Borate glasses with high lanthanide oxids solubility for the cold crucible induction melter(CCIM) applications

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1. Introduction

Pyro-processing is being investigated to reuse radioactive uranium and trans-uranium elements from the spent fuels [1]. Previous researches regarding wasteforms for rare-earth oxides waste generated from pyro-processing reported low elemental release (< 10^4 g/m^2) of RE ions at the product consistency test (PCT) [2]. Current work reports the continuing effort on the enhancement of the waste loading and process-ability using cold crucible induction melter(CCIM). Borate glasses are well-known for their low melting temperatures with high rare-earth oxide solubility compared to silicate glasses [3]. Borate glasses were investigated as potential wasteforms with high waste loading for immobilization of lanthanide ion wastes produced by pyro-processing. Process-ability of them was investigated by characterizing several important processing parameters for cold crucible induction melter (CCIM) process.

2. Methods

Since silicate glasses require high processing temperature (> 1600 ºC), we searched for the borate glasses with melting point ≤ 1300 ºC. Alkaline earth-borate glasses [3] are known to dissolve ~20 mol% of Nd_2O_3 and therefore, we melted the glass of $50B_2O_3$ – 30CaO – $20Nd_2O_3$ (mol%) composition at 1300 ºC for 30 min. Although we obtained a transparent glass, results from the product consistency test (PCT) in Table I did not meet the requirement for a stable host.

Table I: Released concentration and normalized released value of alkaline earth-borate glasses.

	Concentration (ppm)	Normalized values (g/m^2)
Ca	36.72	$9\cdot10^{-3}$
B	16.99	$2\cdot10^{-2}$
Nd	LOD (<0.1ppm)	LOD

To enhance the chemical durability, Al_2O_3 was added to make the final composition of (1-x) (0.25 CaO - 0.19 Al_2O_3 - 0.56 B_2O_3) - x Nd_2O_3 where x varies from 0, 0.1, 0.2 and 0.3. The starting powders were mixed and melted at 1300 ºC for 30 min. The glasses containing 0, 10 and 20 mol % of Nd_2O_3 were transparent with a light blue color. The melt containing 30mol % of RE crystalized during quenching.

3. Results

3.1 Chemical durability

We performed product consistency test (PCT) to evaluate chemical durability of the glasses containing 20 mol % of Nd_2O_3. The normalized released amount of Ca, Al and B were 10^{-3}-10^{-4} g/m^{2}day (Table II) and the concentration of Nd released was below the limit of dectection of ICP-MS (< 0.1 ppb).

Table II: Released concentration and normalized released value of final specimen performed by PCT.

	Concentration (ppm)	Normalized values (g/m^2)
Ca	1.82	$1\cdot10^{-2}$
Al	0.11	$7\cdot10^{-4}$
B	2.00	$1.3\cdot10^{-2}$
Nd	LOD (<0.1ppb)	**< $1.2\cdot10^{-7}$**

3.2 Composition analysis and waste loading

Composition of the representative glasses was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and compared with its nominal compositions (Fig.1). Nominal composition (mol%) of 20 CaO - 15 Al_2O_3 - 45 B_2O_3 - 20 Nd_2O_3 remained without significant volatilization of components during melting processes.

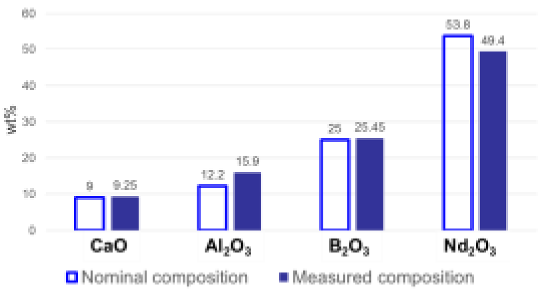

Fig.1 Comparison of nominal composition analyzed by ICP-AES.

Maximum solubility of the rare-earth oxides in the glasses was evaluated as 22 mol% (56.8 wt%) when the batch was melted at 1300^{O}C for 30 min. Processing temperature of these glasses were 150 ^{O}C lower than the melting points of the lanthanide aluminosilicate glasses with slightly lower rare-earth solubility[4].

3.3 Thermal stability of glasses

Stability of glass phases against the heat was evaluated by additional heat-treatments at 600~800^{o}C for 5 hours. The needle-like crystals appeared when the glass was heat-treated at T>800^{o}C and this major crystalline phase was determined as $NdBO_3$ (Figs. 2 and 3). The glasses were stable and remained amorphous after heat-treatment at T<800^{o}C.

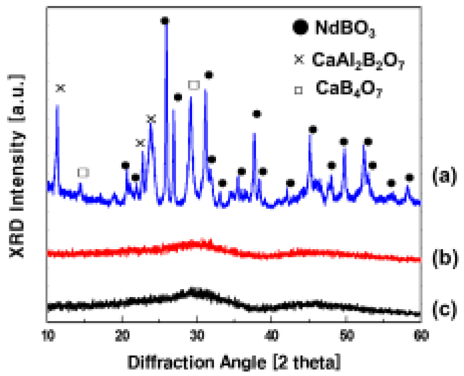

Fig.2 X-ray diffraction patterns of the specimens (20 mol% of Nd_2O_3) heated at temperatures (a) 800 ^{o}C, (b) 700 ^{o}C and (c) 600 ^{o}C for 5 hours.

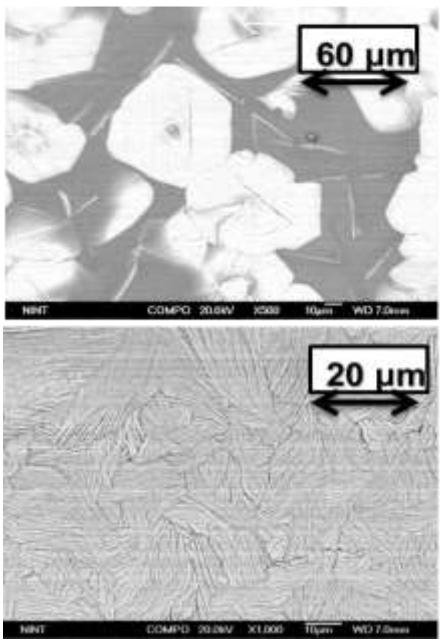

Fig.3 SEM micrographs of crystals in specimen heat-treated at 800 ^{o}C for 5 hours.

3.4 CCIM applications

Three major constraints of glasses to apply CCIM is chemical durability, viscosity and electric conductivity. Chemical durability of these glasses was already analyzed by PCT and meets the requirement (r < 2g/m^2). And viscosity should be between 10-100 poise and conductivity be in the range of 0.1~1 S/cm. All our specimens meet the regulations, therefore, it suggests that these glasses are acceptable to apply to CCIM.

4. Conclusions

Borate glasses containing 0 - 20 mol% Nd_2O_3 were fabricated by melting the starting powders at 1300 ^{O}C for 30 min with maximum loading of 56.8 wt % (22 mol %). The released concentration of Nd were < 0.1 ppm. Crystallization did not appear at the temperature below 800^{O}C. Viscosity and electric conductivity of these glasses meet requirements to apply to CCIM.

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