JOURNAL OF MATERIALS SCIENCE **32** (1997) 1775–1779

# Glass-ceramic from sewage sludge ash

S. SUZUKI, M. TANAKA
*Department of Inorganic Chemistry, Tokyo Metropolitan Industrial Technology Centre, 3-13-10 Nishigaoka, Kita-ku, Tokyo 115, Japan*

T. KANEKO
*Environmental Plant Engineering Department, Tsukishima Kikai Co. Ltd, 2-17-15 Tsukuda, Chuo-ku, Tokyo 104, Japan*

Glass-ceramic was produced by adding limestone to sewage sludge incinerated ash. Black glass was produced by melting a blended ash batch at 1450 °C. For nucleation, this glass was reheated at 800 °C for 1 h, and reheated at 1100 °C for 2 h to form glass-ceramic. The main components of sewage sludge incinerated ash are $SiO_2$ and $Al_2O_3$. Because small amounts of $Fe_2O_3$, sulfur and carbon are included, the addition of limestone alone can generate the crystal nucleant, FeS, to form anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) crystal. The glass-ceramic showed superior characteristics of high strength and acid resistance for use in construction materials.

## 1. Introduction

The wastewater generated from our daily lives, and industrial wastewater, are treated at the sewage treatment plant, and the clean treated water is discharged into the river. Most of the sewage sludge is landfilled after reducing the volume by incineration. At present, the sewered population in Japan is about 50%, and 400 000 ton sewage sludge incinerated ash is generated annually. In the future, the increase in the sewered population will be accompanied by an increase in the volume to be treated. For the Tokyo Metropolitan area, whose sewered population reached 100%, about 60 000 ton sewage sludge incinerated ash are generated annually, costing 8000 yen/ton to landfill.

In Tokyo, securing a new site for landfill disposal is becoming difficult, so converting sewage sludge incinerated ash into a resource has been an emergency theme for the administration. To date, the following technology effectively to use sewage sludge incinerated ash has been developed [1].

1. After forming the sewage sludge incinerated ash by pressing, interlocking brick is made by baking.
2. Sewage sludge incinerated ash is granulated then fired to generate voids to make a lightweight aggregate.
3. Slag is formed by melting sewage sludge incinerated ash at a high temperature for use as concrete aggregate or lower roadbed materials.

However, these technologies face problems with cost and quality, so a highly useful technology with added value is favoured.

Vitrification is effective for reducing the volume of waste, making waste non-hazardous, and creating a resource from waste. If glass-ceramic can be produced, then a higher value added use can be obtained. Up to now, a number of reports [2–6] have been published on glass-ceramics using waste materials such as coal ash, iron and steel slag; however, very few reports have appeared on glass-ceramics using sewage sludge incinerated ash.

This study focused on the main components of sewage sludge incinerated ash, which are silicic acid and alumina, as well as the components for nucleation. Based on this idea, the production of glass-ceramic using sewage sludge incinerated ash as the main material has been attempted.

## 2. Experimental procedure

A sample was taken from the organic sewage sludge incinerated ash from the dewatered cake with polymer. Tables I and II show the chemical composition and particle-size distribution of incinerated ash which is a very fine yellowish brown powder. Fig. 1 shows the measured results using thermogravimetry and differential thermal analysis. Industrial calcium carbonate (limestone), dolomite, silica sand under 200 mesh, and soda ash were used as conditioning materials for component control.

Conditioning materials such as limestone were blended in different ratios of 200 g incinerated ash, then mixed for 30 min in the automatic ceramic mortar to make blended ash batch samples (batches). Each batch was placed in a covered 130 $cm^3$ SSA-H alumina crucible, then melted in the silicon carbide electric furnace. The temperature increased at 10 °C $min^{-1}$, and was kept at 1400 °C, then a 250 g batch was remelted five times, at 1450 °C for 2 h. The cover was sealed and a reducing atmosphere was maintained. After refining for 1 h at 1300 °C, the glass was allowed to flow over the iron plate. The temperature of the obtained original glass was increased at

TABLE I Chemical composition of sewage sludge incinerated ash

| Component | (wt %) | Component | (wt %) |
|---|---|---|---|
| $SiO_2$ | 48.2 | $TiO_2$ | 1.8 |
| $Al_2O_3$ | 18.7 | $MnO_2$ | 0.4 |
| $Fe_2O_3$ | 8.5 | $P_2O_5$ | 5.6 |
| $Na_2O$ | 0.6 | ZnO | 0.5 |
| $K_2O$ | 0.9 | CuO | 0.2 |
| CaO | 4.1 | S | 2.6 |
| MgO | 1.9 | C | 0.3 |
|  |  | Others | 5.6 |

TABLE II Grain-size distribution of sewage sludge incinerated ash

| Grain size (μm) | (wt %) |
|---|---|
| $> 125$ | 0.0 |
| 62–125 | 6.2 |
| 31–62 | 22.2 |
| 16–31 | 22.1 |
| 7.2–16 | 16.2 |
| $< 7.2$ | 33.3 |

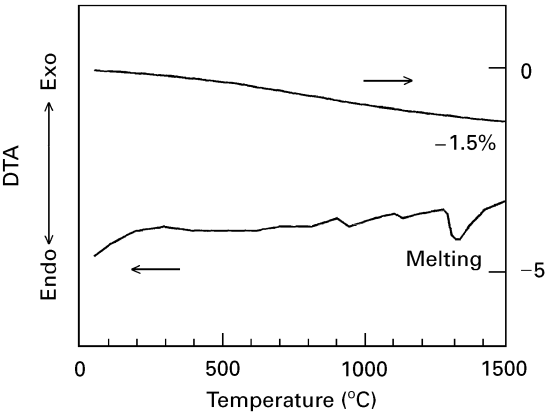

*Figure 1* TG–DTA curves of sewage sludge incinerated ash.

10 °C $min^{-1}$, and maintained for 1 h at 800 °C for nucleation and then held at 1000–1200 °C for 1–8 h to promote crystallization.

After annealing, the manufactured original glass and glass-ceramic were analysed using X-ray diffraction, differential thermal analysis, scanning electron microscopy, and thermodilatometry. Hardness was based on the Japan Industrial Standard M-0302 using a sample of 20 mm diameter and 40 mm height. Acid resistance was tested for the amount of weight reduction after being kept for 650 h at 25 °C in a 1% $H_2SO_4$ solution using a 15 mm × 15 mm × 10 mm sample.

## 3. Crystallization process

By melting sewage sludge incinerated ash containing a limestone additive, $CaO–Al_2O_3–SiO_2$-type glass is formed. Sewage sludge incinerated ash contains iron, sulfur, and carbon. As iron and sulfur are assumed to form many kinds of compounds, assuming that those compounds exist as ferric oxide or sodium sulfate, iron sulfide is generated as shown in Reactions 1–3 in the melting and heat-treatment processes.

$$Na_2SO_4 \rightarrow Na_2O + SO_3 \quad (1)$$

$$SO_3 + 3C \rightarrow S + 3CO \quad (2)$$

$$2Fe_2O_3 + 4S \rightarrow 4FeS + 3O_2 \quad (3)$$

For sulfur and carbon to remain in the glass, melting should occur in a reducing atmosphere. That is, as shown in Fig. 2, iron sulfide colloid is formed when the sulfur bonds with iron at a low temperature of about 800 °C during the heat-treatment process. For crystallization of $CaO–Al_2O_3–SiO_2$-type glass, iron sulfide works [7] effectively as a nucleant. When the temperature increases further to a high temperature above 1100 °C, a columnar crystal, anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$), etc., generates homogeneous nucleation in the glass. The glass-ceramic with homogeneous nucleation and columnar crystals is known to exhibit very high strength. The formation model of the crystallization process is shown in Fig. 3.

## 4. Results and discussion

Sewage sludge incinerated ash and the batch melted easily, producing a shiny black glass. The black colour was due to the iron, sulfur and carbon in the incinerated ash. Because this glass contained a large volume of iron and its viscosity was low, the crucible tended to

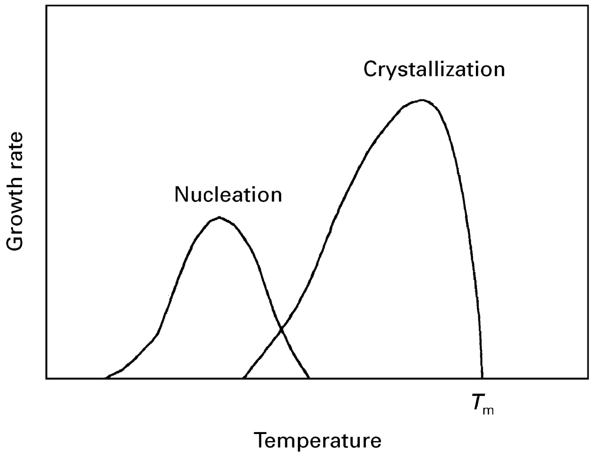

*Figure 2* Relationship between crystal growth and temperature.

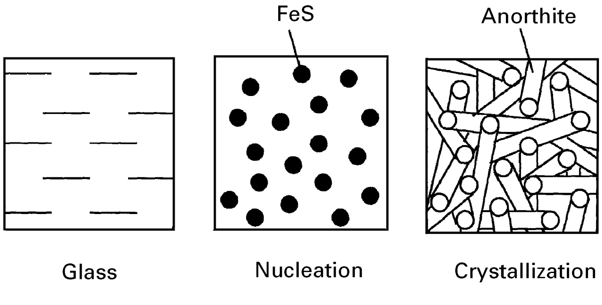

*Figure 3* Schematic illustration of the crystallization process of glass.

corrode easily, so the amount of alumina in the acquired glass-ceramic was found to increase from 1%–2% more than the calculation.

In the oxidizing atmosphere of the electric furnace, keeping open the cover of the crucible or having a space between the cover and the crucible caused the sulfur and carbon to oxidize and vaporize, so that even when the glass was heat treated, crystal nucleation of iron sulfide did not occur. In this case, crystals precipitated from the surface of the glass and grew inwards. Such crystals undergoing orientation showed low strength, because they cracked easily when hammered. Microscopic examination showed cavities in the fracture surface of the glass-ceramic.

When the crucible was sealed completely, the melted glass was kept in a reducing atmosphere and crystal nucleation of iron sulfide was generated by heat treatment. As a result, by precipitating homogeneous crystals all over the glass, a glass-ceramic could be obtained. The glass exhibited a high strength, because hammering did not break the glass easily.

For crystal nucleation of iron sulfide to occur, maintaining the temperature at 800 °C for 1 h was sufficient. Crystal nucleation was found to occur only on slow cooling and increasing the temperature. $P_2O_5$ is known remarkably to promote the speed of crystal nucleation [8], and because sewage sludge incinerated ash also contains a few per cent of $P_2O_5$, crystal nucleation can be assumed to occur quickly. Heat treatment for 2–4 h at 1100 °C was required for crystal precipitation and sufficient crystal growth. When heat treatment was over 8 h, various crystals other than anorthite precipitated, and cavities developed with increasing crystallization; therefore, the strength of glass-ceramic tended to decrease. Fig. 4 shows the conditions suitable for heat treatment.

When the weight per cent of limestone additive was less than 30% of the sewage sludge incinerated ash, the precipitation would be deficient in anorthite crystal. When the limestone additive was over 70%, crystals would begin to precipitate in the melting or refining stage, so moulding would be difficult. When limestone additive was 40%–60%, crystals did not start to precipitate before moulding, therefore a glass-ceramic with a high strength of 30%–50% crystallinity was obtained by heat treatment. X-ray diffraction showed anorthite to be the main crystal of this glass-ceramic, but also showed precipitation of small quantities of other unidentified crystals.

When limestone alone was added to the sewage sludge incinerated ash, crystallization occured easily, because the ratio of network formation oxide (such as silicic acid) was small and the viscosity low, therefore, under different heat-treatment conditions from those in Fig. 4, brittle glass-ceramic was formed. When observing the cross-sectional diagram, crystals other than anorthite precipitated from the surface, decreasing the fluidity of the glass, and a void, were generated, together with internal crystal growth.

When an appropriate amount of silica sand was added together with the limestone, a stable, high-strength glass-ceramic was produced even under changing heat-treatment conditions. When there was surplus silica sand, the viscosity increased and crystal formation was not processed, but by adding a small amount of soda ash, the viscosity became the right consistency to form good-quality glass-ceramic.

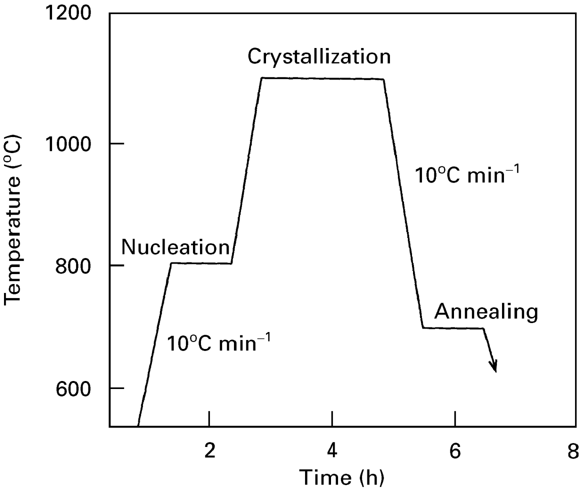

*Figure 4* Heat-treatment schedule.

When using dolomite conditioning material instead of limestone, the same tendency of crystallization as with limestone was confirmed. When 40%–60% dolomite dosage was added to sewage sludge incinerated ash, a high-strength glass-ceramic was produced with 30%–50% crystallinity. X-ray diffraction showed precipitated crystals to be anorthite, diopside, and forsterite, all being prismatic. When hammered or cut with a diamond cutter, it was found that the glass-ceramic was higher in strength and hardness than that produced with a limestone additive.

Table III shows examples of proper conditions of component control. When plotting the main components CaO, $Al_2O_3$, $SiO_2$ of conditions 1–3 on the equilibrium diagram for three components [9], it was found that all fit into the region of anorthite, as shown in Fig. 5, on the condition that the three components totalled 100%.

## 5. Properties of glass-ceramics

The results of the characteristic test are given below when producing a glass-ceramic tile using condition 1 of controlled composition in Table III, which is the lowest cost for raw material, that is, with a 2 : 1 proportion of sewage sludge incinerated ash and limestone.

The chemical composition of the developed product is shown in Table IV and the main components are silicic acid, alumina and lime. From the small amount of silicic acid and phosphoric acid as oxide, totalling 42.1%, it can be considered that alumina, iron and titanium also work effectively for network formation. From the X-ray diffraction chart of Fig. 6, the main crystal can be confirmed to be composed of anorthite with a crystallinity of about 40%. When all the alumina, (the smallest amount of the three main components) is assumed to migrate to the anorthite crystal, then the crystallinity is about 40%; however, a number of unidentified crystals other than anorthite

TABLE III Examples of good batch composition (weight ratio)

| Material | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Sewage sludge incinerated ash | 100 | 100 | 100 | 100 | 100 |
| Limestone | 50 | 50 | 60 | | |
| Dolomite | | | | 50 | 60 |
| Silica sand | | 10 | 30 | | 20 |
| Soda ash | | | 10 | | 10 |

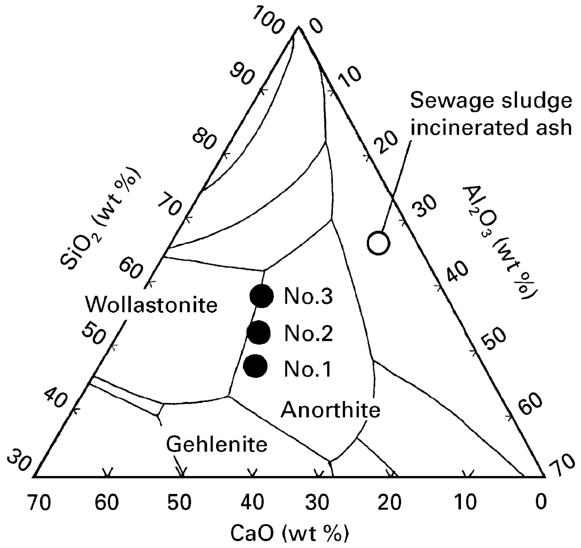

*Figure 5* Phase equilibrium diagram of the CaO–$Al_2O_3$–$SiO_2$ system.

TABLE IV Chemical composition of glass-ceramic

| Component | (wt %) | Component | (wt %) |
|---|---|---|---|
| $SiO_2$ | 37.7 | $TiO_2$ | 1.4 |
| $Al_2O_3$ | 14.6 | $MnO_2$ | 0.3 |
| $Fe_2O_3$ | 6.7 | $P_2O_5$ | 4.4 |
| $Na_2O$ | 0.5 | ZnO | 0.4 |
| $K_2O$ | 0.7 | CuO | 0.2 |
| CaO | 25.1 | S | 2.0 |
| MgO | 1.5 | C | 0.2 |
| | | Others | 4.4 |

should exist. The highest peak in Fig. 6 is presumed to be overlapping of a number of crystal peaks, such as apatite.

From the thermal expansion curve of Fig. 7, the glass-ceramic compared to the original glass showed a smaller thermal expansion coefficient, and showed no change even at high temperature. That is, crystallization greatly improved the heat resistance and thermal shock resistance, due to the low thermal expansion coefficient of the anorthite crystal at $40 \times 10^{-7}\,°C^{-1}$, and the high melting point of 1550 °C.

Fig. 8 shows the photograph of the fractured section of glass-ceramic taken with the scanning electron microscope. Numerous prismatic crystals (anorthite), 0.5 μm × 0.5 μm × 2 μm are entangled and precipitated.

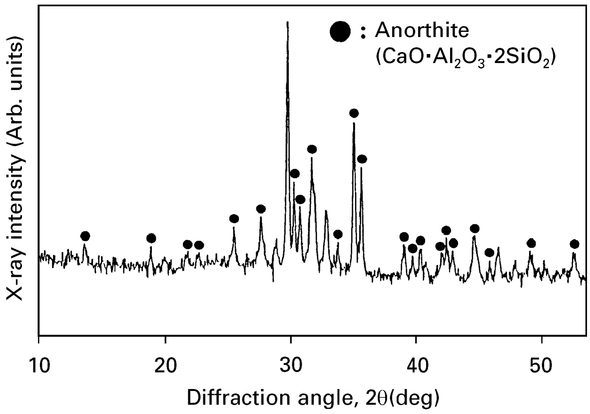

*Figure 6* Powder X-ray diffraction pattern of glass-ceramic 1.

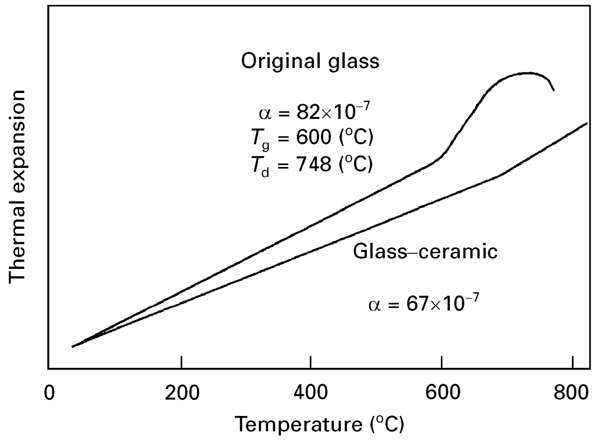

*Figure 7* Thermal expansion curves of glass-ceramic 1.

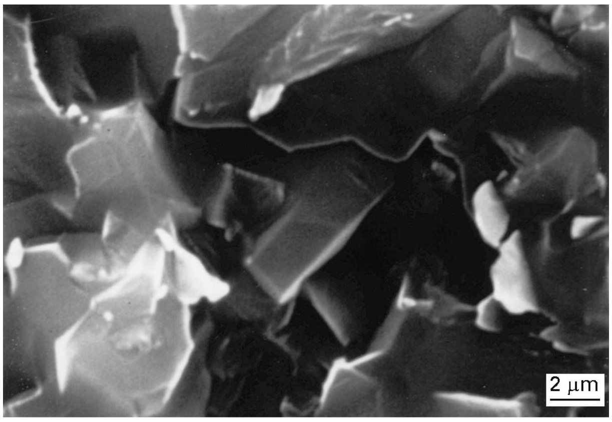

*Figure 8* Scanning electron micrograph of glass-ceramic 1.

Fig. 9 shows the glass-ceramic tile sample. Shiny black original glass becomes brown glass-ceramic on heat treatment. The uneven surface was due to the shrinkage accompanying crystallization. On polishing this dark-coloured material, a beautiful marble-like pattern appeared. This can add a high-value to a high-quality material for construction.

Table V shows the physical and chemical properties of the development product compared with natural stone. The developed product shows especially high strength and superior acid resistance.

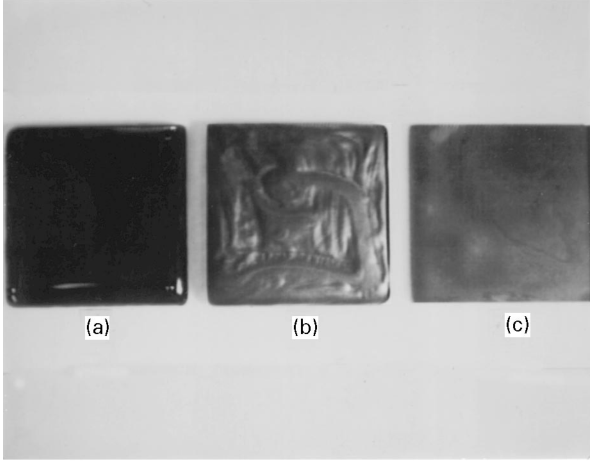

*Figure 9* Experimentally made tile. (a) Original glass, 1; (b) glass-ceramic 1, (c) polished glass-ceramic 1.

TABLE V Properties of glass-ceramic and natural stone

| Item | Glass-ceramic | Granite |
|---|---|---|
| Modulus of rupture (kg cm$^{-2}$) | 500 | 150 |
| Density (g cm$^{-3}$) | 3.0 | 2.7 |
| Moh's hardness | 6 | 5–6 |
| Thermal expansion coefficient (10$^{-7}$ °C$^{-1}$) | 67 | 50–150 |
| Acid resistance (wt loss %) 1% $H_2SO_4$ 25 °C, 650 h | 0.1 | 1.0 |
| Water absorption (%) | 0.00 | 0.35 |

## 6. Conclusions

1. A glass-ceramic with homogeneous anorthite prismatic crystal was formed by blending an ash batch sample of 100 wt % sewage sludge incinerated ash with 50 wt % limestone.

2. This glass-ceramic was high in strength and superior in acid resistance, and has been shown to be a good material for construction purposes.

3. From the batch substituting dolomite for limestone, a glass-ceramic that is high in strength and superior in acid resistance also was obtained. The main homogeneous crystals were anorthite, diopside, and forsterite.

4. Without adding a crystallization catalyst, iron, sulfur, and carbon were contained in sewage sludge incinerated ash, therefore crystal nucleation of iron sulfide was possible when melted in a reducing atmosphere.

5. When adding a small amount of silica sand to the batch, the network formation oxide increased, therefore promoting easier glass-ceramic formation.

## Acknowledgement

The authors thank Professor Umegaki Takashi, Tokyo Metropolitan University, Faculty of Engineering, for his assistance.

## References

1. Tokyo Metropolitan Sewerage Bureau, "Annual Technical Report".
2. Y. TANAKA and T. KATO, *J. Ceram. Soc. Jpn* **86** (1978) 559.
3. E. M. RABINOVICH, in "The Fifth Conference on Mineral Engineering", Israel (1980) p. 108.
4. *Idem*, *Adv. Ceram.* **4** (*Nucl. Cryst. Glasses*) (1982) 334.
5. Y. MA and B. SUN, *J. Non-Cryst. Solids* **52** (1982) 541.
6. M. PELINO, C. CANTALINI, F. VEGLIO and P. P. PLESCIA, *J. Mater. Sci.* **29** (1994) 2087.
7. N. M. PAVLUSHKIN, "Osnovy Tekhnologii Sitallov (Introduction to Technology of Glass-Ceramics)" (Stroiizdat, Moscow, 1970).
8. H. HARPER and P. W. McMILLAN, *Phys. Chem. Glasses* **13** (1972) 97.
9. E. E. OSBORN and A. MUAN, "Phase Diagrams for Ceramists" (American Ceramic Society, 1964) p. 210.

*Received 16 February*
*and accepted 31 July 1996*