IMMOBILIZATION OF RARE EARTH WASTE STREAM FROM REPROCESSING USING VITRIFICATION

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Abstract

One of the waste streams generated during pyroprocessing of spent nuclear fuel is a mixture of rare earth (RE) oxides. The study investigated RE solubility in aluminoborosilicate glass (AG) using microscopy and x-ray diffraction (XRD). Various types of crystals were identified: Ce3BSi2O10, Al-containing crystals, and CeO2. Liquidus temperature of these crystalline phases was determined as a function of glass composition.

1. INTRODUCTION

Accumulation of this spent fuel became a long-term issue for operating and proposed nuclear power plants [1]. The hydro-chemical radioactive waste reprocessing technology that separates U and Pu from spent fuel via dissolution in nitric acid [2] and extracting U and Pu with a chemical solvent was adopted in many countries, including United Kingdom, France, Japan, India, and Russia. Pyroprocessing is an alternative technology, which has been designed to prevent nuclear proliferation, was adopted in the Republic of Korea. The pyroprocessing of spent fuel produces various waste stream, such as transuranic waste, fission products, rare earth oxide waste, and salt waste [2,3]. These waste streams must be immobilized for the long-term storage.

In this work, aluminoborosilicate glass (AG) was examined as a waste form for the rare earth (RE) waste from pyroprocessing possessing a high waste loading and excellent chemical durability [4]. In particular, the study focused on RE solubility as a function of temperature and glass composition. Mathematical models for the melt and glass properties facilitate glass formulation for a wide variety of wastes [5]. Following the approach developed for the equilibrium concentration of spinel in high-level waste glasses [6], the present work applies mathematical modelling to multiple crystalline phases produced in AG glasses with RE components.

2. METHODOLOGY

Table 1 lists compositions of AG glasses designed and fabricated for this study. The crystal fraction in heat-treated glasses was obtained by combining the x-ray diffraction (XRD) analysis with the optical and scanning electron microscopy. Liquidus temperature, TL, was obtained by plotting the crystal fraction as function of temperature and extrapolating the relationship to zero percent crystals using the standard procedure [7]. Details of the experimental steps and the analytical techniques are reported in previous studies [3,4].

TABLE 1. AG COMPOSITIONS

Glass Id	SiO_2	B_2O_3	Al_2O_3	RE-oxides	Sum
L-53	0.1973	0.0797	0.1930	0.5300	1.0000
L-53-HS3	0.2273	0.0767	0.1858	0.5102	1.0000
L-53-HS5	0.2473	0.0747	0.1810	0.4970	1.0000
L-53-LS3	0.1673	0.0826	0.2002	0.5498	1.0000
L-53-LS5	0.1473	0.0846	0.2051	0.5630	1.0000

L-53-HB3	0.1909	0.1097	0.1867	0.5127	1.0000
L-53-HB5	0.1866	0.1297	0.1825	0.5012	1.0000
L-53-LB3	0.2037	0.0497	0.1993	0.5473	1.0000
L-53-LB5	0.2080	0.0297	0.2035	0.5588	1.0000
L-53-HA3	0.1900	0.0767	0.2230	0.5103	1.0000
L-53-HA5	0.1851	0.0747	0.2430	0.4972	1.0000
L-53-LA3	0.2046	0.0826	0.1630	0.5497	1.0000
L-53-LA5	0.2095	0.0846	0.1430	0.5629	1.0000
L-53-HC3	0.1899	0.0767	0.1858	0.5477	1.0000
L-53-HC5	0.1849	0.0747	0.1809	0.5594	1.0000
L-53-LC3	0.2047	0.0827	0.2003	0.5123	1.0000
L-53-LC5	0.2097	0.0847	0.2051	0.5005	1.0000
L-53-HN3	0.1885	0.0761	0.1844	0.5510	1.0000
L-53-HN5	0.1826	0.0737	0.1787	0.5650	1.0000
L-53-LN3	0.2061	0.0832	0.2016	0.5091	1.0000
L-53-LN5	0.2120	0.0856	0.2074	0.4951	1.0000

The TL data of theses glasses are reported in our previous study [4], including mathematical models and statistical characteristics, such as the correlation coefficients and root mean square errors [8]. The standard leaching procedure known as product consistency test (PCT) was also performed, confirming good chemical durability of the glasses [3, 9].

3. RESULTS AND DISCUSSION

RE glasses may produce a complex blend of crystalline phases. Previous study has found alkaline earth with rare earth silicates crystals in glass adopting from well-known French glass composition – international simple glass. Figure 1 shows oxyapatite (Ca2RE8Si6O26) needle-like shape crystals which was found in the French glass composition containing rare earth [3]. The liquidus temperature of oxyapatite was found to be 1052°C in 15 wt% rare earth loading in simple glass composition. The PCT result of this glass showed normalized release of silicon (Si), boron (B) and sodium (Na) are 0.14, 0.42 and 0.47 g/m2, respectively [3].

On the other hand, Fig. 2 shows cubic CeO2 crystals of <10 µm size that were found in the bottom part of the glass with typical borosilicate glass containing >25 wt% alkaline oxides [4]. This CeO2 crystals was found to nucleate at the bottom of the sample which shows that the melt viscosity is very high, and this has been discovered during room temperature quenching. Even though, no attempt on viscosity measurement has been carried out for this study. In 25 wt% rare earth waste loading, liquidus temperature of CeO2 recorded as 1118°C and the crystal fraction of CeO2 crystals which is below than 0.1 wt% does not have any implications on performance of alkaline rich glass. However, the PCT indicate poor durability of the glass due to high normalized release of Si, B and Na which are 10.5, 36.9 and 30.4 g/m2, respectively [3].

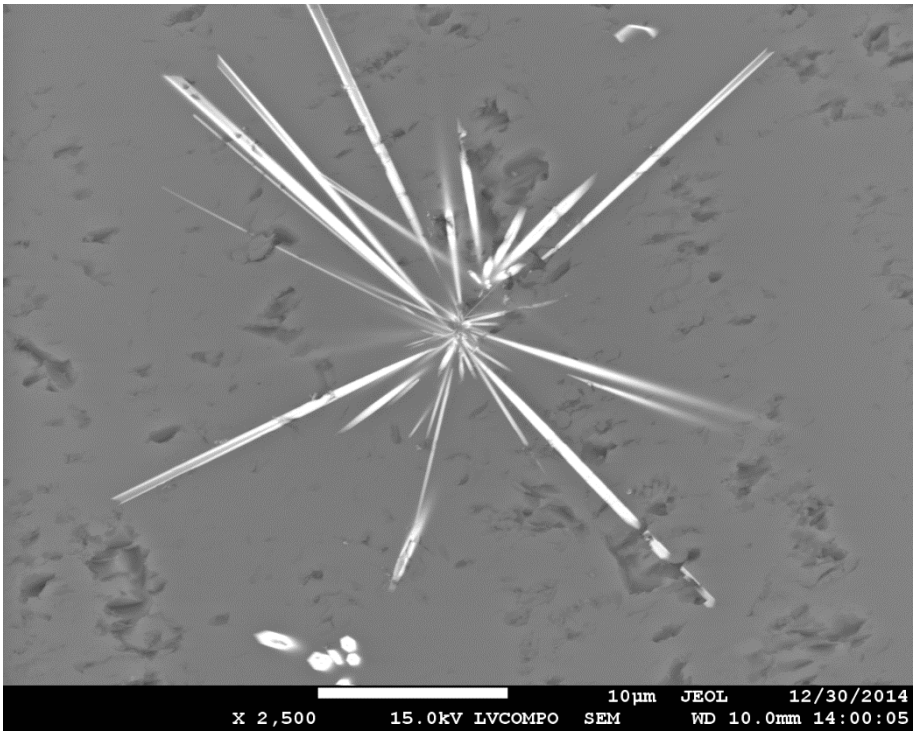

FIG. 1. Oxyapatite ($Ca_2RE_8Si_6O_{26}$) crystal morphology.

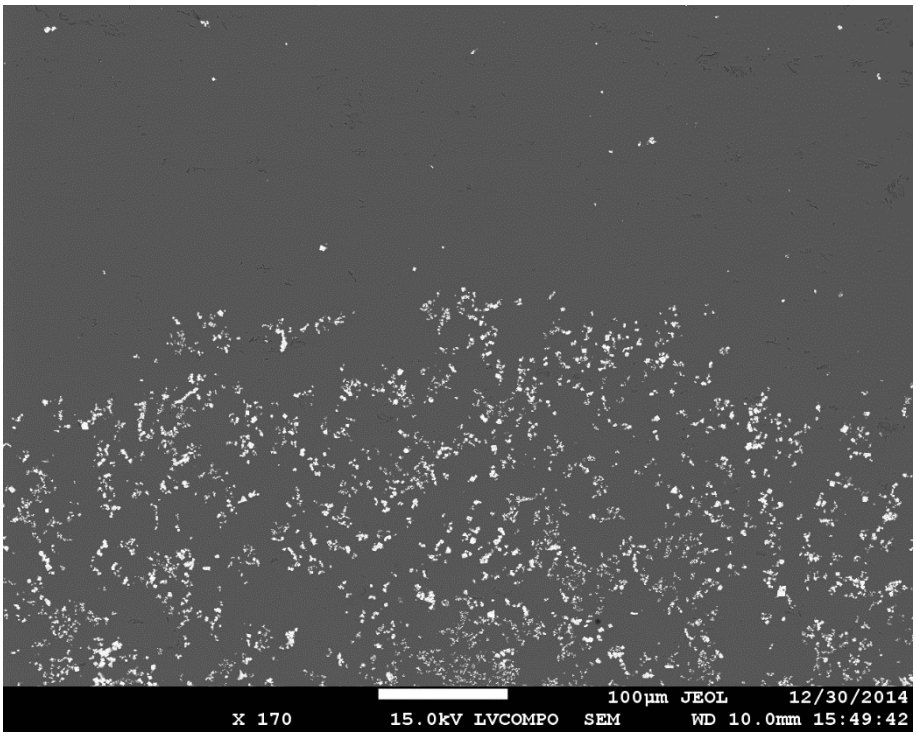

FIG. 2. CeO_2 crystals.

The liquidus temperature for various crystals in AG glass has been carried out previously at 53 wt% rare earth loading which found at 1201°C [3]. The study also showed very good durability of the glass with normalized release of Si and B are 0.01 and 0.03 g/m2, respectively, for PCT result. Hence, further crystallization study was carried out for this AG glass [4]. Almost 140 data points were generated for AG glasses listed in Table 1 at the temperature range from 949 to 1202°C. More than one crystalline phase was

observed in heat-treated samples; 116 samples contained RE-borosilicate (RE3BSi2O10) crystals, 126 had Al-containing crystals (Al10Si2O19 and Al2O3), and 136 contained CeO2 crystals after heat treatment. The morphology of crystals is showed in Fig. 3.

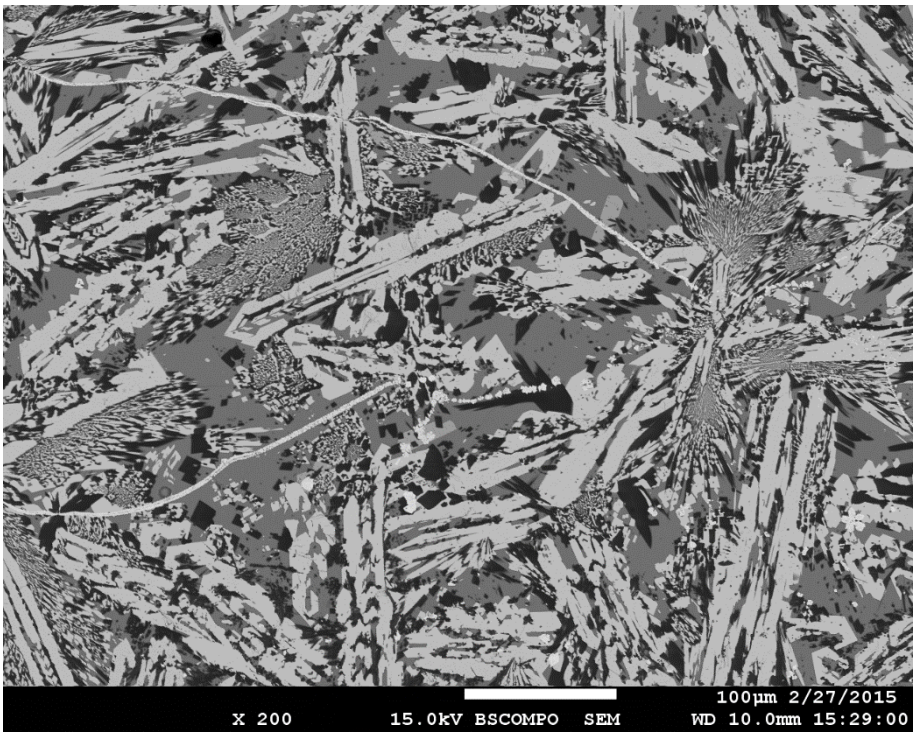

FIG. 3. Morphology of crystalline phases in AG glass with the highest (56.5 wt%) waste loading.

Figure 4 to Fig. 6 display the effects of compositions on the TL for Ce3BSi2O10, Al-containing crystals, and CeO2 as primary crystalline phases. Data points represent the measured values and the lines are based on linear TL models fitted to data. As Fig. 4 shows, the B2O3 reduced the TL more than SiO2 and that Nd2O3 increased TL more than CeO2 and Al2O3. The model predicted poorly the B2O3 effect on the TL for glasses with low B2O3 content. In these glasses, precipitated also Nd2Si2O7 crystals, possibly affecting the Ce3BSi2O10 liquidus. The effect of Nd2O3 on the TL was more significant than that of CeO2. This might be attributed to the presence of Nd atoms in the Ce sites.

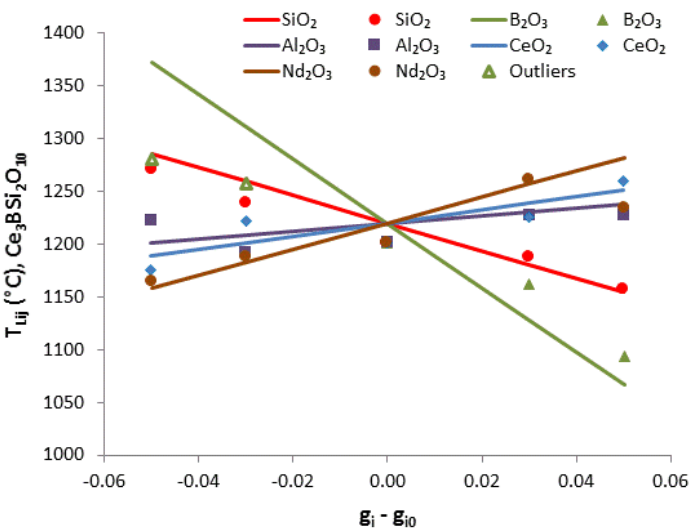

FIG. 4. Effects of component mass fraction change on T_L of $Ce_3BSi_2O_{10}$.

Figure 5 shows the effects of AG components on the TL for Al-containing crystals; B2O3 exhibits a stronger TL decreasing effect than SiO2 while Al2O3 increases the TL as expected; Nd2O3 and CeO2 have little effect.

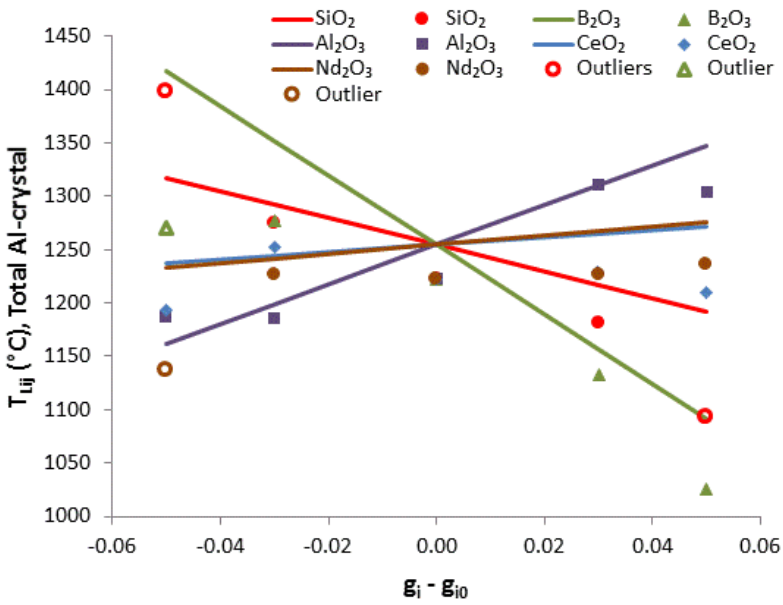

FIG. 5. Effects of components mass fraction change of T_L for total Al-containing crystals.

Figure 6 displays the effects of components on the mass fraction of CeO2 crystals, which did not change with the temperature [4]. The strong effect of B2O3 indicates that the CeO2 crystalline phase was probably conjointly present with other crystalline phases effected by B2O3. Not surprisingly, the fraction of CeO2 crystals increases with the CeO2 content in glass.

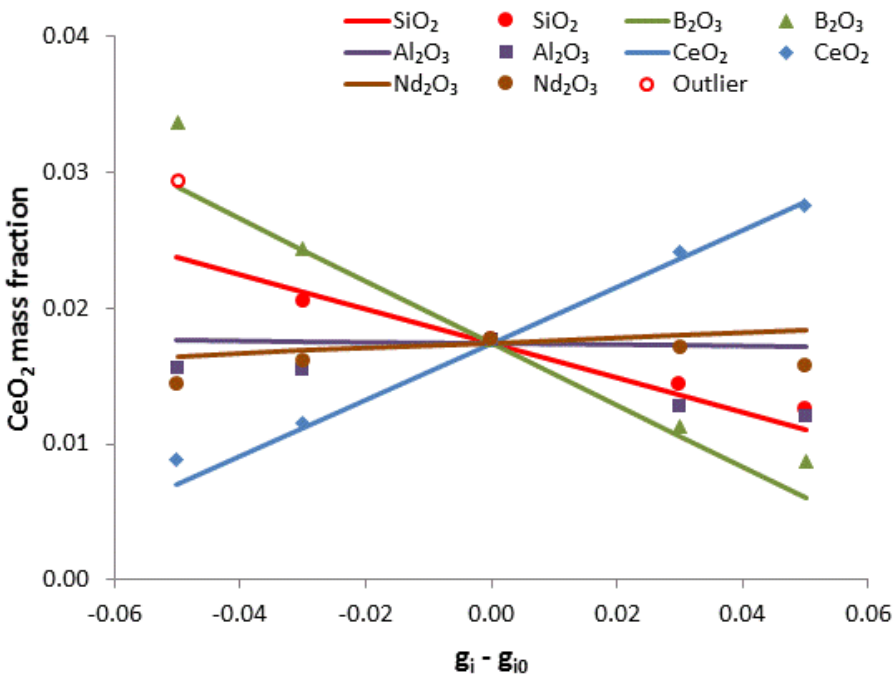

FIG. 6. Effects of components mass fraction change of CeO_2 mass fraction.

Overall, B2O3 and SiO2 appear to affect all crystalline phases by reducing their solubility. As expected, RE components increase the TL of RE-containing phases and Al2O3 increases the TL of Al-containing crystals.

4. CONCLUSION

As the component effects show, the TL models work reasonably well considering the complexity of the phase behaviour of AG glasses with RE oxides. Thus, the phase behaviour of AG glasses could be reliably represented by linear models.

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