Comparative study of Cs silicates properties between DFT calculation and experimental data

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Abstract

For the construction of the Cs chemisorption model on the stainless steel surfaces under LWR severe accident, the structural and thermodynamic properties of potentially formed Cs chemisorbed species were estimated theoretically and compared with experimental data in order to reduce the uncertainties in Cs-(Fe)-Si-O thermodynamic database. The DFT predicted values allowed to reduce drastically the uncertainties on $Cs_2Si_2O_5$ substance and agreed in overall for other ones.

Keywords: Cesium, silicates, chemisorption, DFT, thermodynamic, LWR

1. Introduction

Estimation of cesium distribution in the reactor pressure vessels of the Fukushima Dai-ichi Nuclear Power Station by the present severe accident analysis codes causes large uncertainties. A major source of the uncertainties originates from the implemented models. A mass transfer type model [1] is being developed for the reduction of uncertainties. This model treats the chemical features of the Cs chemisorption process, which requires accurate thermodynamic data for the Cs chemisorbed compounds. For this purpose, we compared thermodynamic properties of major formed/predicted Cs silicates, Cs-(Fe)-Si-O, obtained from DFT calculations with ones from experimental data to mutually estimate the accuracy of both methodologies.

2. Methodology

Density Functional Theory (DFT) was applied to obtain the structural and energetic properties of the target species coupled with statistical physics to predict the thermodynamic properties [2]. The experimental data were derived from low-temperature heat-capacity measurements by using PPMS device [3].

3. Results and discussion

Table 1 shows comparison of thermodynamic properties between the DFT predicted values, experimental measurements and literature references. The mean absolute error for heat capacities (C_p) is 0.74-3.9% between literature and DFT, while 18.7% between literature and experiments. As for entropies (S), it is about 3.9-8.7% between literature and DFT, while 15.7% between literature and experiments.

Table 1 Comparison of the values of Heat capacity, Cp(T), Entropy, S(T), and Enthalpy increment, H(T)-H(0)

Properties	$Cs_2Si_2O_5$			Cs_2Si4O_9			$CsFeSiO_4$	
	DFT	Exp.[3]	Lit.[4]	DFT	Exp.[3]	Lit.[5]	DFT	Exp.[3]
Cp (298 K) [J/mol. K]	163	231	165	238-253*	249	239	133	144
S (298 K) [J/mol. K]	241	308	230	303-277*	321	313	177	188
H (298K) -H(0) (kJ/mol)	32	43	-	43	46	-	24	26

** Two crystal structures were found stable*

It appears that experimental evaluation of $Cs_2Si_2O_5$ would require further certification considering the large discrepancies from others. A great accordance is found for the thermodynamic assessment of $Cs_2Si_4O_9$ and $CsFeSiO_4$ substances from all sources.

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References

[1] S. Nishioka et al, AESJ Fall meeting, 2P09, 2017. [2] F. Miradji et al, AESJ Spring meeting, 2M14, 2018. [3] E. Suzuki et al, AESJ Spring meeting, 2D18, 2018. [4] Spencer, NPL report, 1973. [5] R. Ball et al., J.Nucl. Mater. 201 (1993) 81.