

Interactions between Platinoid Fission Products and Chalcogen Elements

Thermodynamics of the Pd-Rh-Ru-Se-Te-(O) System

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Introduction: Thermodynamics of the Platinoid Fission Products in Nuclear Reactors

Platinoid (Pd-Rh-Ru) and chalcogen (Se-Te) fission products are formed under irradiation of nuclear fuels. Under operating conditions, the main formed Platinum Group Metal (PGM) is ruthenium. It accumulates in the fuel in the form of metallic precipitates in higher concentration than the other PGMs: palladium and rhodium. In the fuel, under low oxygen potential, ruthenium can be partly oxidized into RuO_2 . This oxide is relatively stable at high temperature (about 1800 K) but in case of accidental high temperatures, it may partly decompose into metallic Ru-HCP and radiotoxic volatile gaseous species ($\text{RuO}_{3(g)}$, $\text{RuO}_{4(g)}$). On the contrary, Pd and Rh tend to form intermetallic phases or solid solutions by reaction with the very volatile Se and Te fission products.

During the nuclear fuel irradiation, Palladium, Rhodium and Ruthenium FPs are produced in higher quantities than the metalloids Tellurium and Selenium. However, Tellurium is of the utmost importance because it is involved in the Fuel Cladding Interaction, mainly due to the formation of numerous intermetallic compounds and to possible low temperature eutectic reactions. Tellurium and Selenium are also very volatile: under thermal gradient, they tend to condensate in lower temperature regions.

The Pd-Rh-Ru platinoids often interact with the low melting point elements Tellurium and Selenium. Because the resulting Pd-Rh-Ru-Te-Se alloys or liquid phases may affect the properties of the nuclear materials (fuel, cladding, glass), a thermodynamic modeling of this system is required.

Method: Development of a Thermodynamic Database devoted to Platinoid Fission Products

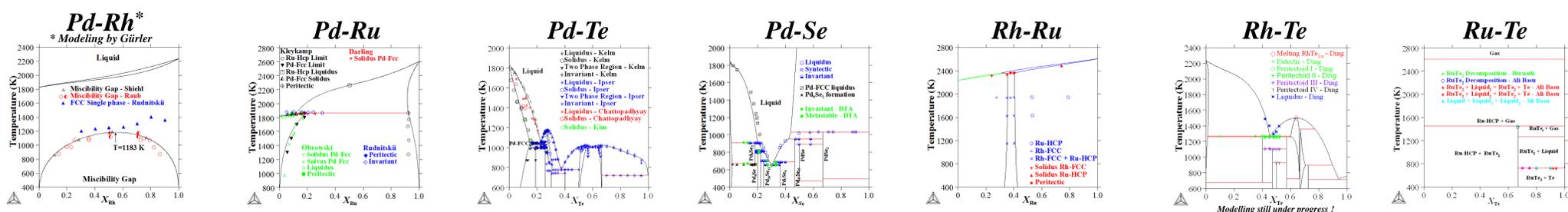
Several studies are being undertaken at CEA to investigate the chemical interactions between the platinoid and chalcogen elements in order to predict the phases to be formed in the fuel under irradiation or in the glass during the vitrification process of high level nuclear wastes. The aim of this study is to develop a thermodynamic database which describes the platinoid phases that form during the different steps of the fuel cycle (Irradiated Fuel, Fuel Cladding Interaction in Gen III and Gen IV Reactors, Accidental conditions, Vitrification process).

This thermodynamic database enables to calculate both phase diagrams and all thermodynamic properties of the platinoid based phases formed. It constitutes a flexible tool to predict the thermodynamic behavior of platinoid (Pd,Rh,Ru) and chalcogen (Te,Se) FPs.

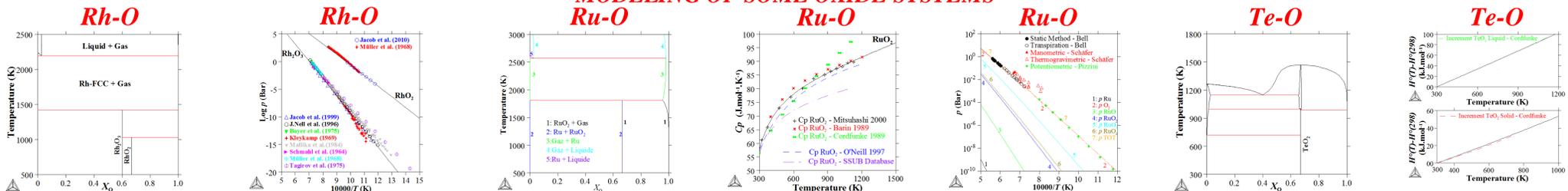
These calculations are performed using the CALPHAD method.

Results: Modeling of the Pd-Rh-Ru-Te-Se-(O) Quinary System

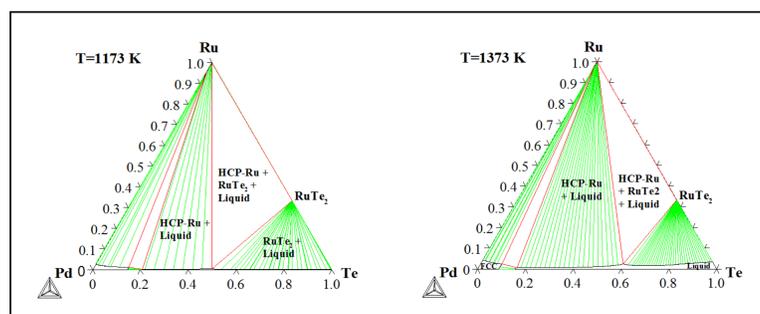
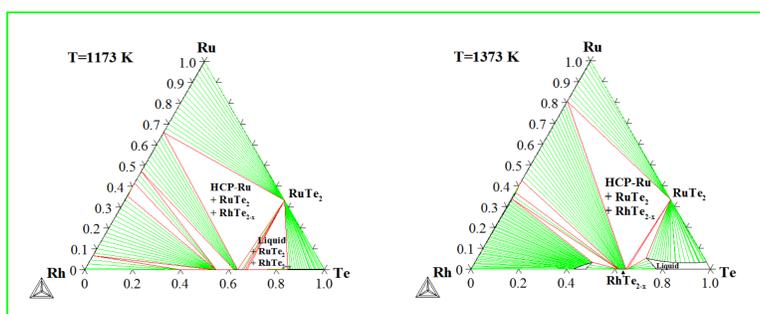
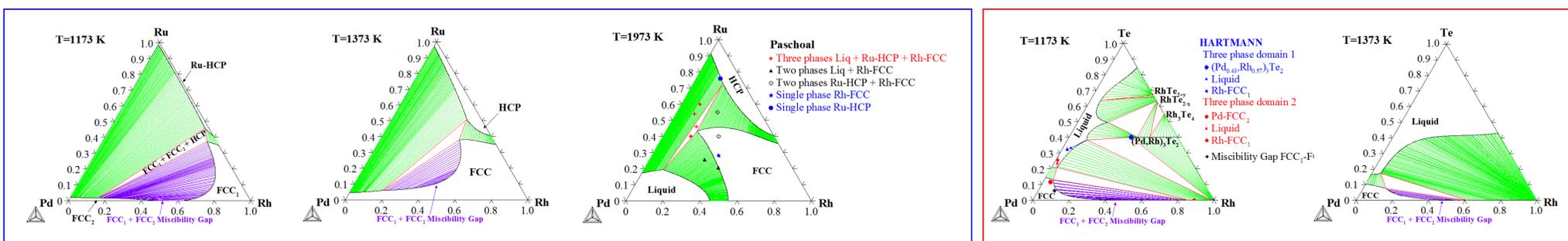
BINARY SYSTEMS: Calculated Phase Diagrams of the Pd-Rh*, Pd-Ru, Pd-Te, Pd-Se, Rh-Ru, Rh-Te, Ru-Te Systems



MODELING OF SOME OXIDE SYSTEMS



Calculated Phase Diagrams of the Pd-Rh-Ru, Pd-Rh-Te, Rh-Ru-Te, Pd-Ru-Te Ternary Systems



Conclusions

A database is being developed to predict the thermodynamic data and phase equilibria of the platinoid phases in the irradiated fuel and in the glass of high level nuclear wastes. The current database describes both metallic and oxide fission products of the Pd-Rh-Ru-Se-Te-(O) systems. This tool makes it possible to predict the relative stability of the metallic and oxide phases in function of both temperature and oxygen potential fixed in the fuel or in the glass melt.

Shortly, other FPs elements (Mo) and fuel materials will be introduced so as to extend its application field.