Use of high-temperature oxide melt solution calorimetry in understanding long-term behaviors of ceramic waste forms

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1. Introduction

Thermochemical data are essential in understanding materials stability and compatibility in technological applications as well as in evaluating their long-term behaviors for the long-term safety assessments. However, it is technically difficult to obtain the information for materials that do not dissolve in the aqueous phase (*e.g*., a strong acid or base). The high-temperature oxide melt solution calorimetry [1,2] provides thermochemical properties of materials of interest which do not dissolve in aqueous solutions. Thus, use of high-temperature oxide melt solution calorimetry technique can be a unique and crucial approach for issues of stability and as a starting point for kinetics of materials relevant to energy and environment.

Here, we introduce the study on development of potential ceramic waste forms and understanding their long-term behaviors using high-temperature oxide melt solution calorimetric technique. Understanding the underlying waste form structures and their properties is considered a prerequisite for establishing ceramic waste forms. The relations among crystalline and amorphous or glassy states for waste forms are of importance because, in the long-term, they can produce unstable materials through amorphization from radiation damage and during nuclear vitrification. Moreover, as for the waste forms to immobilize radioactive nuclides with relatively intermediate half-lives (~ 30 years), such as Cs-137 and Sr-90, the stability related to their decay products is of particular concern. How do the waste forms structures and their stability respond to the changes from decay processes (*i.e.*, Cs to Ba, and Sr to Zr to Y)?

2. High-temperature oxide melt solution calorimeter

As shown in Figure 1, the high-temperature oxide melt solution calorimeter is based on a twin microcalorimeter of the Tian-Calvet type. It consists of two sample chambers each surrounded by a thermopile of thermocouples in series. The operating temperature of the calorimeter is usually at 600 ~ 900 $^{\circ}$C. At this temperature, the buffer materials (e.g., lead borate and sodium molybdate) exist as molten oxide solvents, thus the metal oxide samples which do not dissolve in aqueous solvents can be dissolved. With a sample drop into the solvent, the calorimeter measures the heat of sample in the system. This includes the heat obtained from room temperature to operating temperature and that from dissolution. With proper thermodynamic cycle, the enthalpy of formation ($\Delta H_{\text{f,ox}}$) can be calculated. With thermodynamic information obtained (e.g., $\Delta H_{\text{f,ox}}$), one can predict the stability of materials of interest and evaluate their long-term behaviors.
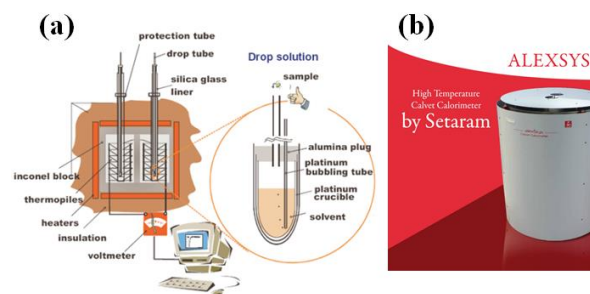

Fig. 1. (a) Schematics of high-temperature oxide melt solution calorimetry, (b) image of a commercial high-temperature oxide melt solution calorimeter.

3. Ceramic waste forms and thermochemistry

Titanosilicates as waste forms for Cs and Sr are attractive due to their successful function as selective ion exchangers and their chemical, mechanical, and structural stability comparable to that of borosilicates or aluminosilicates. Processing schemes to utilize Cs/Sr-loaded titanosilicate waste forms resemble those already well-developed to produce Synroc.

Cesium titanosilicate ($CsTiSi_2O_{6.5}$) is the titanium analogue of aluminosilicate ($CsAlSi_2O_6$, pollucite) and a possible ceramic form for immobilization of Cs. Pollucite ($CsAlSi_2O_6$), a naturally occurring mineral, is an analogue of leucite ($KAlSi_2O_6$) and analcime ($NaAlSi_2O_6$). The basic structures consist of an open framework of corner-sharing $(Al,Si)O_4$ tetrahedra with cations (e.g, Cs^+, K^+, and Na^+) occupying the cavities. The naturally occurring mineral phases prove the long-term stability in nature.

Not only the stability related to the $CsTiSi_2O_{6.5}$, but also that to the decay products (*i.e.*, Ba incorporation into the Cs site) is of fundamental importance. The decay schemes possibly happen in nature are shown in Fig. 2. Scheme (a) represents charge-balances route (e.g., $2Cs^{1+} = Ba^{2+} +$ vacancy, whereas scheme (b) represents a reaction of 1:1 replacement of Cs by Ba. With samples

relevant to the corresponding phases for decay schemes, one can perform the high-temperature oxide melt solution calorimetry to obtain the enthalpies of formation from oxides.
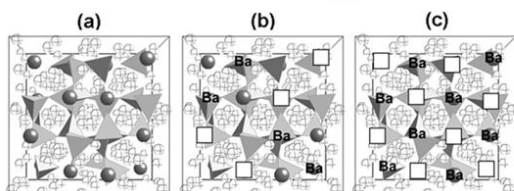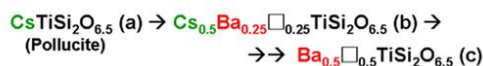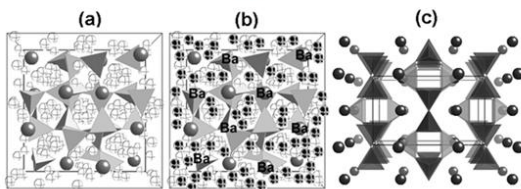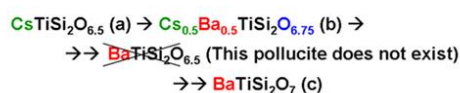

Fig. 2. A schematic diagram that represents the potential decay processes in the Cs-pollucite. Decay scheme (a) includes the potential decay product series with charge-balance in pollucite, whereas (b) includes the series with one-to-one replacement of Cs by Ba.

The measures from sample drops into the high-temperature oxide melt solution calorimeter show the enthalpy of drop solutions (ΔH_{ds}). With proper thermodynamic cycle, one can calculate the enthalpy of formation from oxides ($\Delta H_{f,ox}$) for the sample. Representative thermodynamic cycle is shown in Table 1.

Table 1. Thermodynamic cycle used to calculate the enthalpy of formation of $CsTiSi_2O_{6.5}$ from constituent oxides.

	Reaction	Enthalpy
1	$CsTiSi_2O_{6.5}$ (solid, 25 ºC) → $CsTiSi_2O_{6.5}$ (dissolved, 702 ºC)	$\Delta H_1 = \Delta H_{ds}$ (sample)
2	Cs_2O (solid, 25 ºC) → Cs_2O (dissolved, 702 ºC)	$\Delta H_2 = \Delta H_{ds}(Cs_2O)$
3	TiO_2 (solid, 25 ºC) → TiO_2 (dissolved, 702 ºC)	$\Delta H_3 = \Delta H_{ds}(TiO_2)$
4	SiO_2 (solid, 25 ºC) → SiO_2 (dissolved, 702 ºC)	$\Delta H_4 = \Delta H_{ds}(SiO_2)$
5	$0.5Cs_2O$ (solid, 25 ºC) + TiO_2 (solid, 25 ºC) + $2SiO_2$ (solid, 25 ºC) → $CsTiSi_2O_{6.5}$ (solid, 25 ºC)	$\Delta H_5 = \Delta H_{f,ox}$ (sample) = $\Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_1$

With a similar process using proper thermodynamic cycles, the enthalpy of formations of decay products are also calculated. For the samples, $\Delta H_{f,ox}$ are exothermic and become less so with increasing Ba content. This implies the decay process will affect negatively to the stability of potential ceramic waste forms. The effect of vacancies in the pollucite structure is more dominant factor in the thermochemical stability than that of Ba replacement.

4. Conclusions

The calorimetric techniques to understand the long-term behaviors of potential ceramic waste forms are introduced. With high-temperature oxide melt solution calorimetry and the proper thermodynamic cycles, the thermodynamic data can be obtained and calculated. The relative stability from oxide constituents for materials of interest, in this present study, the decay product series of potential ceramic waste forms, can be analyzed to predict the long-term behaviors for potential ceramic waste forms.

Acknowledgement

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