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Sodium borosilicate glass produced from coal fly ash upon vitrification in an induction-melting furnace

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Sodium borosilicate glasses were produced from coal fly ash and their properties were investigated. Fly ash could be vitrified completely by induction heating at 1500℃ for 30 min with Na_2O or B_2O_3 additions of more than 10 wt.%. The induction furnace incorporated a new method, namely, induction susceptor heating and employed a cyrindrical graphite rod as the susceptor that could efficiently capture the electromagnetic energy. The alkali borosilicate glasses produced had Vickers microhardness of 3000-4000 MPa, bending strength of 30-40 MPa and indentation fracture toughness of 0.7-1.1 MPa· $m^{1/2}$. With suitable Na_2O and B_2O_3 addition, their melting points decreased down form 1500℃ to less than 1200℃. Finally, their chemical resistances against acid leaching indicated that heavy metals were immobilized well under environmental regulation. Therefore, alkali borosilicate fly ash glasses should be recycled as materials with good chemical resistance.

Key words: fly ash, alkali borosilicate glass, vitrification, induction furnace, susceptor

1. INTRODUCTION

Fly ash is defined as the fine mineral residue resulting from the combustion of coal in an electric power plant. Ash is usually generated in the range of 4~25 wt.% of the total coal used [1]: approximately 90 wt.% of this ash is fly ash and the rest is called bottom ash. Fly ash consists of the unburned inorganic materials that exist in coal fused during the combustion. Since the fly ash particles are collected by an air pollution control (APC) system while they are suspended in the exhaust gases, they are generally spherical. Fly ash consists mostly of silicon dioxide (SiO_2), aluminum oxide (Al_2O_3) and iron oxide (Fe_3O_4) and it also contains various heavy metals such as Cr, Cd, Cu, Pb, Mn, Ni, Co, etc. Such heavy metals are toxic and dangerous to human beings and an ecosystem. Therefore, fly ash should be stabilized in order to prevent the environmental impact its exposure would cause. This necessitates an appropriate treatment process. The vitrification treatment effectively immobilizes heavy metals in glass matrix, and it can therefore solve the abovementioned problem. However, the vitrification treatment is extremely energy-consuming. Thus, vitreous fly ash should be recycled in the manufacture of glass-based articles such as tiles [2], fibers [3], glass-matrix composites [4], spheroidal beads [5] and high voltage insulators [6].

Borosilicate glass is widely used as a chemical resistant material especially, for the sequestration of nuclear waste [7]. This glass may be also one of the suitable applications for recycling of the vitreous fly ash. Particularly, Alkali borosilicate glass is interesting because its phase separation yields a porous glass through acid leaching, thereby enabling the control of the physical properties of borosilicate glass. This decomposition was exploited by the Corning Glass Works in the form of a technology known as the Vycor process. For this process, alkali borosilicate glass is heat-treated at around 500-600℃. Its compositions are separated from a mixing phase and an interconnecting microstructure forms. It is then immersed in 3N H_2SO_4 at about 90℃ to dissolves the continuous sodium borate phase and yield a 96% silica skeleton. Finally, fine droplet structure was made in the glass. Pore diameter of the glass is about 20-50Åand total porosity is roughly 25-40%. Such fine droplet structure would allow vitreous fly ash to recycle as new application, as well as a high chemical resistance.

In addition, an advanced melting furnace has also given an economical advantage to the vitrification treatment. Especially, an induction furnace is a valuable tool of providing fast, consistent and uniform heat for melting a variety of wastes. However, the wastes comprising only plastic or non-conductive materials cannot be heated by using an induction furnace. Accordingly, the fly ash vitrification process must incorporate with susceptor heating using conductive materials. An electrically conductive susceptor can heat such wastes very effectively because it is used to capture the electromagnetic energy. Although technically advanced, the induction furnace with a susceptor has yet high electrical energy consumption because a water-cooling coil around a crucible leads to significant energy loss.

This study reports the conversion of fly ash to alkali borosilicate glass in the first step for the production of a porous glass. The effects of fly ash - as a SiO_2 resource - on the physical and chemical properties of alkali borosilicate glass have also been investigated. Moreover, the induction furnace is introduced in a new process of susceptor heating that can enhance the energy efficiency of the vitrification process.

2. EXPERIMENTAL

The coal fly ash used in this study was collected from a coal-fired power station in Fukushima, Japan. The fly ash was a fine powder that contained almost spherical particles. This was mixed several times by hand to make the mixture as homogeneous as possible. The chemical composition of the fly ash was analyzed using an X-ray fluorescence (XRF) spectroscope and an inductively

Table I Chemical composition of coal fly ash

Chemical composition (wt.%)										
SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	Na_2O	MgO	P_2O_5	MnO	LOI
75.625	16.393	3.051	0.858	0.818	0.695	0.392	0.353	0.013	0.78	2.195
Heavy metals (ppm)										
Cd	Cr	Cu	Mn	Ni	Pb	Co	Sr	Li		
<10ppm	119.6	91.52	297.4	87.51	<10ppm	117.6	665.1	464.0		

coupled plasma (ICP) spectrometer. Table I shows that the fly ash mainly contained Si, Al and Fe – together they constituted more than 95 wt.% of the total fly ash weight. X-ray diffraction (XRD) patterns were obtained at 30kV, 20mA with a scan speed of 4°/min over the 2Θ values of 10°~80° at a step interval of 0.05°, using the Cu Kα radiation. In the fly ash, crystalline compounds were present in the form of oxide minerals consisting of major elements: quartz, mullite and magnetite (Fig. 1).

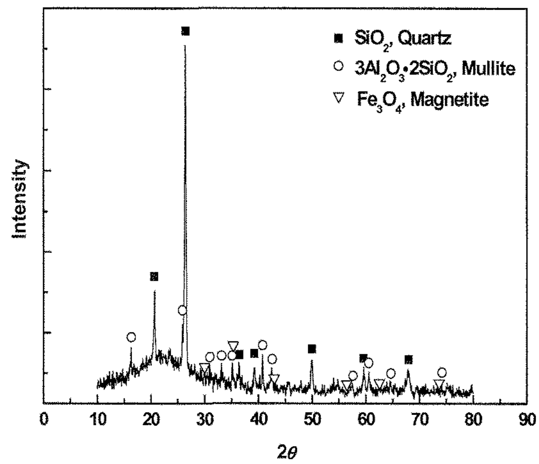


Fig. 1 XRD pattern of fly ash

As shown in Fig. 2, the induction-melting furnace (20kW, 30kHz) was coupled with a graphite susceptor installed at its center. This arrangement minimized the heat loss caused by the water-cooling line. In this system, the fly ash surrounding the graphite susceptor acted as a good thermal insulator. The solenoid coil of the furnace consisted of 12-turns of copper tube (Φ = 10 mm). The coil had a diameter of 110 mm and height of 120 mm. A detailed numerical analysis of the induction furnace is in progress and will be reported elsewhere.

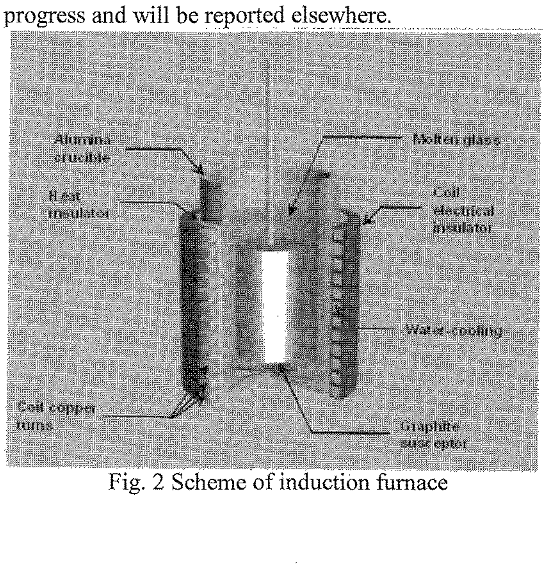


Fig. 2 Scheme of induction furnace

Alkali borosilicate glasses were prepared from coal fly ash mixed with the desired ratio of the reagents mixed Na_2CO_3 and B_2O_3. For good workability, considering the viscosity of the melts, the total amount of reagents was maintained constant at 30 wt.%. The mixtures were melted by heating them at 1500℃ for 30 min in an alumina crucible. The melts were poured onto a copper plate in air and allowed to solidify, thus forming a glass. The glasses so formed were then annealed at 650℃ for 1 h and slowly cooled down to room temperature.

The mechanical and the physical properties of these glasses were determined by using the general approaches. Their densities were measured by the Archimedes method. Vickers hardness was measured by the indentation method using a Vickers indenter [8]; a load of 200 g and loading time of 10 s were employed for this purpose. The Vickers indentation test (200 g, 10 s) was also used to evaluate the fracture toughness of these glasses. The fracture toughness K_{IC} was calculated by the equation suggested by Evans [9]. The four-point bending strength of the specimens (3.0 mm × 3.0 mm × 40.0 mm) was measured using the inner and outer spans of 10 and 20mm, respectively, at the cross-head speed of 100 μm /min, following the American Society of Testing Materials (ASTM) specifications [10]. Each specimen was polished using No. 1500 sandpaper and a polishing cloth with 0.1 μm -diamond paste.

Thermal analysis was performed using a differential scanning calorimeter (DSC) at a heating rate of 10℃ /min over a temperature range of 25~1500℃ in an air atmosphere using an a alumina cell. The glass transition temperature (*Tg*) was measured as the point of intersection of the baseline with a line drawn through the inflection point of the change in heat capacity. The crystallization temperature (*T*x) and the maximum exothermic temperature (*Tc*) were determined as the starting point and the maximum point, respectively, of the exothermic peak in the DSC thermogram.

The chemical durability of the samples was assessed according to the toxicity characteristic leaching procedure (TCLP) developed by the US Environmental Protection Agency (EPA) [11]. For the leaching tests, the glass samples were ground and sieved to a particle size of 10~45 μm that corresponds to the fly ash particle size so that a direct comparison between the glass samples and fly ash was possible. Subsequently, the samples were leached in acetic acid; the leachates were filtered through a glass fiber filter, and then the concentration of heavy metals in the leachates was quantified by using the ICP spectrometer.

3. RESULTS AND DISCUSSION

Because of its high SiO_2 content, coal fly ash can be transformed into glass; this transformation is possible without any reagent. Although the fly ash used in this study had a sufficient amount of glass formers, because of its high melting point (>1700℃) and the high viscosity of the melt, its vitrification required high energy. However, the addition of a small amount of a glass modifier, even 10 wt.% Na_2O, to the fly ash significantly reduced its melting point to less than 1500℃ and the viscosity of its melt. Fig. 3 is a ternary diagram that presents the glass-forming region when B_2O_3 and Na_2O are added. Glasses can be formed by fly ash with the addition of Na_2O up to 60 wt.%. With an increase in the wt.% of a glass modifier, the color of a glass changed to light green with Na_2O and to light brown with B_2O_3.

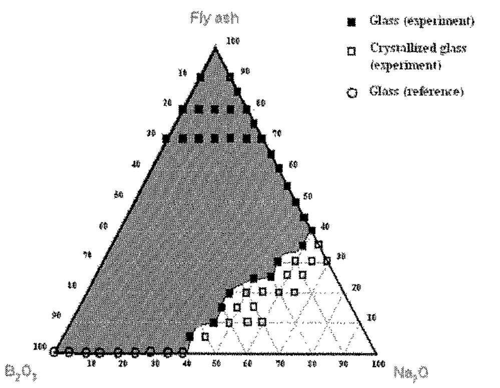


Fig. 3 Fly ash-B_2O_3-Na_2O Ternary diagram (wt.%)

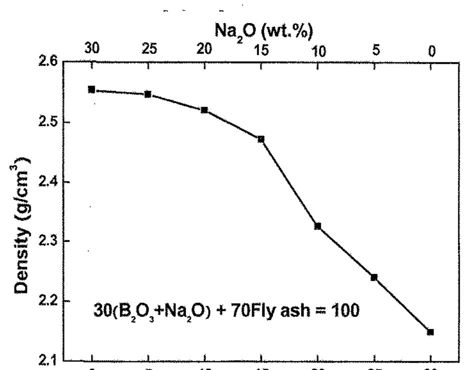
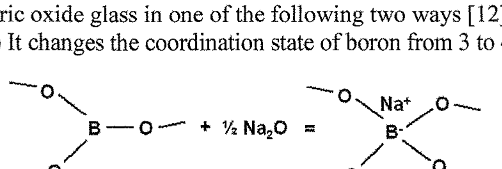


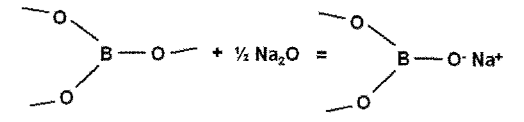
Fig. 4 Changes in the density of fly ash glass with B_2O_3 and Na_2O addition

The density of the fly ash glasses decreased as the amount of B_2O_3 addition increased (Fig. 4); this is because B2O3 has a lower density (1.5 g/cm^3) than that of fly ash glass (2.55 g/cm^3) that contains 30 wt.% of Na_2O alone. However, the decrease in density was maximal when the B_2O_3 content increased from 15 wt.% to 20 wt.%. This is because the alkali ion Na^+ modifies boric oxide glass in one of the following two ways [12]:

(a) It changes the coordination state of boron from 3 to 4.



(b) It creates non-bridging oxygen (NBO).



Consequently, the network connectivity in fly ash glasses was modified by the convert of boron from a 4-coordination state to a 3-coordination state.

The changes in network connectivity modified the Vickers microhardness and fracture toughness (Fig. 5). Initially, the microhardness increased with the B_2O_3 content and reached 4030 MPa at 15 wt.% B_2O_3 + 15 wt.% Na_2O. However, with a further increase in the B_2O_3 content, it decreased and attained the minimum value of 2800Mpa at 25 wt.% B_2O_3 + 5 wt.% Na_2O. On further addition of B_2O_3, the microhardness increased again, attaining the maximum value of approximately 4500 MPa at 30 wt.% B_2O_3 + 0 wt.% Na_2O. This is explained as follows. It is expected that initially, the addition of B_2O_3 decreased the NBOs; this explains the initial increase in the microhardness with the B_2O_3 content. However, with a further addition of B_2O_3, the 3-coordination boron increased in the glass matrix; this explains the observed decrease in the microhardness from 15 wt.% to 25 wt.% B_2O_3. As regards the glass with 30 wt.% B_2O_3, although it should also consist of 3-coordinated boron, the hardness and toughness exhibited high values because this glass could not have NBOs. Some fly ash glasses attained high values of microhardness, comparable to that of window glass (4,100 MPa). The fracture toughness exhibited a trend similar to that of the microhardness, except for the glasses having the composition of 20 wt.% B_2O_3 + 10 wt.% Na_2O.

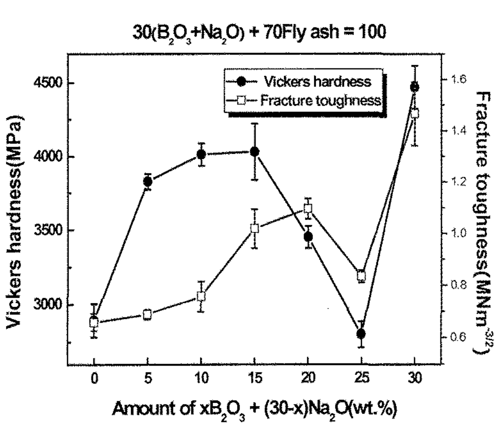


Fig 5 Changes in Vickers microhardness and fracture toughness with Na_2O and B_2O_3 addition

The bending strength (Fig. 6) exhibits a different pattern from that of the changes in the Vickers microhardness (Fig. 5). Since the bending strength is related to various factors such as microstructure, defects, production process etc., its observed pattern cannot be explained considering only one of the many factors. Its values for the fly ash glasses were found to be approximately half that for common window glass (~80 MPa).

Table III Results of leaching tests by TCLP (ppm)

	Standard	Fly ash	F+30N	F+20N+10B	F+15N+15B	F+10N+20B	F+30B
Cr	1.5	**2.53**	0.01	0.02	0.041	0.041	0.055
Cd	0.3	0.016	N.D.	N.D.	N.D.	N.D.	N.D.
Cu	-	1.189	0.145	0.155	0.046	0.145	0.285
Pb	0.3	**5.107**	0.438	0.383	0.196	0.224	0.194
As	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Se	0.3	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

* N & B denote Na_2O and B_2O_3, respectively, F = fly ash and N.D. = not detected.

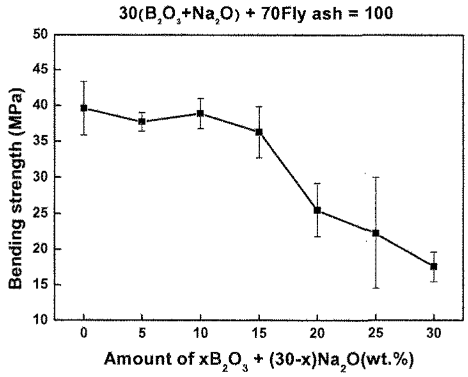


Fig 6 Changes in bending strength with Na_2O and B_2O_3 addition

With an increase in the amount of B_2O_3 added to fly ash + Na_2O glass, the melting temperature (Tm) of the glass increased from 1080 ℃ to 1210 ℃, and the glass transition temperatures (Tg) also increased within the range of 480°C to 550°C (Fig. 7). On the other hand, no specific tendency was exhibited by the crystallization temperatures (Tx) and the maximum exothermic temperatures (Tc).

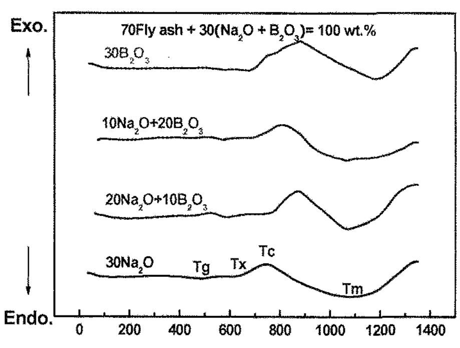


Fig 7 DSC curves of glasses as the amount of Na_2O and B_2O_3 changed

Table III shows the results of leaching tests performed on the fly ash glasses based on the TCLP protocol. The fly ash used in this study had week chemical resistance to the acid leaching of chromium and lead. Particularly, the lead content of the fly ash (5.107 ppm) was 17 times higher than its standard value; however, it stabilized to a lower value (0.194 ppm) through the vitrification process. The leaching of heavy metals was slightly enhanced with the addition of Na_2O; consequently, this weakened the network structure of the fly ash glasses. On the other hand, B_2O_3 served as glass former and enhanced the chemical stability of the fly ash glasses. A general technique to improve the chemical stability of a glass is based upon reducing the concentration of alkali ions in the glass surface [13]. Some results of the leaching tests satisfy Japanese environmental regulations and suggest that the vitrification process is effective in reducing the toxicity of fly ash.

4. CONCLUSIONS

Alkali borosilicate glass can be produced by vitrifying coal fly ash with the additions of Na_2O and B_2O_3. The fly ash glasses with a composition of 15 wt.% B_2O_3 + 15 wt.% Na_2O exhibited high Vickers microhardness of 4030 MPa, bending strength of 37 MPa, fracture toughness of 1.0 MPa· $m^{1/2}$ and low melting point of less than 1200℃. These values are comparable to those for Corning Pyrex® (7740) (4100 MPa, 0.77 MPa· $m^{1/2}$). Moreover, the results of the leaching tests based on the TCLP protocol clearly indicated that the glass with B_2O_3 and Na_2O possessed good chemical stability. Alkali borosilicate glasses produced from fly ash exhibit good chemical resistance and can be employed for the recycling of vitreous fly ash and producing porous glasses.

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