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研究課題名（和文）Prepation of Generic Oxides Melt Model for Late-Phase Severe Accident Analysis

研究課題名（英文）Prepation of Generic Oxides Melt Model for Late-Phase Severe Accident Analysis

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研究成果の概要（和文）：軽水炉での重大事故におけるセシウムの高温挙動の理解を深めるために、H2O+H2ガス中のCs2Mo04の高温挙動について研究した。二元系であるCs2Mo04-Mo03をRedlich-Kister式を用いて熱化学的にモデル化し、IMCCモデルを用いてCs2Mo04とCs2Mo207の液体混合物を行った。短時間の全電源喪失特有のLWR炉心劣化状態において、熱化学モデルを適用した。
Cs2Mo207の蒸発挙動を明らかにされて、Cs2Mo04とSUSとの反応を研究した。乾燥状態にはCrとの反応でCs2Mo04が主であり、湿潤状態には、モリブデンは酸化スケールでの取り込み、反応は限られているようだった。

研究成果の概要（英文）：The high-temperature behavior of Cs2Mo04 in H2O+H2 gas was studied in order to better understand the behavior of cesium in the severe accident of the LWR. The pseudo-binary system, Cs2Mo04-Mo03, was thermochemically modeled with Redlich-Kister formulation, and the IMCC model has been also examined for the liquid mixtures of Cs2Mo04 and Cs2Mo207. Thermochemical model was further applied to predict the partitioning of cesium and molybdenum among gaseous species in the LWR core degradation condition, which is typical of Short-Term Station Blackout.
Vaporization behavior of Cs2Mo207 was clarified. Reactions of Cs2Mo04 with SUS in dry and humid atmosphere were studied. It was clarified that Cs2Mo04 was decomposed mostly by the reaction with Cr in dry condition. In humid condition, the reaction seemed to be limited to result in a very small fraction of molybdenum incorporation in the oxide scale.

研究分野：　materials science

キーワード：　cesium molybdate　vaporization　Cs2Mo04-Mo03　Cs-Mo-O-H system　Cs2Mo207　thermodynamics　severe accident

１．研究開始当初の背景

Cesium is one of the key fission products in the consequence analysis of severe accident of the Light Water Reactor (LWR) and Pressurized Water Reactor (PWR). Traditionally, cesium has been considered to form mainly CsOH, while some Cs forms CsI to an extent corresponding to the iodine inventory. Recently, some research recently confirmed the form of Cs during releasing is cesium molybdate, Cs_2MoO_4. However, the knowledge on the behavior of vaporization and deposition of Cs_2MoO_4 was limited for understanding the fission product releasing during severe accident.

During the whole course of the severe accident of BWR, the oxygen potential, $p(O_2)$ should be high enough for stabilization of Cs_2MoO_4 in the steam dome region. Besides, it should have the effect of steam on the partitioning of Cs_2MoO_4 and CsOH. In the equilibria, higher molybdates of cesium such as $Cs_2Mo_2O_7$ also play some roles. Therefore, the detailed analyses of Cs-Mo-O-H system at high temperatures is necessary.

Moreover, when Cs_2MoO_4 transported under gaseous form, it could deposit and react on steam generator, steam dryer and reactor coolant system that were made by stainless steel. The behavior of Cs_2MoO_4 and the chemical reaction with SUS in the complex conditions with temperature, steam contents components need to be cleared.

２．研究の目的

This study aims to extend the ideal mixing the complex components (IMCC) model to vaporization of Cs_2MoO_4-MoO_3 system in various environments. Thermochemical model was further applied to predict the partitioning of cesium and molybdenum among gaseous species in the BWR core degradation condition typical of Short-Term Station Blackout.

Based on the behavior of species at high-temperature, the final's goal is to identify the possible phases could be formed, in order to have further insight on the effect of Cs_2MoO_4 on SUS oxidation at high temperature.

３．研究の方法

3.1 Thermogravimetric method

The high-temperature mass loss of Cs_2MoO_4 and $Cs_2Mo_2O_7$ were monitored with a thermogravimetry equipment (SETARAM SETSYS TG DTA18) which is coupled with a humidity generator (SETARAM WETSYS). The heating temperature ranging from 1273 to 1573 K. The heating rate was 10 K/min. The carrier gas was argon at a flow rate of 40 ml/min, to which steam was added with 90%RH at 343K, giving a partial pressure $p(H_2O)$=0.281 bar.

The obtained data was used for $Cs_2Mo_2O_7$ enthalpy calculation.

3.2 Thermochemical modeling

Based on the measurement and reference data, IMCC model of Cs_2MoO_4-MoO_3 liquid solutions were calculated and then was compared with RKMP model of Cs_2MoO_4-MoO_3 liquid solutions and

3.3 Reactions involving Cs_2MoO_4 in the BWR core degradation

Fukushima Daiichi Unit-1 (1F) was taken as an example, with the amount of Cs is 1140 mol/core and molybdenum inventory was about 1850 mol/core. Molybdenum is enough to form Cs_2MoO_4 as long as the inventory is concerned. the average molar flow ratio of $H_2O(g)$/Cs was choose as about 2,000. The molar flow ratio $H_2(g)/H_2O(g)$ would typically range from 1/100 to 2 due to the analysis. Referring to the MELCOR time-to-failure model, T (fuel) < 2600 K was assumed in the calculation. The calculations were done at the total pressure of 75 bar and 3.5 bar, which represent the RPV pressure before and after the depressurization. Free energy minimizer ChemSage was used for the calculation. Iodine was excluded in this analysis in order to focus on the equilibria in the Cs-Mo-O-H system.

3.4 Transpiration test

Either Cs_2MoO_4 or $Cs_2Mo_2O_7$ were placed in a platinum boat and heated at 1573 K. Either SUS304 or platinum plates were placed downstream at different distances corresponding to temperatures ranging from 1554 to 547 K. The carrier gas was Ar or Ar saturated with steam at 70°C. The deposits were examined by the scanning electron microscope equipped with an energy dispersive X-ray spectroscopy (SEM/EDAX), micro-Raman spectroscopy and X-ray diffraction equipment.

４．研究成果

4.1 Enthalpy vaporization of $Cs_2Mo_2O_7$

Comparing the high-temperature mass losses of $Cs_2Mo_2O_7$ by thermogravimetry with that of Cs_2MoO_4, the equilibrium vapor pressure of $Cs_2Mo_2O_7$ was estimated. The vapor pressure of $Cs_2Mo_2O_7(l)$ in its liquid state

was calculated to be:

$\log_{10}P\ (Cs_2Mo_2O_7(l)) = (8.95 \pm 0.07) - (1.03 \pm 0.01) \times 10^4 / T \quad (T = 1273 - 1573\ K)$

which gives ΔH_v of $Cs_2Mo_2O_7(l)$ as 197 ± 31 kJ.mol^{-1}. **Fig. 1** compares the vapor pressures of Cs_2MoO_4 in the literature and $Cs_2Mo_2O_7$ in this work.

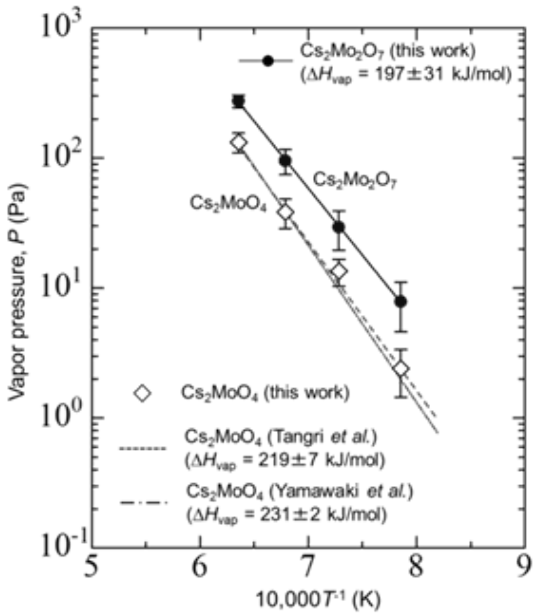

Fig. 1. The Arrhenius plot of the vapor pressure of Cs_2MoO_4 and $Cs_2Mo_2O_7$. The lines for Yamawaki *et al.* and Tangri *et al.* are extrapolated beyond their measurement ranges.

4.2 Thermochemical modeling

In this study, the IMCC model was also tested for the liquid mixtures of Cs_2MoO_4 and $Cs_2Mo_2O_7$. In accordance with IMCC, the molten Cs_2MoO_4 - $Cs_2Mo_2O_7$ phase was simply assumed as their ideal mixtures.

The liquidus was calculated with the IMCC model to be compared with that by the RKMP model (**Fig. 2**) although the agreement deteriorates toward the $Cs_2Mo_2O_7$ end, it is excellent near the Cs_2MoO_4 end.

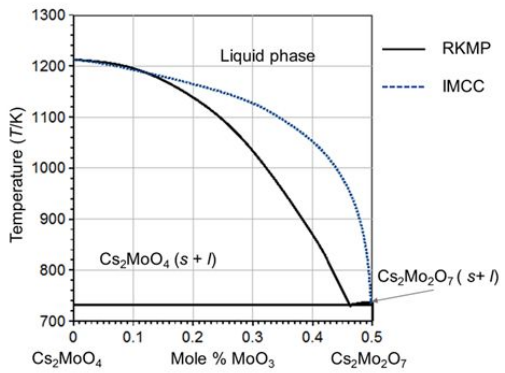

Fig. 2 The liquidus of Cs_2MoO_4 was calculated by the IMCC model and by the RKMP model.

4.3 Reactions involving Cs_2MoO_4 in the BWR core degradation

Fig. 3 shows the partial pressure of different species at in the total pressures at 75 bar and 3.5 bar. The solid and dash lines correspond to the molar ratio of H_2/H_2O at 1 and 1/100, respectively. The relative importance of Cs_2MoO_4 and CsOH is not very sensitive to the H_2/H_2O ratio. On the other hand, the total pressure has a significant effect: CsOH(g) becomes more predominant at lower temperature regions with increasing pressure. Although Mo is preferentially partitioned also to H_2MoO_4 at the damaged core region, it will be transferred to cesium molybdates as the gas phase cools. Importance of Cs(g) decreases rapidly, but that of $Cs_2Mo_2O_7(g)$ increases as the gas cools. The deposition of molybdates starts at ~1900K at 75bar and ~1550K at 3.5 bar.

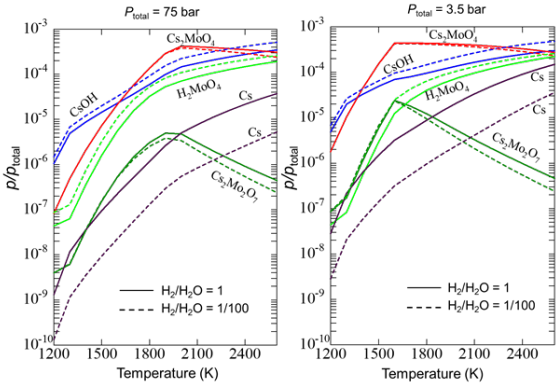

Fig. 3 Partial pressure of species in core region with different molar ratio H_2/H_2O

4.4 Reactions on SUS 304

Mo was found on the surface and inside of SUS oxide scales at the temperature higher than 1230°C but it did not correspond to any type of cesium molybdates. At lower temperature (944°C), the deposit was identified as MoO_2 (**Fig. 4**). These observations were compared with the deposit on platinum plate. At the same temperature, the deposit on platinum was Cs_2MoO_4. The observation suggests that there were some reactions between Cs_2MoO_4 and SUS304 at the temperature higher than melting point of Cs_2MoO_4 (940°C). At the lower temperatures the deposits were Cs_2MoO_4.

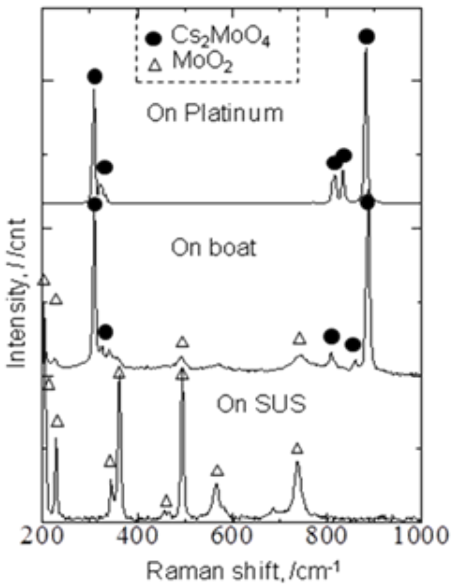

Fig. 4 Raman spectra of deposits on Pt tape, boat and SUS at 944°C.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計　1 件）

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Title: Cs2Mo04-Mo03系の高温化学; 2. Cs2Mo207融解挙動を組込んだCs2Mo04-Mo03系のモデル化.

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Author: Thi-Mai-Dung Do, Supamard Sujatanond, Toru Ogawa

〔図書〕（計　0 件）

〔産業財産権〕

○出願状況（計　0 件）

名称：
発明者：
権利者：
種類：
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国内外の別：

○取得状況（計　0 件）

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権利者：
種類：
番号：
取得年月日：
国内外の別：

〔その他〕
ホームページ等

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