator fly ashes—part I: the influence of the heating rate on the sinter-crystallisation

Alexander Karamanov[a], Mario Pelino[a,*], Alessandro Hreglich[b]

[a]Department of Chemical Engineering and Materials, University of L'Aquila, Monteluco di Roio, 67100, Italy

[b]Stazione Sperementale del Vetro, Via Briati, 10, Murano-Vinice, 30141, Italy

Received 16 November 2001; received in revised form 12 June 2002; accepted 16 June 2002

Abstract

A glass composition, made by mixing 70% of MSW ashes and 30% of waste from feldspar production, was studied. The batch was melted at 1350 °C and the melt was quenched in water. The chemical stability of the glass was investigated by TCLP leaching test. DTA experiment, at 10 °C/min heating rate in the 20–1200 °C range, showed that the glass has a high crystallisation trend with a gehlenite ($2CaO.Al_2O_3.SiO_2$) formation at 935 °C. The percentage of crystal phase formed as a function of the heat treatment was measured by density variation and XRD. In order to obtain sintered glass ceramics, the frit was heat treated in Al_2O_3 moulds at 950, 1000 and 1050 °C by 2 and 20 °C/min heating rates. At high heating rate predominantly surface crystallisation occurred with fibre-like crystals growing perpendicularly from the surface; at low heating rate bulk crystallisation took place. At low rate, the sintering was inhibited by the crystallisation process. Non porous sintered samples were obtained by a 30 °C/min heating rate and a 40 min isothermal step at 1120 °C, near the liquidus temperature.

Keywords: Fly ash; Glass-ceramics; Sintering; Waste recycling

1. Introduction

The combustion of the wastes may be considered a very old and common method employed to reduce the volume and to eliminate the risks of disposing of human waste. Traces of this technology are even found in the Bible where it is reported that at the time of King Solomon the waste from Jerusalem was brought outside the city and burned in an open fire.[1] More recently, the infections generated by the disposal on open land of the municipal solid waste (MSW) were ascertained and the first incinerator facility was realised in England about 130 years ago.[1]

Today the incineration of MSW is a mature technology by which the environmental and safety aspects are taken into consideration at all phases of the process. In the EU countries, about 40% of the 150 million tonnes of annual MSW production is currently incinerated.[2] Combustion in the modern incinerators decreases the volume of the waste by more than 90% and allows recovery of thermal energy by producing electricity and by heating public buildings. During the incineration about 70% of the MSW is transformed into gases and the other part remains in the form of slag and ashes. Depending on the composition of MSW, the slag is usually classified as inert material while the ash collected in the electrofilters is classified as hazardous because it contains various percentages of heavy metals vaporised during the combustion. The results of the leaching tests show that the concentration of some elements, usually Cd, Cr, Zn, exceeds the regulatory limits and cannot be disposed of in the present form and therefore require a stabilisation or inertisation treatment prior to disposal.

Vitrification is a known technology for the inertisation of various industrial residues[3,4] and, by properly selecting the glass composition and thermal treatment, the re-utilisation of the glass or glass ceramic as raw material for different industrial applications is possible. In this regard, several studies with MSW ashes

---

* Corresponding author. Tel.: +39-0862-434224; fax: +39-0862-434233.

E-mail addresses: karama@ing.univaq.it (A. Karamanov), pelino@ing.univaq.it (M. Pelino).

0955-2219/03/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0955-2219(02)00210-8

(MSWA) were carried out in recent years on the chemical durability of the vitrified products,[5,6] on the crystallisation behaviour of the parent glasses,[7,8] on the structure and properties of bulk glass-ceramics,[9–11] as well as on the possibility of obtaining sintered glass-ceramics from powdered MSW glasses.[11–16]

In the present work the possibility of obtaining glass-ceramics from MSWA by sinter-crystallisation of glass frit, placed loosely in refractory moulds, is discussed. This technique makes it possible to obtain products with an agreeable appearance and properties superior to natural stones, i.e. marble and granites, by properly selecting the glass frit granulometry and thermal treatment. Sinter-crystallisation was commercially applied, for the first time, in the production of marble-like "Neoparies" material,[3,17] made by crystallisation of glass particles with 1–7 mm sizes. The glass-ceramic is made up of 35–40 wt.% wollastonite ($CaO.SiO_2$) crystal phase and after grinding and polishing, has an appearance similar to marble, together with outstanding mechanical and chemical properties. More recently, sintered glass-ceramics with diopside crystal phase ($CaO.MgO.2SiO_2$) were developed by means of natural raw material[18] as well as that of different industrial wastes.[19–22] In these materials, surface crystallisation is predominant and fibre-like crystals in the order of millimeters grow perpendicularly from the surface. As a result, the sintered particles are well distinguishable in the structure of the materials and the appearance imitates the grained structure of granites.

The research activity was divided into two parts; in the first part, here presented, the results based on 100 and 70% of MSWA glass compositions, are described. The sintering and crystallisation, at different heating rates, were investigated by means of DTA, XRD, density measurements and optical microscopy.

In the second part, the glass composition was somehow modified by the addition of sand, glass cullet and B_2O_3 and the sinter-crystallisation process parameters were adjusted to improve the appearance and the chemical, mechanical and thermal properties of the glass-ceramics.

2. Experimental

Fly ashes from an incinerator plant, burning mainly MSW, were employed in the present study. The plant produces 230 kg slag and about 28 kg fly ashes per 1000 kg of burned wastes. The slag was classified as inert while the fly ash, since it contains high percentages of chlorides and sulphates together with heavy metals, i.e. Cd, Cr, Cu, Hg, Se, was classified as hazardous.

In order to separate the soluble salts such as NaCl and Na_2SO_4, the initial ash was washed several times and filtered. During washing, the pH of the solutions decreased from 12.3 to 8.3. After drying, a total 43–45% weight-loss was recorded.

Two glasses were prepared. The first, labelled G-100, was obtained by melting washed and dried MSWA without any additives. The second, labelled G-70, was prepared by mixing 70 parts of MSWA with 30 parts of wastes from feldspar production (FW). The chemical compositions of the wastes, G-100 and G-70 glasses are reported in Table 1.

The melting was carried out in a gas furnace utilising 1 l Al_2O_3 crucibles. The batch was heat-treated at 1350 °C for 4 h and the melt was quenched in water. The frit was crushed and sieved. In the present study, the fraction from 4.0 to 5.6 mm was used.

The chemical stability of G-100 and G-70 glasses was characterised by leaching in 0.5 M acid acetic for 24 h (TCLP test). The analyses of the leaching media summarised in Table 2 showed that both samples exceed the environmental regulatory limits.

The crystallisation process was investigated by DTA technique, (Netzsch STA 409 apparatus), using 100 mg glass powder at a heating rate of 10 °C/min. The crystalline phase formed was determined by XRD technique (Philips PW1830 apparatus and CuK_α radiation).

The frits were placed in Al_2O_3 moulds ($3\times2\times2$ cm^3) and heat-treated at 2 and 20 °C/min to different temperatures.

The densities of the sintered samples were measured by He displacement Pycnometer (AccyPyc 1330). Then the samples were crushed and milled to a size below 45 μm and the densities were measured again. The density differences before and after milling were used to estimate the percentages of close porosity, P, through the relation:

Table 1
Chemical compositions of the wastes and corresponding G100 and G70 glasses (wt.%)

	MSWA	FW	G-100	G-70
SiO_2	24.42	65.11	30.59	41.24
TiO_2	1.91	0.12	2.32	1.10
Al_2O_3	11.52	18.73	14.91	15.24
Cr_2O_3	0.10	0.003	0.08	0.07
Fe_2O_3	2.35	1.52	2.93	2.45
CaO	30.0	1.92	37.24	24.65
MgO	4.21	1.02	5.23	3.68
BaO	0.14	0.02	0.15	0.12
ZnO	1.42	0.01	1.71	1.09
PbO	0.14	–	0.16	0.11
CuO	0.05	0.002	0.06	0.03
CdO	0.015	–	0.02	0.01
NiO	0.01	0.01	0.01	0.01
Na_2O	2.12	7.83	2.52	4.36
K_2O	0.62	1.11	0.83	0.92
SO_3	2.31	–	–	–
P_2O_5	1.48	0.12	–	–
L.O.I	17.12	2.53	–	–

Table 2
The TCLP leacing test results of the washed and dried MSW ash and obtained glasses

	MSWA	G-100	G-70	Applied Limits
Cd	0.0723	0.045	0.0003	0.02
Pb	<0.001	0.007	0.001	0.2
Cu	0.068	0.069	0.0042	0.1
Cr^{VI}	0.499	0.076	0.001	0.2
Se	0.446	–	–	0.03
Mn	0.004	0.011	0.002	2
Zn		0.28	0.05	2
Ni	<0.1	0.06	<0.01	2
Fe	0.17	<0.01	0.02	2
Hg	0.0015	–	–	0.005

$$P = 100\frac{\rho_{gc} - \rho_i}{\rho_i} \tag{1}$$

where ρ_i and ρ_{gc} are the densities of the heat-treated samples before and after milling respectively. The helium displacement pycnometer measures the skeleton density of the sample. Therefore, relation (1) provides the percentage of close porosity not reachable by the gas. The experimental associated error to this measurements was evaluated as ±0.16%.

The crystalline fraction, x (wt.%), was evaluated by measuring the change of the density between the parent glass (2.716 g/cm^3) and the heat-treated and then powdered sintered sample. The method used is based on the variation of density during crystallisation through the following equation.[21]

$$x = 100\frac{1/\rho_g - 1/\rho_{gc}}{1/\rho_{g(cr)} - 1/\rho_{cr}} \tag{2}$$

where ρ_g is the density of parent glass, ρ_{gc} is the density of measured powdered sample, $\rho_{g(cr)}$ is the density of a hypothetical glass with the composition of the formed crystal phase and ρ_{cr} is the density of the crystal phase.

In the method, it is assumed that the volume of the parent glass, V_g, consists of two parts: $V_{g(cr)}$—with the composition as the crystal phase which is going to be formed and $V_{g(r)}$—with the composition of the residual glass. Then, during crystallisation, only the $V_{g(cr)}$ part is transformed in the crystal phase with volume V_{cr}. A detailed description of the methodological approach and application to the crystallisation of glasses is reported elsewhere.[23]

In the case of gehlenite formation, ρ_{cr} is 3.04 g/cm^3 [4,24] while the corresponding density of hypothetical $Ca_2Al_2SiO_7$ glass, $\rho_{g(cr)}$, estimated by the Appen method,[25] is 2.87 g/cm^3. The experimental associated error to the measurements, employing a 5–6 g glass powdered sample, was evaluated as ±0.003 g/cm^3, which allows the detection of differences of ±2% in the crystal phase.

The influence of the heating rate and holding temperature on the sintering and crystallisation processes was determined by optical microscopy observation and visual impression.

3. Results and discussion

The results of the TCLP test carried out on G-100 glass show a high Cd concentration in solution, while Cr and Cu are slightly below the regulated limits. For this reason G-100 composition was not considered appropriate for further studies. In G-70 glass, the chemical durability was improved by increasing the percentages of the glass formers, obtained by the addition of waste from feldspar production. The TCLP test shows that concentration in solution of all pertaining metals is considerably lower than the regulated limits. The results are shown in Table 2, where the test carried out on MSWA is reported for the sake of comparison, together with the limits for each of the regulated elements.

The crystallisation of the G-70 glass was investigated by DTA. Fig. 1 reports the DTA plot of a powdered glass sample. The glass transformation temperature, T_g, is relatively high and occurs at 660 °C while a clear and sharp crystallisation exo-peak is at 935 °C, suggesting an intensive crystallisation process in the 900–1000 °C temperature range. In the DTA trace, the melting endo-effect was revealed at 1150 °C. The crystal phase formed was identified as gehlenite ($Ca_2Al_2SiO_7$) by XRD. The spectrum of the glass-ceramic is shown in Fig. 2.

The glass frit was placed in moulds (3×2×2 cm^3) and heat-treated at 950, 1000 and 1050 °C for 1 h by means of a 2 and 20 °C/min heating rates, respectively; they were then cooled at a rate of 20 °C/min. The densities of the sintered samples before and after milling are reported in Table 2. Tables 3 and 4 summarise the results of the percentages of crystal phase formed, evaluated by

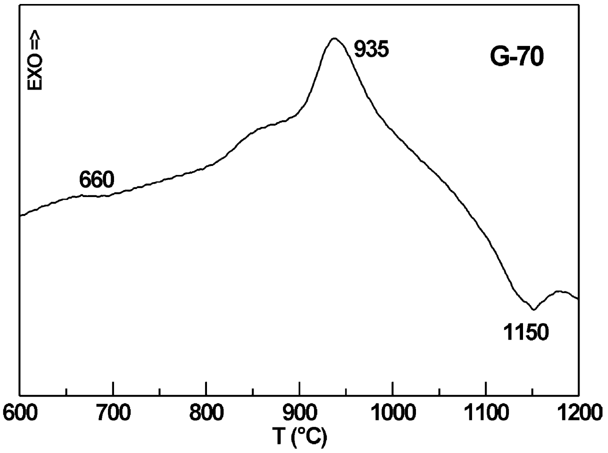


Fig. 1. DTA trace of the parent G-70 glass.

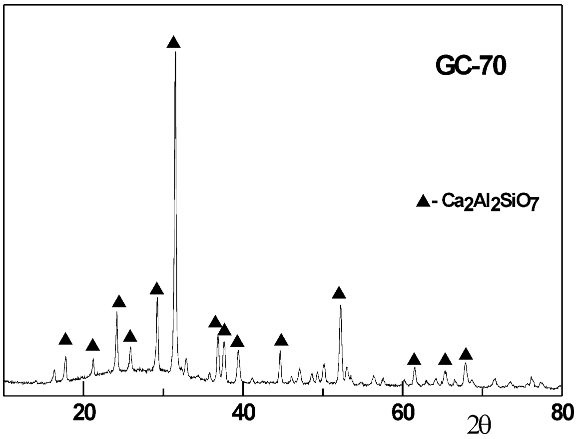


Fig. 2. XRD spectrum of the sintered glass-ceramic.

Table 3
The densities before (ρ_i) and after crushing (ρ_{gc}) of the samples obtained at 2 and 20 °C/min and 1 h holding step at different temperatures

Isothermal (1 h)	Heating rate (2 °C/min)		Heating rate (20 °C/min)	
	ρ_i	ρ_{gc}	ρ_i	ρ_{gc}
950 °C	2.742	2.782	2.732	2.753
1000 °C	2.748	2.779	2.731	2.745
1150 °C	2.743	2.785	2.728	2.749

Eq. (2), and the closed porosity, evaluated by Eq. (1), respectively.

It is evident that the evolution of the crystalline phase is not sensibly influenced by the holding temperature but depends on the heating rate. At 2 °C/min the amount of gehlenite phase is about 2 times higher than the one formed at 20 °C/min heating rates. Optical microscopy showed that, at high heating rate, the surface crystallisation is predominant while at low heating rate bulk crystallisation takes place. Therefore, the higher percentage of crystal phase formed in the samples heat-treated at 2 °C/min is a result of bulk crystallisation.

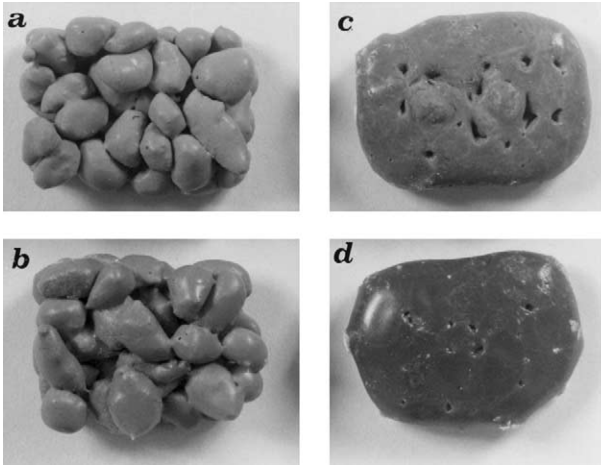
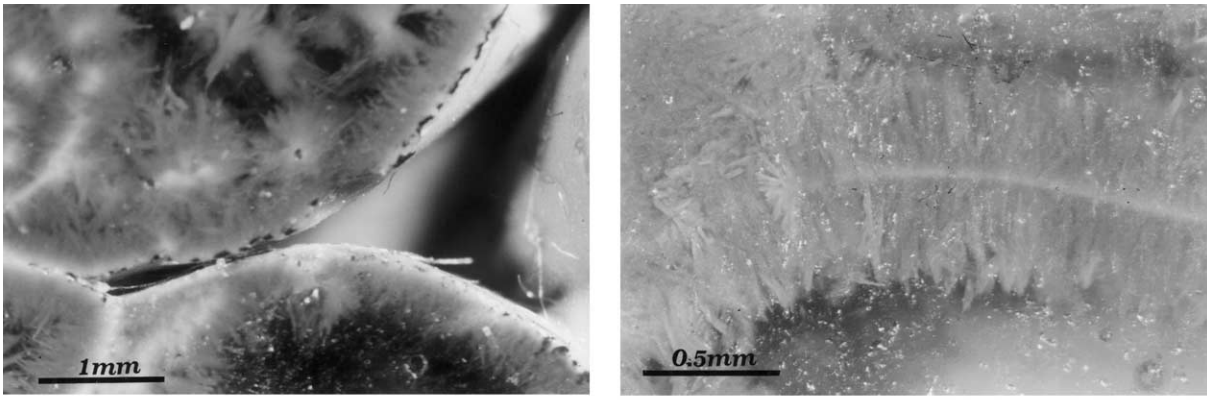


Fig. 3. Pictures of samples (3×2 cm) heat-treated at 2 °C/min and 1 h at 950 °C (a) and 1050 °C (b) ; samples heat-treated at 20 °C/min and 1 h at 950 °C (c) and 1050 °C (d).

The closed porosity is also influenced by the heating rate; its value for the samples obtained at 2 °C/min ranges between 1.20 and 1.50% while it is between 0.50 and 0.80 for the samples sintered at 20 °C/min.

Fig. 3 shows pictures of sintered samples. Photos "*a*" and "*b*" are the samples obtained at 2 °C/min after 1 h holding at 950 °C and 1050 °C respectively; photos "*c*" and "*d*" present the samples obtained by 20 °C/min heating rate and holding at the same temperatures. At 2 °C/min the sintering process is inhibited even if the holding at 1050 °C is prolonged for 24 h; no evident differences were noticed in the degree of sintering. On the other hand, the degree of sintering of samples treated by 20 °C/min improves by increasing the temperature and prolonging the time of the isothermal step.

By treating the glass frit by 2 and 20 °C/min to 950 and 1050 °C and then immediately cooling by 20 °C/min the percentage of gahlenite formed was related to the heating step. By 2 °C/min heating rate up to 950 and 1050 °C a 21 and 29 wt.% crystal phase were formed, respectively. Fig. 4 a shows an optical microscopy photo



(a) (b)

Fig. 4. Optical microscopy photos of samples heated to 1050 °C at 2 °C/min (a) and at 20° C/min (b).

of a cut and polished sample, heated at 1050 °C where surface and bulk crystallisation are evident as well as a residual close and open porosity. By 20 °C/min heating rate up to 950 and 1050 °C a 7 and 13% crystal phase was formed, respectively. The optical microscopy observation, Fig. 4b, of the sample heated at 1050 °C highlighted that only surface crystallisation took place; the glass grains were sintered and only a minimum porosity was retained.

At low temperatures, 650–850 °C, due to high viscosity (10^{13}–10^{10} dPa.s.), the crystal growth and the sintering are negligible while a nucleation process can take place. At higher temperatures, these nuclei can act as centres of crystallisation influencing the rate of phase formation. The number of nuclei formed in the low temperature region increases as a function of the heating rate,[26,27] i.e. the lower the heating rate the higher the number of nuclei formed. This aspect would play a role in the sintering carried out at higher temperatures, i.e. in the 950–1150 °C range. In this regard, a series of experiments were carried out to highlight the role on the sintering of the heating rate in the nucleation region. Glass frit were heated up to 850 °C by 2 and 20 °C/min, respectively. Both samples retained the amorphous structure while a low degree of sintering was attained. The samples are shown in Fig. 5a and b, respectively. The temperature of both samples was then raised for sintering to 950 °C by 2 or 20 °C/min thus obtaining 4 sintered samples, labelled GC2/2, GC20/2, GC2/20, and GC20/20, respectively, where the first number represents the heating rate to 850 °C and the second the one to 950 °C. The percentages of gehlenite, determined by density measurements, were 17% in GC20/2, 21% in GC2/2; 12% in GC2/20 and 7% in GC20/20. The difference between GC20/2 and GC2/2 was attributed to the bigger number of active nuclei formed at low heating rate. The same consideration applied for the samples GC2/20 and GC20/20. Fig. 5c and d show the samples GC2/20 and GC20/20, respectively, where sintering is evident only in the last case.

From the results it follows that the sintering is inhibited if the crystal phase formation in the low temperature region is higher than 10%, i.e. if the heating rate is lower than 15–20 °C/min. At high heating rates, i.e. around 20 °C/min or higher, sintering is attained and low or no close porosity remains in the glass ceramics.

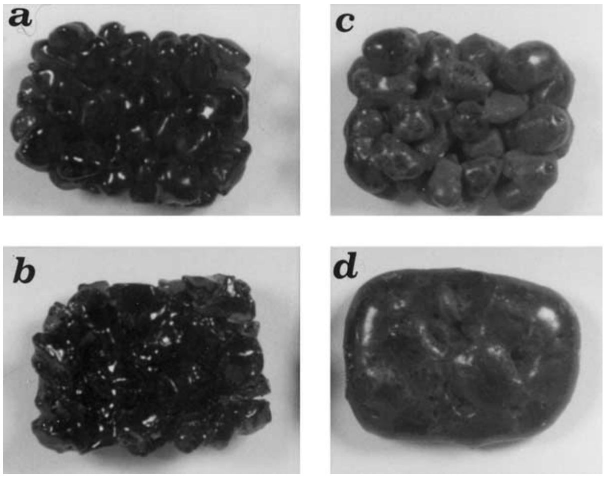


Fig. 5. Pictures of samples (3×2 cm) heated to 850 °C at 2 °C/min (a) and at 20 °C/min (b); picture of GC 2/20 (c) and GC 20/20 (d).

Sintered glass-ceramic non-porous tiles with a brownish colour ($100/100/20$ mm^3) were obtained at 30 °/min heating rate followed by 40 min isothermal step at 1120 °C, i.e. 30 °C below the liquidus temperature, followed by a 10 °C/min cooling. After polishing, due to predominate surface crystallization, the glass-ceramics showed a texture similar to natural granite.

4. Conclusion

In this study, a gehlenite glass-ceramic was obtained by sintering glass frit from municipal solid waste ashes. The crystallisation resulted in being influenced by the heating rate: at high heating rate, 20 °C/min, surface crystallisation is predominant while at low heating rate, 2 °C/min, bulk crystallisation takes place.

The formation, during heating at low rates, of a degree of crystallisation higher than about 15% inhibits the sintering so that open and close porosity remains in the glass-ceramics. Non porous sintered samples were obtained at high heating rate, 30 °C/min, by 40 min

Table 4
Percentage of the crystal phase formed and the closed porosity in the samples obtained at 2 and 20 °C/min and 1 h holding step at different temperatures

Isothermal (1 h)	Heating rate (2 °C/min)		Heating rate (20 °C/min)	
	Crystal phase (%)	Closed porosity (%)	Crystal phase (%)	Closed porosity (%)
950 °C	39	1.44	20	0.76
1000 °C	37	1.17	16	0.52
1150 °C	41	1.51	18	0.64

isothermal step at 1120 °C, i.e. near the liquidus temperature.

Acknowledgements

The authors are grateful to the National Council of Research (CNR) for the financial support given to this paper through the project: "Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate II".

References

1. IAWG International Ash Working Group: Van der Sloot, H.,. Sawell, S., Chandler, A., Hjelmer, O., Eighmiy, T., Kosson, D., Hartlen, J. and Vehlow, J., *Municipal Solid Waste Incineration Residues*, Elsevier, Amsterdam, 1997.
2. Vehlow, J., Thermal treatment of wastes in europe–regulatory framework and implemented technology. In *Proceedings of I Congresso Nazionale* Valorizzazione e Riciclaggio del Residui Inustriali, L'Aquila, Italy, 1997, pp. 265–278.
3. Strnad, Z., *Glass-Ceramic Materials*. Elsevier, Amsterdam, 1986.
4. Pavlushkin, N., *The technology of Glass and Glass-Ceramics (in Russian)*. Stroiisdat, Moscow, 1983.
5. Menzler, N., Mortel, H., Weibmann, R. and Balec, V., Examination of two glass compositions for the vitrification of toxic products from waste incineration. *Glass Technology*, 1999, **40**, 65–70.
6. Boccaccini, A., Petitmeret, M. and Wintermantel, E., Glass-ceramics from municipal incinerator fly ash. *The American Ceramic Society Bulletin*, 1997, **11**, 75–78.
7. Romero, M., Rawlings, R. and Rincon, J., Development of a new glass-ceramics by means of control vitrification and crystallization of inorganic wastes from urban incineration. *J. Eur. Ceram. Soc.*, 1999, **19**, 2049–2058.
8. Kraub, M., Vitrification of waste materials. *Glastech. Ber., Glass Sci. Tech.*, 1997, **70**, 375–381.
9. Krauss, M., Vitrification of filter dust from incineration- relation between batch composition, resulting glass composition and waste glass properties. *Proc. of XVIIIth ICG*, Am. Ceram. Soc, 5–8 July 1998, San Francisco, USA.
10. Romero, M., Rawlings, R. and Rincon, J., Crystal nucleation and growth in glasses from inorganic wastes from urban incineration. *J. Non-Crystalline Solids*, 2000, **271**, 106–118.
11. Ferraris, M., Salvo, M., Smeacetto, F., Augier, L., Barbieri, L., Corradi, A. and Lancellotti, I., Glass matrix composites from solid waste materials. *J. Eur. Ceram. Soc.*, 2001, **21**, 453–460.
12. Barbieri, L., Ferrari, A., Lancellotti, I., Leonelli, C., Rincon, J. and Romero, M., Crystallization of (Na2O–MgO–CaO–Al2O3–SiO2 glassy systems formulated from waste products. *J. Am. Cer. Soc.*, 2000, **83**, 2515–2520.
13. Barbieri, L., Corradi, A. and Lancellotti, I., Bulk and sintering glass-ceramics by recycling municipal solid bottom ash. *J. Eur. Ceram. Soc.*, 2000, **20**, 1637–1643.
14. Boccacini, A., Schawohl, G., Kern, H., Schunck, B., Rincon, J. and Romero, M., Sintered glass-ceramics from municipal incinerator fly ash. *Glass-Technology*, 2000, **41**, 99–105.
15. Kipka, A., Luckscheiter, B. and Lutze, W., Melting of Fly Ashes and product properties. *Glastech. Ber.*, 1993, **66**, 215–220.
16. Gutman, R., Thermal technologies to convert solid waste residuals into technical glass products. *Glastech. Ber., Glass Sci. Tech.*, 1996, **69**, 285–299.
17. Nakamura, S., Crystallized Glass Article Having a Surface pattern, US Patent 3 955 989, 1976.
18. Karamanov, A., Gutzow, I. and Penkov, I., Diopside marble-like glass-ceramics. *Glastech. Ber., Glass Sci. Tech.*, 1994, **67**, 202–208.
19. Karamanov, A., Gutzow, I. and Chomacov, I., Synthesis of wall-covering glass-ceramics from waste raw materials. *Glastech. Ber., Glass Sci. Tech.*, 1994, **67**, 227–231.
20. Gorobinskay, V., Kravtcenchko, I., Bossert J. and Stablein, J., Sintered crystallization of waste containing harmful components, *Proc. of XVIIIth ICG, Section A7*, Am. Ceram. Soc. 5–8 July 1998, San Francisco, USA.
21. Karamanov, A., Taglieri, G. and Pelino, M., Iron-rich sintered glass-ceramics from industrial wastes. *J. Am. Ceram. Soc.*, 1999, **82**, 3012–3016.
22. Nicolescu, M., Boroica, L., Boroica, I. and Ursu, D., Mosaic and granite type products from glass and other industrial wastes. In *Proc. of I-st.Balcan Conference on Glass Science and Technology*, Volos- Greece, 9–10 October 2000, pp. 221–226.
23. Karamanov, A. and Pelino, M., Evaluation of the degree of crystallisation in glass-ceramics by density measurements. *J. European Cer. Soc.*, 1999, **19**, 649–654.
24. Hlavac, J., *The Technology of Glass and Ceramics: an Introduction*. Elsevier, Amsterdam, 1983.
25. Appen, A. A., *The Chemistry of Glasses (in Russian)*. Himiq, Leningrad, 1974.
26. Matusita, K. and Sakka, S., Kinetic study on crystallization of glass by differential thermal analysis—criterion on application of Kissenger plot. *J. Non-Crystalline Solids*, 1980, **38**, 741–746.
27. Karamanov, A. and Pelino, M., Influence of time-lag on the activation energy in non-isothermal crystallization. *J. Non-C rystalline Solids*, 2001, **290**, 173–179.