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A Thermodynamic Approach to predict the Metallic and Oxide Phases Precipitations in Nuclear Waste Glass Melts

S. Gossé[a]*,C. Guéneau[a], S. Bordier[a], S. Schuller[b], A. Laplace[b], J.Rogez[c]

[a] *DEN,DPC,SCCME,LM2T CEA Saclay 91191 Gif-sur-Yvette, France*
[b] *DEN,DTCD,SECM,LDMC, CEA Marcoule, 30207 Bagnols-sur-Cèze, France*
[c] *IM2NP, Faculté des Sciences et Techniques – Service 262, 13397 Marseille Cedex 20, France*

Abstract

Among the large number of matrixes explored as hosts for high-level nuclear wastes, conditioning of fission products and minor actinides into a homogeneous borosilicate glass is the most promising technique already implemented at the industrial scale. The advantage of this vitrification process is the volume reduction of the high level waste coming from the spent fuel reprocessing and its stability for the long-term storage. Nevertheless, some fission products are poorly soluble in molten glasses:

- Platinoids (Pd, Ru, Rh) which precipitate as (Pd-Te, Ru-Rh) metallic particles and (Rh,Ru)O_2 oxide phases with acicular or polyhedral shapes during the vitrification process.
- Molybdenum oxide (MoO_3) which can form complex molybdates.

In order to point out the chemical interactions between the glass and these precipitated phases issuing from the calcinated waste, a thermodynamic approach is developed using the Calphad method. The objective of this work is to calculate thermodynamic properties for complex fission product systems in order to predict the precipitation of platinoids or molybdate phases.
This thermodynamic database is being developed on the Mo-Pd-Rh-Ru-Se-Te-O complex system. This flexible tool enables to predict phase diagrams, composition and relative stability of the metallic or oxide precipitated phases as a function of both temperature and oxygen potential in the glass melt.

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Keywords: Thermodynamic; Calphad; Nuclear Waste Glasses; Platinoid; Molybdenum; Fission product

* Corresponding author. Tel.: +33 (1) 69 08 97 39; fax: +33(1) 69 08 92 21.
E-mail address: stephane.gosse@cea.fr

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1. Introduction

During vitrification process of high level radioactive glasses, slightly soluble Pd-Rh-Ru platinoid metals and molybdenum as complex oxides exhibit low loading rate (Figure 1) [1-3]. Platinoids mainly form (Pd-Te, Ru-Rh) metallic particles [1-5] and/or $(Rh,Ru)O_2$ oxide phases [3-5] in the vitreous matrix of high level waste containment glasses. At high concentration, molybdenum oxide tends to demix as a complex molybdate phase enriched mainly in sodium molybdates, calcium and other alkalines (Cs, Li) and alkaline-earth (Ca, Sr, Ba, Mg) [6-9].

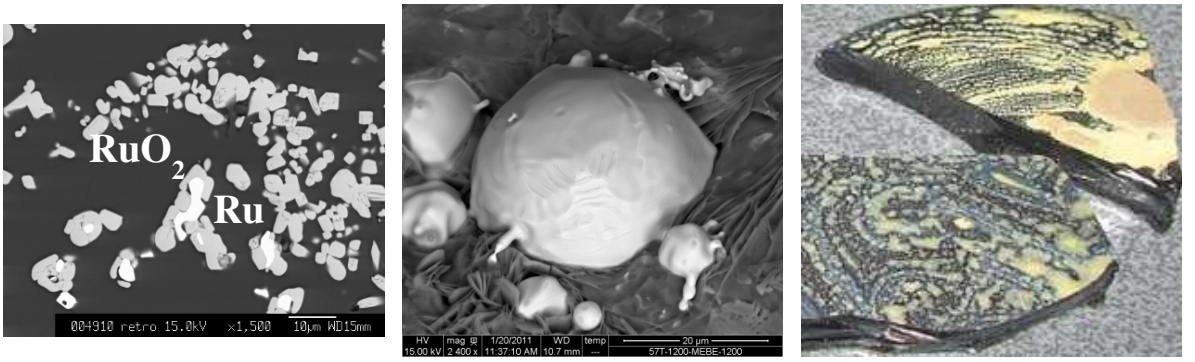

Figure 1: Crystallized metallic and oxide phases in nuclear borosilicate glasses: a) Ru-HCP and RuO_2 polyhedra, b) Pd_xTe_y Intermetallics observed by ESEM and c) Visual observation of a complex yellow phase obtained by high temperature reaction between glass frit and calcine

This paper presents the development of a thermodynamic modelling for typical nuclear waste compositions. Using the Calphad method [10], a database was developed on the Mo-Pd-Rh-Ru-Se-Te-O system. The objective is to use a thermodynamic approach to develop solution models for fission products and oxide melts systems that are predictive with regard to composition, phase separation, and volatility observed during vitrification of nuclear waste glasses.

In this work, the Gibbs free energy function of each phase (solid, liquid and gas) is modelled to provide an overall thermodynamic description of the stability of the molybdates and the platinoid phases in nuclear waste glasses:

- Because platinoids are sparingly soluble, their thermodynamic properties can be calculated without considering the glass chemistry. In this case, the melt is only taken into account through its oxygen potential.
- Concerning molybdenum, the interactions with the oxides from the melt (CaO, Na_2O, SiO_2) are considered through the assessments of the CaO-MoO_3, MoO_3-Na_2O and MoO_3-SiO_2 binary and MoO_3-Na_2O-SiO_2 ternary phase diagrams.

The main objective of the database is to calculate phase diagrams and thermodynamic properties: stability and composition of the phases at equilibrium, eutectics and demixing phenomena. This flexible tool also enables to predict the relative stability between metallic and oxide phases as a function of temperature and oxygen potential (RedOx equilibrium) somehow fixed by the glass frit.

The present thermodynamic database was used to predict the platinoid fission products and the molybdenum oxide behaviours at high temperature. These calculations partly explain the precipitation phenomena of platinoid metallic droplets and the demixing of molybdates in nuclear waste glasses.