Use of Ceramics, Glass and Other Materials in the Disposition of Nuclear and Hazardous Wastes
Organized by S. Marra, and J.E. Marra
Materials Science and Technology (MS&T) 2006: MATERIALS AND SYSTEMS - Volume 2

Recycling of municipal waste slag using phase separation of glass

T. Imaoka[1], S. Sakida[2], T. Nanba[1], Y. Miura[1]

[1]Department of Environmental Chemistry and Materials, Okayama University
3-1-1, Tsushima-Naka, Okayama 700-8530, Japan
[2]Health and Environment Center, Okayama University
3-1-1, Tsushima-Naka, Okayama 700-8530, Japan

Keywords: slag, recycling, colorless glass, phase separation

Abstract

A novel recycling process of municipal waste slags was developed by using a phase separation of borosilicate glass. B_2O_3 was added to a simulated waste slag to promote the phase separation. The slag glasses were heat-treated above glass transition temperatures, from which phase separation was successfully induced. In the phase-separated slag glasses, small droplets formed by the nucleation and growth process were observed in high B_2O_3 specimens heated at higher temperatures. The spinodal decomposition was also confirmed mostly in low B_2O_3 specimens. The slag glasses were colored in brown or black due to Fe ions, and after soaking in acid, they were bleached, obtaining colorless solids. According to EDX analyses, no Fe ions were confirmed in the remaining insolubles, indicating that Fe ions were preferentially incorporated into the borate-rich phases soluble in acid. The main constituent of the colorless solids was SiO_2, and the end products obtained in the present process were expected as an alternative of pure silica glass.

1. Introduction

In Japan, nonindustrial wastes such as municipal wastes have been disposed of with incineration. However, endocrine disrupters such as dioxin have been exhausted from the incinerators together with the gas and fly ash, which became a serious social problem. As a countermeasure against the dioxin problem, an incineration method melting wastes at high temperature has been introduced. Dioxin are decomposed at high temperature, and the wastes are finally discharged as glassy melt slags. The slags are reused as aggregates such as asphalt paving, concrete product, interlocking block. In this way, 2/3 of the discharged slags are reused, but the residuals are sent for landfill disposals. The amount of slag emissions is increasing yearly, and new recycling routes other than the reuse as aggregates are anticipated.

The main constituents of waste slags are SiO_2, CaO and Al_2O_3, and due to Fe_2O_3 present in ~10%, the slags are colored black. If Fe_2O_3 is selectively removed from the slags, colorless glass should be obtained, which is expected as an ingredient of plate glasses. It will be a new recycling route of waste slags. In the present study, a novel removal method of Fe ions from waste slags has been developed, where phase separation of glass was used.

It is well known that alkali borosilicate glasses separate into two glassy phases, that is, silica-rich and alkali borate-rich phases [1,2]. Fe ions prefer basic environment rather than acidic one, and hence Fe ions present in alkali borosilicate glasses preferentially enter into alkali borate-rich phase. Alkali borate

phase is easily dissolved in acid, and it is therefore expected that if Fe-containing borosilicate glass is soaked in acid after phase separation, Fe-free colorless silica glass is obtained. However, waste slags contain no B_2O_3 component as ingredient, and hence B_2O_3 should be added to waste slags to promote phase separation. As for waste glasses, a recycling method using the phase separation has been proposed [3].

In the present study, B_2O_3-containing slag glasses were prepared by adding B_2O_3 to a simulated Fe-containing waste slag prepared from reagents, and phase separation behavior due to heat treatment was observed. Finally, it was examined whether Fe ions were removed from the phase-separated slag glass by acid treatment.

2. Experimental Procedures

The schematic experimental procedure is shown in Figure 1. Firstly, a simulated municipal waste slag with the chemical composition of $SiO_2 : CaO : Al_2O_3 : Fe_2O_3 : Na_2O = 43 : 25 : 17 : 8 : 7$ (mass%) was prepared from reagents. The mixture was calcined in a Pt crucible at 1000 °C for 30 min and melted at 1600 °C for 30 min. The melt was press-quenched, obtaining the simulated slag. Secondly, B_2O_3 was added to the powdered slag, and the mixture was melted at 1600 °C for 30 min. By quenching the B_2O_3-containing slag melt, slag-derived glass was obtained. Next, for phase separation, the slag-derived glass was heat-treated at the temperatures higher than the glass transition temperature, Tg, which was determined by differential thermal analysis, DTA. The surface and cross-section of the heat-treated glass were observed by scanning electron microscopy, SEM. The heat-treated glass was soaked in hydrochloric acid, and the borate-rich phase was dissolved by the acid treatment. The residual solids were filtered, rinsed in water and dried in a dry oven, obtaining the end product. Compositional analyses were performed with energy dispersion X-ray spectroscopy, EDX. Optical absorption was evaluated from diffuse reflectance spectra by using powdered specimens.
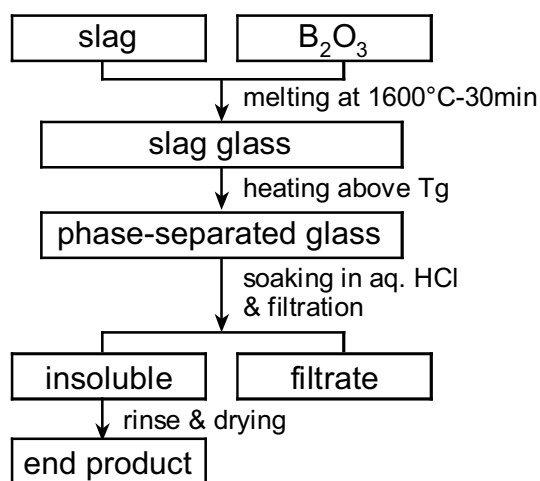

Figure 1: Schematic flow of slag recycling process.

3. Results and Discussion

3.1 SEM Observation of the Phase-Separated Slag Glasses

Figures 2 ~ 4 show the SEM photographs of the B_2O_3-containing slag glasses after the heat treatments under various conditions. As shown in Figs. 2(a) ~ (c), the droplets are found in the slag glasses containing 30 mol% B_2O_3, and the growth of the droplets is clearly confirmed with the prolongation of the heat treatment time, indicating the phase separation of the slag glasses by the nucleation and growth process. The dependence of the heat treatment temperature is shown in Figs. 2(d) ~ (f), where the size of the droplets is 3 ~ 5 μm and is not so different between the specimens heated at different temperatures. In the specimen heated at the lowest temperature shown in Fig. 2(a), larger droplets ~ 10 μm also appear among the smaller droplets. Hence, further growth is expected after the longer heat treatment at lower temperatures.

As shown in Figures 3(a)~(c), the droplets are also found in the slag glasses containing 20 mol% B_2O_3 after the heat treatments at 600 °C, and the growth of the droplets is, however, not confirmed even after the longer heat treatments. As shown in Fig. 3(d), different phase separation is observed in the specimen heated just below Tg, in which micro droplets seem to aggregate just like long leaves. Therefore, the phase separation at 580 °C is associated with the spinodal decomposition due to the diffusion limited aggregation [4,5].

As shown in Figures 4(a) ~ (b), the phase separation by the spinodal decomposition is also confirmed in the slag glasses containing 10 mol% B_2O_3.

In general, the viscosity of glasses at around glass transition temperatures is higher than melts, and hence the migration of atoms to the energetically stable positions is restricted and it takes a longer time. It is also the case in phase separation of glasses, that is, massive movement of atoms is required during the phase separation. It is therefore supposed that heat treatment near the glass transition temperatures prevents the progress of phase separation. Actually, only the insignificant phase separation was observed in the slag glasses containing 30 mol% B_2O_3 when heat-treated at 10 °C above Tg. In the slag glasses containing 30 and 20 mol% B_2O_3, the phase-separated droplets are commonly observed after the heat treatment at 600 °C, and the growth rate of the droplets is, however, much faster in the slag glass containing 30 mol% B_2O_3 with lower Tg.

In the phase separation due to nucleation and growth, concentration gradient between the separated phases is constant, and no compositional change occurs with isothermal treatments. In the slag glasses with lower B_2O_3 content, it must be difficult to keep a constant concentration gradient at around the phase boundaries, and hence the phase separation by spinodal decomposition seems favorable, because in spinodal decomposition the compositions of the separated phases change as time passes.
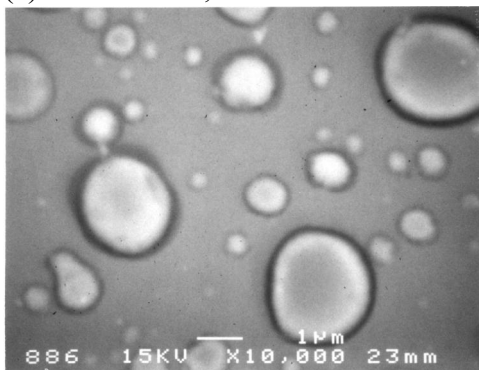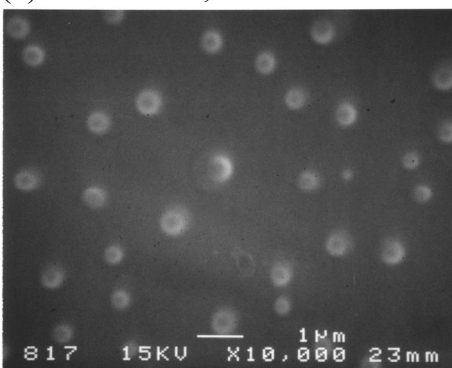
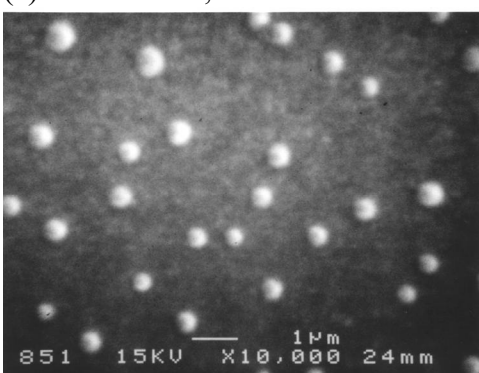(a) 600 °C–2 hr, surface
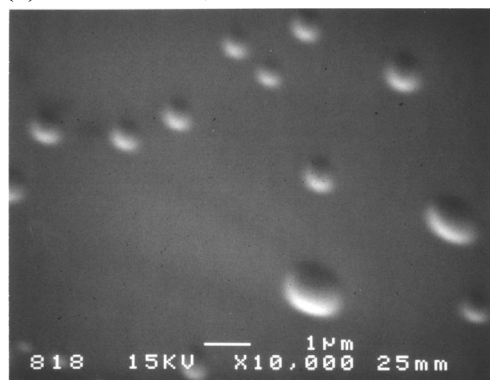
(b) 600 °C–3 hr, surface
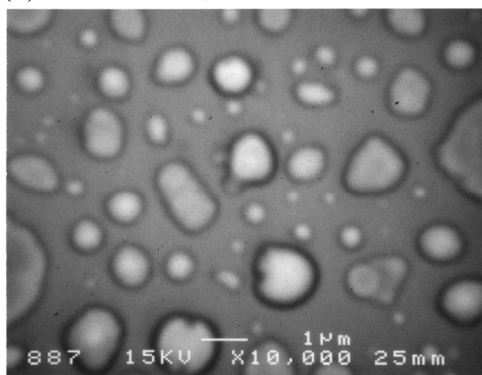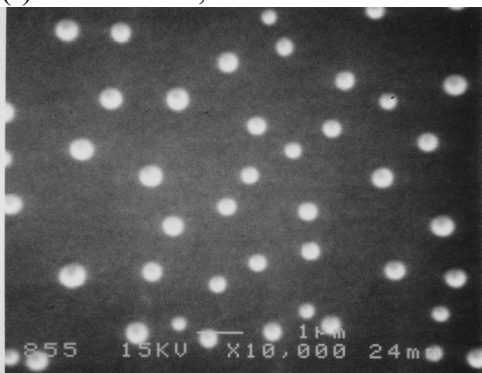
(c) 600 °C–8 hr, surface

(d) 620 °C–2 hr, surface

(e) 680 °C–2 hr, surface
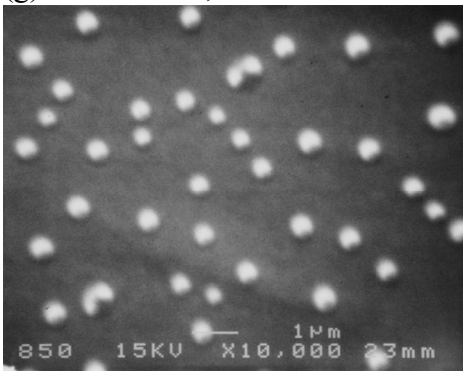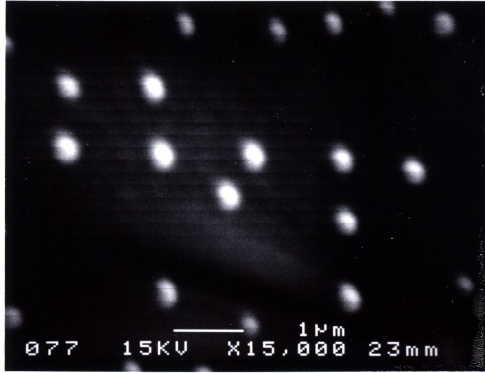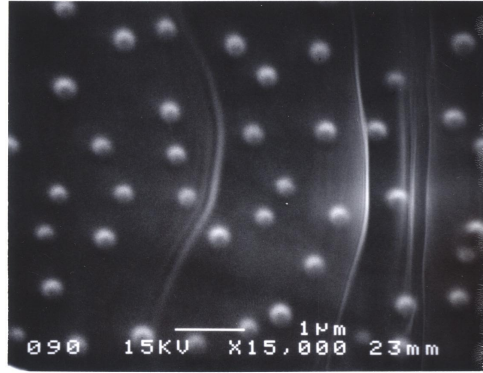
(f) 680 °C–2 hr, cross section

(g) 700 °C–2 hr, surface

Figure 2: SEM photographs of the slag glasses containing 30 mol% B_2O_3 (T_g = 570 °C) after the various heat treatments.
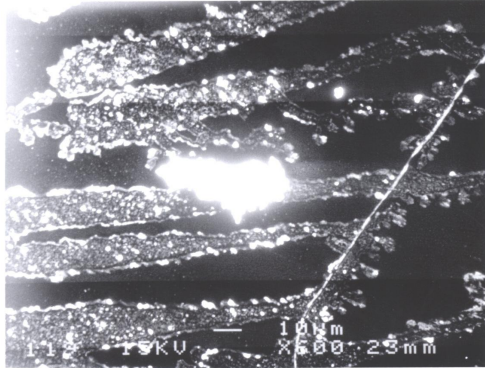
(a) 600 °C–3 hr, surface

(b) 600 °C–8 hr, surface
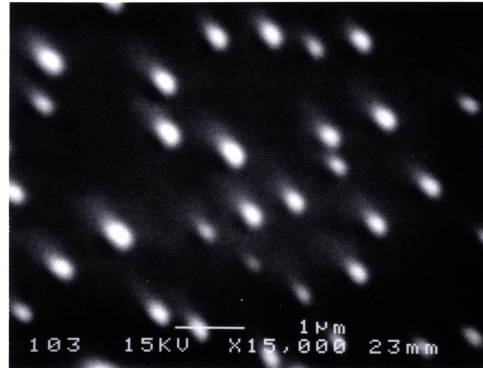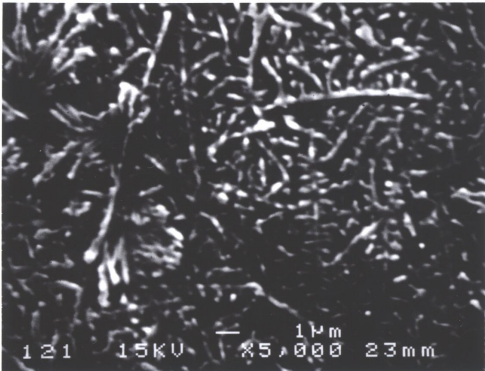
(d) 580 °C–2 hr, surface

(c) 600 °C–10 hr, surface

Figure 3: SEM photographs of the slag glasses containing 20 mol% B_2O_3 (T_g = 585 °C) after the various heat treatments.

(a) 600 °C–8 hr, surface

(b) 600 °C–10 hr, surface

Figure 4: SEM photographs of the slag glasses containing 10 mol% B_2O_3 (T_g = 600 °C) after the various heat treatments.

3.2 Composition of the Phase-Separated Slag Glasses

Figure 5 shows the analytical compositions of the slag glasses containing 30 mol% B_2O_3, where the contents of B and O are excluded in Fig. 5 because they are trustless in EDX. As shown in Fig. 5(a), indispensable amount of Fe is confirmed in the slag glass before the heat treatment for phase separation. In Fig. 5(b), however, Fe atoms are not detected in the insoluble solids after soaking in aq. HCl. It is also noted that the drastic decrease in the amounts of Na, Ca and Al is achieved in addition to the removal of Fe. Thus, the insoluble end product is almost pure SiO_2 glass. In other slag glasses after the heat treatment and acid soaking, Fe and Ca are not detected and small amounts of Na and Al are confirmed other than Si, O and B in EDX. It is therefore concluded that high silica glass is successfully prepared from the B_2O_3-containing slag glasses by using the phase separation technique.
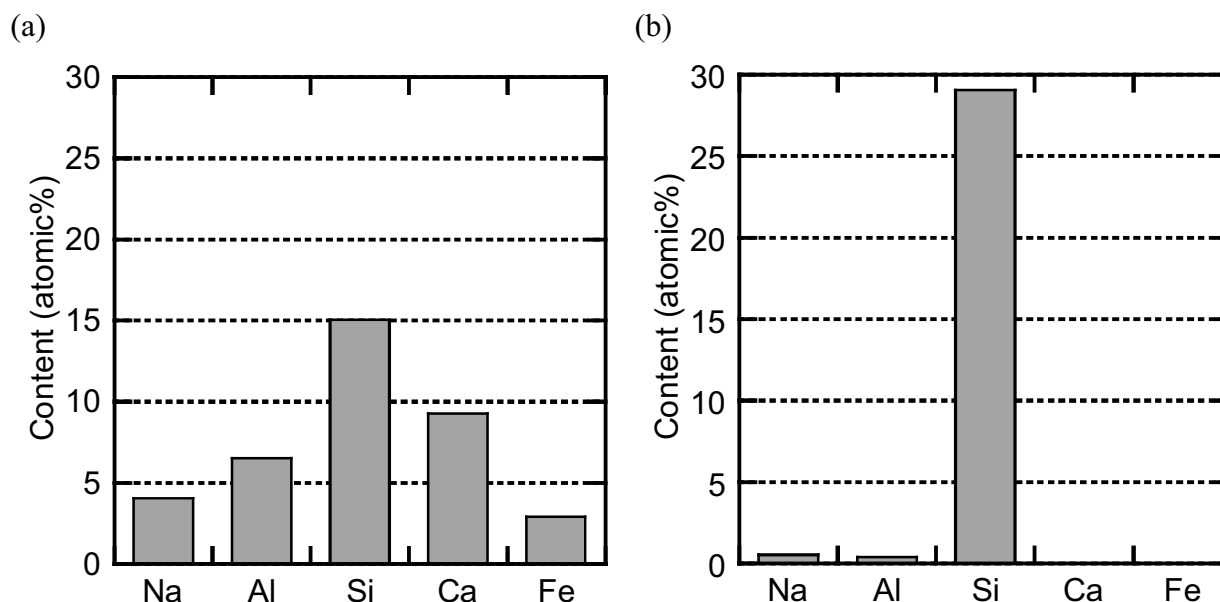

Figure 5: Analytical composition of the slag glasses containing 30 mol% B_2O_3.
(a) before the heat treatment, (b) after heat treatment at 630 °C–3 hr and acid treatment.

The acid soaking was carried out by using the powdered specimens to promote the dissolution of borate-rich phases, and hence the optical absorption was evaluated by diffuse reflectance spectroscopy. As shown in Figure 6(a), the optical absorption edges are located at 2 ~ 3 eV in the slag glasses before phase separation, and the absorption edge moves to larger energy side with increasing B_2O_3 content in the slag glass. As shown in Fig. 6(b), no significant absorption is observed within the region of 0.5 ~ 6.0 eV in the end products after acid treatment (notice the difference in the vertical scale between Figs. 6(a) and (b)). With increasing the heat treatment time, the absorption in the region above 4 eV reduces, indicating the elimination of impurities from the silica phase.
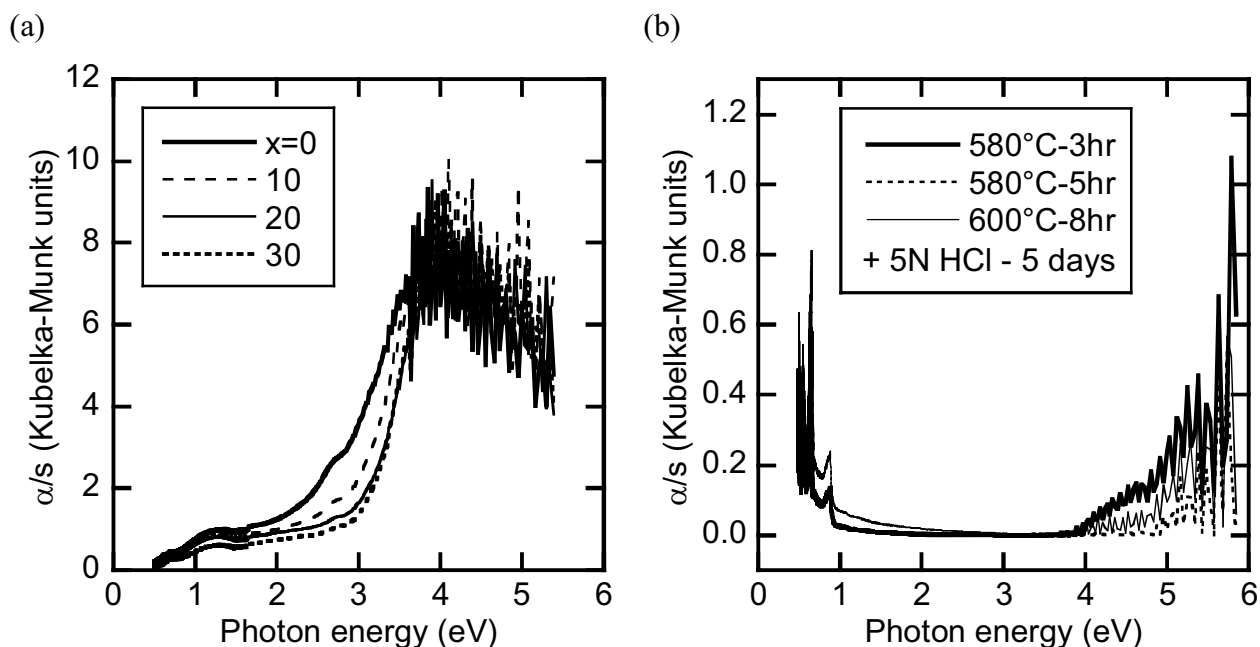
Figure 6: Optical absorption spectra of (a) the slag glasses containing x mol% B_2O_3 before phase separation and (b) the insoluble end products obtained from the slag glass containing 20 mol% B_2O_3 after the heat treatment and the subsequent acid treatment.

Change in color of the slag-derived specimens is shown in Fig. 7. The absorption of visible region below 3 eV seems to be small from Fig. 6(a), but it is obvious from Figs. 7(a) and (b) that the simulated waste slag and B_2O_3-containing slag glass are exactly intense black. As shown in Fig. 6(b), the bleached specimens indicate no absorption below 6 eV, and the end products are therefore expected as an alternative of silica glass.
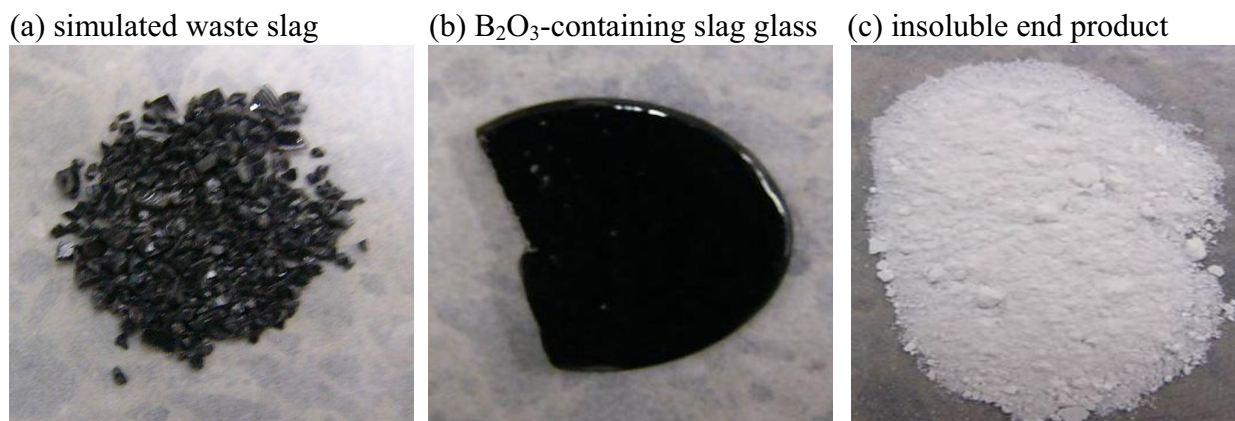

Figure 7: Photographs of the typical specimens prepared in the present study.

In acid treatment, HCl concentration has been changed 10 N, 5 N and 2.5 N. The dissolution rate was not so different between the normalities of 5 N and 2.5 N, and the dissolution in 10 N HCl aqueous solution was slowest. In the view point of environmental burdens, the use of weak acids such as acetic acid is desirable. Furthermore, the cyclic use of B_2O_3 is also desired. It must be a subject of future investigation.

4. Conclusion

A new recycling process of the municipal waste slags was developed. The glasses were prepared from a simulated waste slag by adding B_2O_3. By heating the slag glasses above their respective glass transition temperatures, phase separation was successfully induced, where phase separation processes by nucleation and growth and spinodal decomposition were both observed, which was dependent on the B_2O_3 content and heat treatment temperature. It was found in the slag glasses containing larger amount of B_2O_3 that phase separation due to nucleation and growth preferentially took place and the rate of phase separation was faster than the slag glasses with lower B_2O_3 content. The slag glass specimens were brown or black due to Fe ions, and after the acid treatment in aq. HCl, however, the specimens were bleached to obtain white powders. In the bleached powders, no Fe and Ca atoms were detected by EDX analyses, and the constituent was mostly SiO_2 in every specimen investigated in the present study. Furthermore, no significant optical absorption was observed in visible to ultraviolet region below 6 eV, and the end products were expected as an alternative of silica glass.

References

1. R.J. Charles, F.E. Wagstaff, "Metastable Immiscibility in the B_2O_3–SiO_2 System," J. Am. Ceram. Soc., 51 (1968) 16-20.

2. W. Haller, D. H. Blackburn, F. E. Wagstaff, R. J. Charles, "Metastable Immiscibility Surface in the System Na_2O-B_2O_3-SiO_2," J. Am. Ceram. Soc., 53 (1970) 34-39.

3. D. Chen, H. Masui, T. Akai, T. Yazawa, "Decoloration of waste colored glass through phase-separation and its mechanism," J. Aust. Ceram. Soc., 38(2), (2002) 130-134.

4. R.H. Doremus: Glass Science, Wiley (1973) 44.

5. O.V. Mazurin, E.A. Porai-Koshits, "Phase Separation in Glass," (O.V. Mazurin, E.A. Porai-Koshits ed.), Morth-Holland, (1984) 163.