Cesium – Oxygen – Zirconium

Jean Claude Tedenac, Pierre Perrot

Introduction

Cs is one of the main fission product of uranium and Zr is one of the main constituent of cladding materials. Several cesium zirconates have been reported in the Cs-O-Zr system [1996Das], but only one compound Cs_2ZrO_3 is known to be stable and its thermodynamic properties have been carefully investigated to make detailed predictions of fission products interactions in a fuel rod. A first evaluation of the thermodynamic properties of Cs_2ZrO_3 was carried out by [1983Koh, 1994Koh]. Experimental measurements are summarized in Table 1. Calculations of the equilibrium at 427°C in the Cs-O-Zr system taking into account the oxygen and cesium potential using the Solgasmix program were proposed by [1996Das]. Calculated isothermal sections at 727 and 1727°C were presented by [1999Pou].

Binary Systems

The Cs-O system which has never been thermodynamically assessed, is accepted from [1979Kni]. Using previous experimental determinations, the system O-Zr was assessed by [2004Wan] according to the Calphad method. Cs and Zr are immiscible as well in the solid than in the liquid phases [1996Das].

Solid Phases

Crystallographic data of solid phases are reported in Table 2. In this system only one mixed oxide is well known: Cs_2ZrO_3 which is of the Cs_2PbO_3 type structure. Other compounds, namely Cs_4ZrO_4, $Cs_4Zr_7O_{16}$ and $Cs_6Zr_7O_{17}$ have been reported [1996Das]. However, their crystal structure is unknown. Cs_4ZrO_4 decomposes with formation of Cs_2ZrO_3 + 2 Cs_2O, at 275°C under high vacuum and at 730°C in a sealed container. Cs_2ZrO_3 is stable at least up to 915°C.

Isothermal Sections

Two isothermal sections are proposed by [1999Pou] at the temperatures of 727°C (1000K) and 1727°C (2000 K). These sections were calculated using the Thermocalc package with the nuclear materials databases. The calculation is based on the hypothesis of an ideal behavior of Cs in the (Zr,O) solid solutions. However, such an ideal behavior leads to calculate a slight solubility of Cs in (Zr) and ZrO_2, which contradicts the experimental observations that liquid Cs does not react with Zr, neither with ZrO_2 [1996Das]. Figures 1 and 2 present isothermal sections at 727 and 1727°C under 0.1 MPa pressure, mainly from [1999Pou]. However, the original diagrams have been corrected to take into account the accepted binary diagrams and the lack of any solubility of Cs in zirconium metal and zirconium oxides. According to the thermodynamic modelling [1999Pou] the Cs_2ZrO_3 ternary phase is formed between the room temperature and 900°C by reaction of Cs with zirconia.

Thermodynamics

[1987Cor] measured the standard molar enthalpy of formation of Cs_2ZrO_3. The value $\Delta_f H°(298.15) = -1584.8 \pm 1.9$ kJ·mol^{-1} was obtained by measuring its enthalpy of solution in HF·100H_2O by calorimetry. Same value is reported by [1993Bal] and it is in good agreement with calculated value obtained by [1994Koh] ($\Delta_f H°(298.15) = -1764.2$ kJ·mol^{-1}). It was obtained by measuring $\Delta_f H°$ as a function of temperature from 178°C (451 K) to 378°C (651 K). The resulting value of $\{H(T)-H(298.15\ K)\}$ is presented in Table 3. Gibbs energy of formation of the ternary compound Cs_2ZrO_3 have been obtained by [2001Ali] from vapor pressure of Cs_2O measurements. The value is presented in Table 3. The low temperature heat capacity of Cs_2ZrO_3 was measured between 5 and 393 K by [1999Sch]. The standard entropy at 298.15 K is 199.2 J·mol^{-1}·K^{-1}.

Notes on Materials Properties and Applications

Ytria stabilized zirconia (YSZ) is studied as an inert matrix for an advanced nuclear fuel [1999Pou]. This new fuel generation is foreseen for burning plutonium excesses in light water reactors. Radiocesium is a safety relevant fission product, and both its solubility and retention must be assessed in the fuel. Cesium is known as a volatile fission product which diffuses from the UO_2 pellets towards the gap between the fuel and cladding.

The fission product iodine which is formed in significant amounts combines with another fission product cesium giving CsI [1982Got, 1982Koh, 1985Hof] inside the nuclear fuel pin. In the presence of oxygen, even at its low potential of about 2400 kJ/mol, CsI dissociates to form ternary compounds of cesium such as $Cs_2U_4O_{12}$, Cs_2UO_4, Cs_2ZrO_3, *etc*. and releases elemental iodine [1982Got, 1982Koh, 1985Hof]. The migration of the released iodine to the clad surface and its subsequent reaction with clad material (*e.g.* zircalloy) causes stress corrosion cracking [1982Got, 1982Koh, 1985Hof] which is detrimental to the long-term stability of the nuclear fuel pins. In this context the knowledge of thermochemistry of the compounds of Cs with the other fission products, fuel matrix and the clad materials are important [2001Ali].

Miscellaneous

The synthesis of Cs_2ZrO_3 by a sol-gel procedure following the nitrate-citrate route [2001Mis] leads to nanocrystallites whose average size is 25 nm. Cs_2ZrO_3 vaporizes incongruently with evolution of Cs_2O (gas) and formation of ZrO_2.

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Table 1: Investigations of the Cs-O-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1987Cor]	Dissolution calorimetry in aqueous HF; X-ray measurements	298.15 K / Cs_2ZrO_3
[1993Bal]	Calorimetry /vapor pressure measurements	451-651 K / Cs_2ZrO_3
[1994Koh]	Calorimetry / DSC	310-780 K / Cs_2ZrO_3
[1999Koh]	Heat capacity measurements	310-800 K / Cs_2ZrO_3
[1999Pou]	Implantation / RBS	Cs diffusion in ZrO_2
[1999Sch]	Adiabatic calorimetry and drop calorimetry	5-393 K and 542-703 K / Cs_2ZrO_3
[2001Ali]	Vapor pressure / Knudsen effusion	1142-1273 K / Cs_2ZrO_3

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Cs) < 28.39	*cI*2 $Im\bar{3}m$ W	a = 614.1	at 25°C [Mas2]
(αZr) < 2129	*hP*2 $P6_3/mmc$ Mg	a = 323.16 c = 514.75	at 25°C [Mas2] dissolves up to 31.0 at.% O at 2071°C [2004Wan]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βZr) 1968 - 866	*cI*2 $Im\bar{3}m$ W	a = 360.90	βZr dissolves up to 10.5 at.% O at 1968°C [2004Wan]
αZrO$_2$ < 1203	*mP*12 $P2_1/c$	a = 522 b = 527 c = 538 β = 99.46°	66.6 at.% O [2004Wan]
βZrO$_2$ 2333 - 1203	*tP*6 $P4_2/nmc$ HgI$_2$	a = 511.9 c = 526.0	66.5 to 66.6 at.% O [2004Wan]
γZrO$_2$ 2974 - 1526	*cF*12 $Fm\bar{3}m$ CaF$_2$	a = 509	61 to 66.6 at.% O [2004Wan]
Cs$_2$O < 490	*hR*9 $R\bar{3}m$ Anti-CdCl$_2$	a = 425.6 c = 1899.2	[2005Gem]
Cs$_2$O$_2$ < 590	*oI*8 *Immm* Cs$_2$O$_2$	a = 432.2 b = 751.7 c = 643.0	[Mas2, V-C2]
Cs$_2$O$_3$ < 502	*cI*28 $I\bar{4}3d$ Th$_3$P$_4$	a = 987 ± 1	[Mas2, V-C2]
αCsO$_2$ (r) < 200	*tI*6 *I*4/*mmm* CaC$_2$	a = 446.2 c = 732.6	[Mas2, V-C2]
βCsO$_2$ (h) 432 - 200	*cF*8 $Fm\bar{3}m$ NaCl	a = 662	[Mas2, V-C2]
* Cs$_2$ZrO$_3$ < 915	*oC** *Cmcm* Cs$_2$PbO$_3$	a = 1127.1 ± 0.7 b = 774.3 ± 0.4 c = 595.6 ± 0.5	[1989Min]
* Cs$_4$ZrO$_4$	-	-	[1996Das]
* Cs$_4$Zr$_7$O$_{16}$	-	-	[1996Das]
* Cs$_6$Zr$_7$O$_{17}$	-	-	[1996Das]

Table 3: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J, mol, K]	Comments
Cs_2ZrO_3	869 - 1000	$\Delta_f G° = (-1671.6 + 0.44T\ (\pm 18)) \cdot 10^3$	[2001Ali]
Cs_2ZrO_3	25	$\Delta_f H° = -1748.2 \cdot 10^3$ $\Delta_f G° = -1647.2 \cdot 10^3$ $S° = 197.6$ $Cp = 132.05$	[1999Pou]
Cs_2ZrO_3	25 - 900	$H(T)\text{-}H(298.15\ K) = 167.3315\ T - 2.6252 \cdot 10^{-3}\ T^2 + 35.954 \cdot 10^5 / T - 61715.5$	[1993Bal]

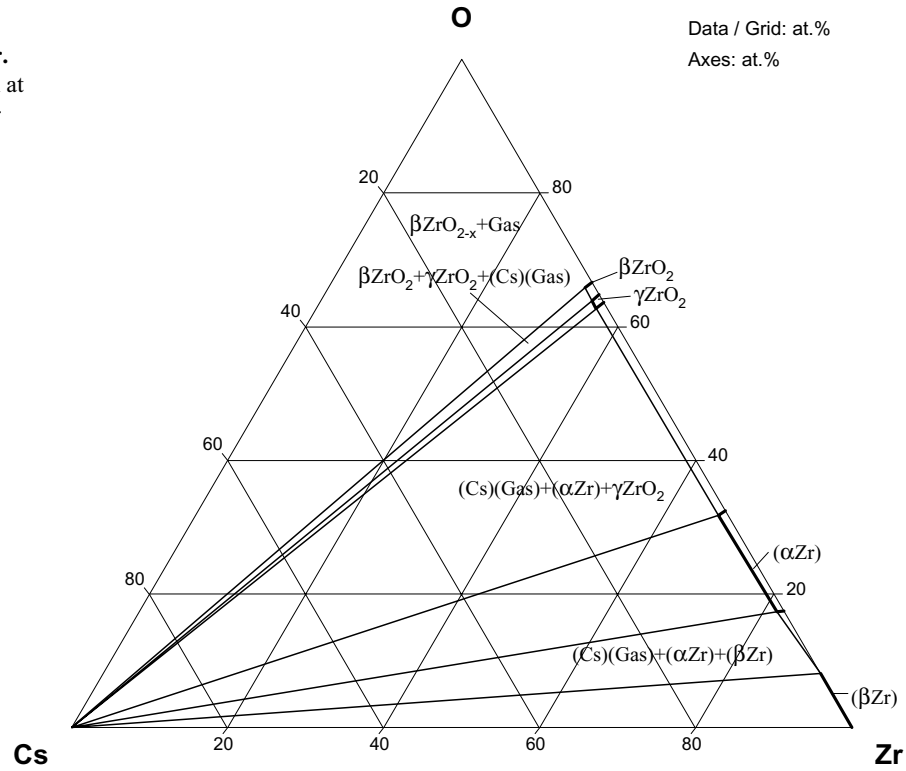

Fig. 1: Cs-O-Zr. Isothermal section at 727°C under 1 bar pressure

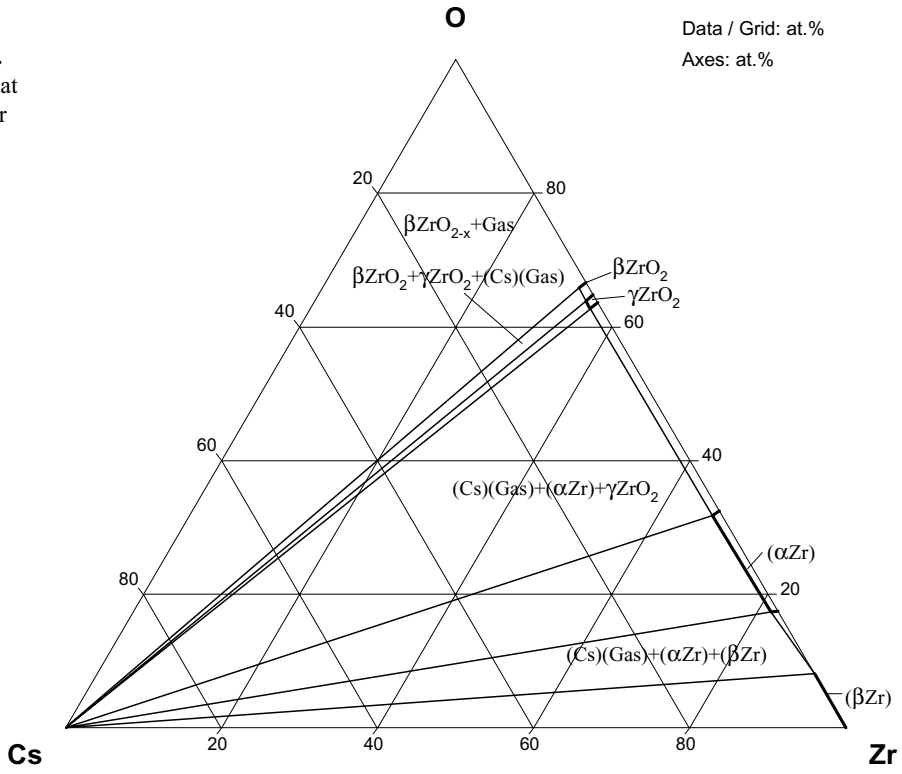

Fig. 2: Cs-O-Zr. Isothermal section at 1727°C under 1 bar pressure