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解　説

Frontiers of Solid-Gas Interaction Research As Extended by Application of Atmosphere-Controlled High Temperature Mass Spectrometer and High Temperature Kelvin Prove

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This study has reviewed (i) improvement of performance of atmosphere-controlled high temperature mass spectrometer (ACHTMS), (ii) application of ACHTMS to studies of high temperature solid-gas reactions of oxide ceramics, and (iii) application of high temperature Kelvin probe (HTKP) to solid-gas interactions on oxide ceramics.

1. Introduction

A finely tunable atmosphere-controlled high temperature mass spectrometer (ACHTMS) was developed and has been used for studies of high temperature reaction equilibia between solid and reactive gases.[1,2] In order to confirm the performance of this newly-developed system in regard of the adequacy for high temperature equilibria studies, temperature dependences of introduced gas pressure in Knudsen cell were measured for hydrogen as well as for other gases.[3] After confirmation of the appropriateness of this system, vapor pressures of lithium-bearing oxide ceramics, the candidates for fusion reactor blanket breeder materials, were measured with hydrogen gas introduced in this system for evaluating the lithium losses of the candidate breeder oxide ceramics.[4] It was observed that the lithium vapor pressure is affected by non-stoichiometry of the oxides. Further, the effect of hydrogen / water vapor addition upon the vapor pressure of complex uranium-alkaline or -alkaline earth oxides was studied using the ACHTMS system for simulating the behavior of highly radioactive fission products during severe accidents of nuclear reactors.[5] Also, high temperature Kelvin probe (HTKP) was applied to study interaction of lithium oxide ceramics with reactive gases.[6] Vacancy formation in such oxides was detected using this method, which was attributed to the irregular vaporization behavior of some lithium oxides as observed with ACHTMS.[4]

2. Characteristics of ACHTMS

The deuterium gas pressure in a Knudsen cell was measured for fixed flow rates of introduced D_2 gas by means of a Nuclide 12-90-HT mass spectrometer attached with a mixed gas inlet system as shown in **Fig.1**. The gas inlet system consists of a pair of outside gas reservoirs, a pair of low conductance capillary tubes and a single fine platinum tube with conductance higher than those of the connecting capillary tubes. The platinum fine tube has the inner diameter of 0.6 mm and was welded into a hole drilled through the center of the bottom of Knudsen cell. The obtained temperature dependence of D_2 pressure in Knudsen cell is shown in **Fig.2**, as compared to that of atomic D pressure.[7] The result confirmed that the experimentally obtained gas pressures are close to the theoretical values over a wide range of temperature from room temperature to 1700 K, though the downward departure of the measured value from the theoretical is clearly identified for temperatures higher than 1173 K. The observed downward departure in temperature dependence of gas pressure in Knudsen cell was not so large as to cause significant errors in the evaluated thermochemical equilibrium constants.[3] From measurements on various kinds of gases, it was shown that the gas supply rate into Knudsen cell depends on the reservoir gas pressure and the mass M of gas molecule or atom. The supply rate decreases almost in proportion to the inverse square root of M corresponding to the molecular flow, while departure from this rule becomes conspicuous

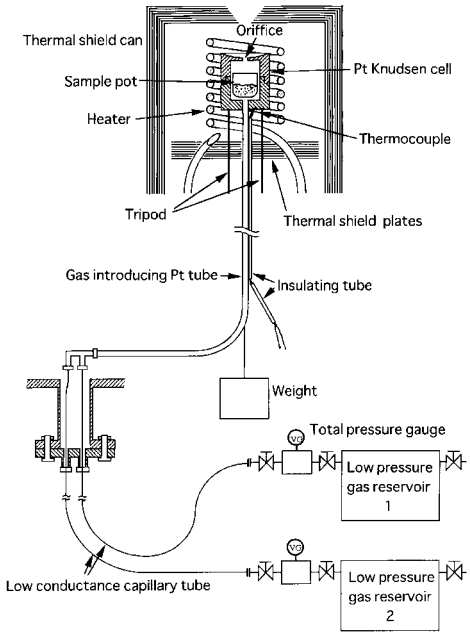

Fig.1 Knudsen cell attached with a mixed gas inlet system for ACHTMS.[3)]

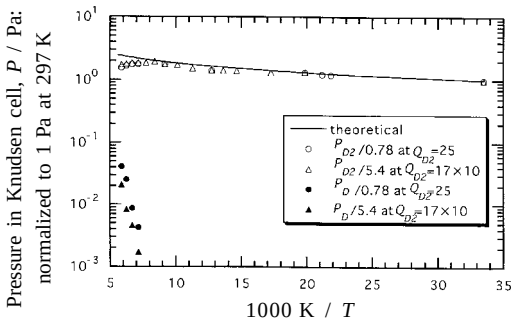

Fig.2 Temperature dependence of gas pressure in Knudsen cell with gas introduction at fixed flow rate $Q_{D_2}/10^{-6}$ Pa m^3 s^{-1}.

with increasing *M*.[3)]

3. Hydrogen Atmosphere Effect on Lithium Evaporation of Lithium-Bearing Oxide Ceramics

Lithium oxide, Li_2O, and lithium-bearing ternary oxides, Li_4SiO_4, Li_2TiO_3, Li_2ZrO_3 and $LiAlO_2$, have been intensively studied as the main candidates for solid breeder material in fusion reactor blankets.[8)] One of the concerns as to using the solid breeders is the lithium loss at high operation

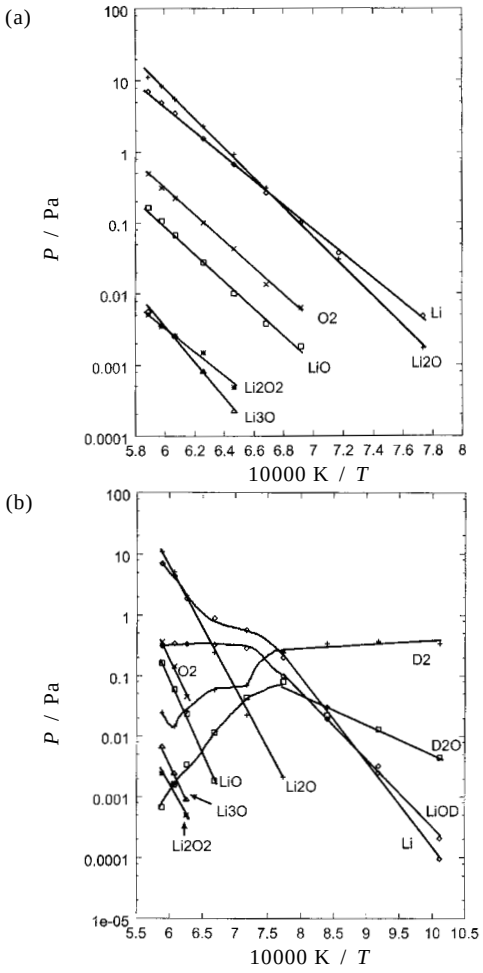

Fig.3 Partial pressures of vapor species in (a) Li_2O (without D_2 or D_2O admission) and (b) Li_2O-D_2 system.

temperature. To evaluate the lithium loss of solid breeders, the vapor pressure over each oxide was measured under addition of hydrogen gas of about 1 Pa into Knudsen cell to simulate the sweep gas of the blanket.[1,9-11)] An example of such a measurement is shown for Li_2O and Li_2O-D_2 system in **Figs.3(a)** and **3(b)**, respectively.[12)] Due to the fact that only a limited amount of D_2 can be admitted in order to maintain "Knudsen flow" regime, a considerable decrease of D_2 partial pressure was observed at temperatures >1300 K. It is likely that most of D_2 reacted with $Li_2O(s)$ in this temperature range to form D_2O and LiOD, which were not observed in **Fig.3(a)**; *i.e.* the case without D_2 admission. From such vaporization results, the equilibrium constants

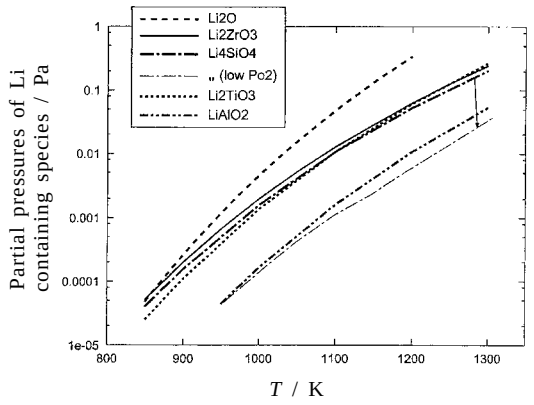

Fig.4 Summation of partial pressures of lithium-bearing species as a function of temperature.

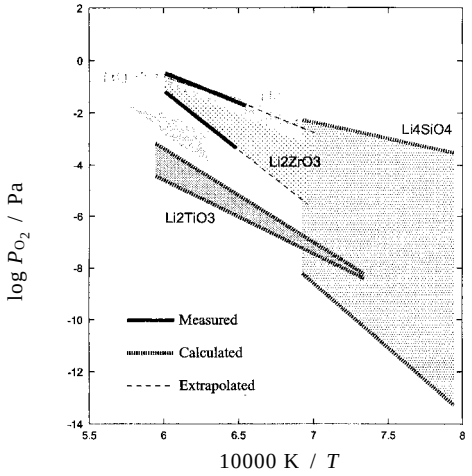

Fig.5 Changes of oxygen partial pressures when hydrogen was admitted.

of the reactions between the vapors of oxides and hydrogen gas were evaluated.

For evaluation of the lithium loss, the typical sweep gas was assumed to be the helium gas at 1 atm pressure added with 100 Pa hydrogen gas. The addition of hydrogen gas is intended to enhance the recovery rate of tritium from the solid breeder during irradiation. As an indicator of the lithium loss, the sum of partial pressures of all the lithium-bearing vapor species was calculated from the evaluated equilibrium constants and the mass conservation law.[3] The obtained sum P_{Li}^{total} of partial pressures of lithium-bearing species over each oxide breeder is exhibited in **Fig.4**. At 1000 K of blanket temperature, P_{Li}^{total} is evaluated to be about 0.005 Pa, 0.002 Pa, 0.0015 Pa, 0.001 Pa and 0.0001 Pa for Li_2O, Li_2ZrO_3, Li_4SiO_4, Li_2TiO_3 and $LiAlO_2$, respectively.[4,12] In the case of Li_4SiO_4, however, a remarkable oxygen potential effect was observed as shown in **Fig.4**. This behavior can be related to the tremendous oxygen pressure drop observed when low pressure (~1 Pa) hydrogen was added into Knudsen cell, as shown in **Fig.5**. A minor oxygen pressure drop was observed in the case of Li_2ZrO_3, while little change in oxygen pressure was identified for Li_2O, Li_2TiO_3 and $LiAlO_2$.[12] Such an exceptional behavior of Li_4SiO_4 was attributed to change of the non-stoichometric composition that Li_4SiO_4 has. The work function measurement of Li_4SiO_4 performed by means of HTKP revealed a strong tendency for this material to produce oxygen vacancies on contacting the reducing atmosphere[13] as described in Section 5 of this report.

4. Hydrogen / Water Vapor Atmosphere Effect on Vaporization of UO_2-Based Complex Oxides with Alkaline Metals or Alkaline Earths

The Cs(g), Sr(g) and Ba(g) partial vapor pressures are especially important to assess the possible impact of severe accidents of light water reactors because of their strong radioactivities and volatilities.

The partial vapor pressure of Cs(g) was found to be more than one order of magnitude higher than those of other vapor species, CsO(g), CsOD(g) etc. over Cs_2UO_4 as well as $Cs_2U_4O_{12}$.[5] As shown in **Fig.6**, the Cs(g) vapor pressure over Cs_2UO_4 was found to be greatly affected by the oxygen potential of the atmosphere; the pressure of Cs(g) was highest when D_2 was introduced into the Knudsen cell, it was secondly highest when D_2O(g) (corresponding to $2D_2+O_2$ mixture) was introduced, while it was lowest when D_2+2O_2 mixture was introduced.[5,14] On the other hand, the pressure of Cs(g) over $Cs_2U_4O_{12}$ was observed not to be so much influenced by the oxygen potential of the atmosphere, *i.e.* by whether D_2 or D_2+O_2 mixture was introduced into the Knudsen cell,[15] as shown in **Fig.7**. The different behaviors observed on Cs_2UO_4 and $Cs_2U_4O_{12}$ can be explained as follows;

The vaporization reaction for Cs_2UO_4 and $Cs_2U_4O_{12}$ can be expressed by the following equations, respectively:

$$2Cs_2UO_4(s)+D_2O(g)=Cs_2U_2O_7(s)+2CsOD(g). \quad (1)$$

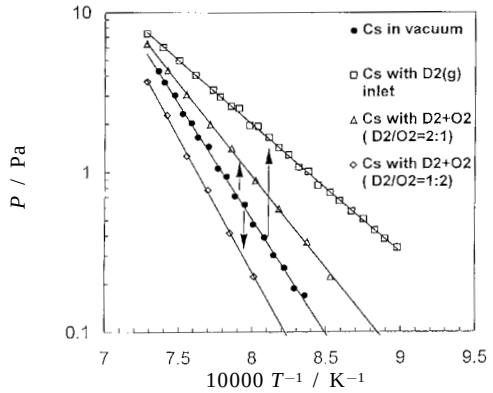

Fig.6　Comparison of Cs pressures over Cs_2UO_4 under different conditions.

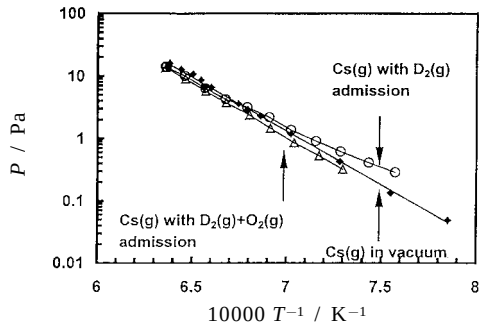

Fig.7　Comparison of changes in Cs pressure over $Cs_2U_4O_{12}$ in different environments.

and

$$Cs_2U_4O_{12}(s) = 4UO_{2+x}(s) + 2(1-x)O_2(g) + 2Cs(g). \quad (2)$$

The reaction product UO_{2+x}(s) in eq.(2) can vary its oxygen content according to the oxygen potential of the atmosphere, so that the impact of the change of the atmosphere composition can be moderated compared to the case without formation of UO_{2+x}(s), *i.e.* the case of Cs_2UO_4(s).

In case of $SrUO_3$ and $BaUO_3$, D_2 or D_2O introduction into Knudsen cell decreased the vapor pressures of Sr(g) and Ba(g), respectively. This can be attributed to the absolute value of Gibbs energy of formation per mole of O_2 of hyperstoichiometric strontium or barium uranate is smaller than that of stoichiometric strontium or barium uranate.[5)]

The above results suggest that the existence states of cesium, strontium and barium in the oxide fuel pellet can greatly influence their vapor pressures and hence the potential risk of release and transportation of their high radioactivities to reach the human environment.

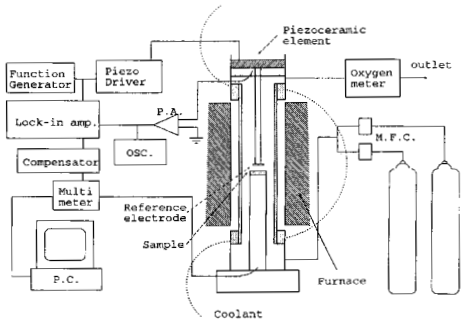

Fig.8　Configuration of the HTKP system.[16)]

5. Work Function Measurement under Controlled Gas Atmosphere at Elevated Temperatures

The high temperature Kelvin probe (HTKP), which is exhibited schematically in **Fig.8**, has been developed and modified by the authors in collaboration with J. Nowotny, the University of New South Wales, with which work function (ϕ) measurement at high temperatures and under controlled atmosphere can be performed.[16)] In order to confirm the performance of the system, the work function change of YSZ (zirconia stabilized with 2 at% yttria) due to the change of oxygen potential was measured at 973 K.[16,17)] The relation between the work function change and the oxygen partial pressure obtained from the experimental results showed good agreement with that predicted based on the defect equilibrium:

$$O_O^x = V_O^{n+} + ne' + 1/2O_2(g), \quad (3)$$

The work function changes of breeder blanket materials caused by the change of composition of the sweep gas were then measured by using the same apparatus. **Fig.9(a)** shows the change of CPD (contact potential difference, corresponding to work function difference with respect to reference electrode) between Li_2ZrO_3 and Pt reference electrode as caused by the change of the composition of flowing gas, while **Fig.9(b)** shows that between Li_2TiO_3 and Pt electrode.[13)] The chemical composition of the sweep gas was either (O): He; (100 cc min^{-1}) or (R): He + 1.06 % H_2 (100 cc min^{-1}). It is shown in **Fig.9(a)** that when the chemical composition of the sweep gas was changed from (O) to (R), the CPD was first decreased abruptly by 500 mV (portion "a"), and then gradually increased to a steady state value (portion "b"). It should be noted that the CPD

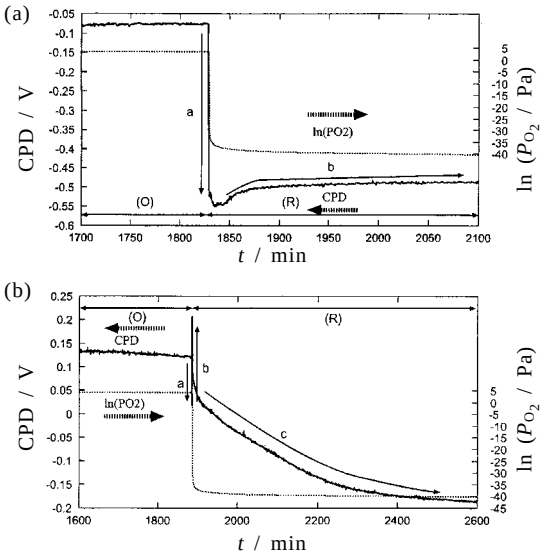

Fig.9 Change of CPD between Li-bearing ternary oxides and Pt electrodes due to the change of chemical composition of sweep gas[13]: (a) Li_2ZrO_3 at 943 K, and (b) Li_2TiO_3 at 933 K. Shown also here is the change of oxygen potential (dashed curve).

change showed good correlation with the change of oxygen partial pressure, P_{O_2}. Assuming that the change "a" is due to production of oxygen vacancies, V_o^{n+}, the decrease of work function and that of P_{O_2} which is determined by a defect equilibrium (eq. (3)) can be related by:

$$1/kT\ (\partial \phi / \partial \ln P_{O_2}) = 1/2(n+1), \quad (4)$$

according to which $1/2(n+1)=1/5.68$ ($n=1.84$) was obtained. This implies that doubly charged $V_o^{\cdot\cdot}$ is predominant. Similar results were obtained for Li_4SiO_4, measurement of work function change of which was performed at 973 K.[18]

In the case of Li_2TiO_3 (**Fig.9(b)**), it is characterized by a single step of the CPD change whose rate was very slow compared with that of Li_2ZrO_3. Such a slow change of work function due to the change of P_{O_2} may be explained, if one assumes that it is governed by adsorption / desorption of H_2 on the surface, whose processes are vitally important in the tritium release from ceramic breeders.

6. Discussion

One of the facts which led the authors to suppose an existence of non-stoichiometric layer in the near surface of Li_4SiO_4 and Li_2ZrO_3 was the finding that in these cases the equilibrium constant, *K*, of LiOD formation was dependent

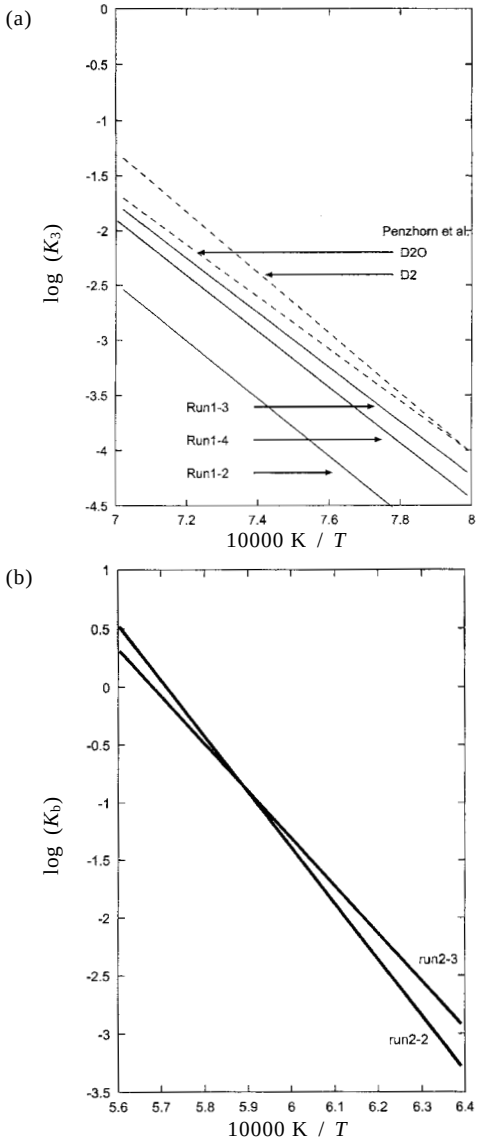

Fig.10 Temperature dependence of equilibrium constant of LiOD formation reaction obtained from several different runs: (a) Li_4SiO_4; for reference, the data by Penzhorn *et al*.[19] are shown with the dashed lines, and (b) $LiAlO_2$.

on oxygen potential.[1,19] In **Figs.10(a)** and **10(b)** are compared the equilibrium constants corresponding to:

$$Li_4SiO_4(s)+D_2O(g)=2LiOD(g)+Li_2SiO_3(s), \quad (5)$$

$$5LiAlO_2(s)+2D_2O(g)=4LiOD(g)+LiAl_5O_8(s). \quad (6)$$

It can be seen from the above equations that the partial pressure of LiOD is considered to be weakly dependent on

that of O_2. According to the figure, it was true in the case of $LiAlO_2$ (**Fig.10(b)**), whereas it was not in the case of Li_4SiO_4 (**Fig.10(a)**). This has led the authors to suppose that a reaction such as;

$$Li_4SiO_{4-x}(s) + x\,O_2(g)/2 + D_2O(g) = 2LiOD(g) + Li_2SiO_3(s) \quad (7)$$

is responsible for the obtained result shown in **Fig.10(a)**. This equation implies that the larger the P_{O_2} is, where P_{O_2} is considered to decrease as Run 1-3 > Run 1-4 > Run 1-2, the larger the $K_3 = (P_{LiOD})^2/P_{D_2O}$ becomes, since $K_3 \propto (P_{O_2})^{x/2}$.

In order to examine whether the oxygen-deficient layer is really formed, the HTKP was employed. The performance of the probe was examined thoroughly by using YSZ as a sample, the defect concentration of which is controlled by the dopant, yttria (Y_2O_3). Thermochemical behavior of defects in YSZ is well known, so that the experimental results can be compared with those cited in literature.[20] By closely comparing with the data of YSZ, the thermochemical behavior of Li-bearing ceramics with respect to defect formation / annihilation was studied. According to the results obtained thus far, two steps of the work function change are normally observed; *i.e.* a fast initial change being followed by a slow change. So long as the defect equilibria hold, the former can be attributed to the oxygen vacancies formation / annihilation, whereas the latter to adsorption / desorption or other surface kinetics, if any.

Another important aspect of the work function measurement in the present system is that the observed work function change may be deconvoluted to several different surface kinetics. It was demonstrated that the defect formation / annihilation process is very fast, which can be clearly distinguished from other processes, such as adsorption and desorption. The HTKP may be effectively combined with other surface-sensitive techniques such as thermal desorption spectroscopy (TDS)[21] or FT-IR,[22] to clarify the mechanism of surface reactions.

In an environment relevant to fusion blanket, not only surface reactions[23] but also irradiation effects[24] may play a vital role in tritium release from ceramic breeders. Kelvin probe can be further extended to investigate the behavior of non-equilibrated irradiation defects. Actually, the authors *et al.* have set up a new apparatus to investigate the effect of beam irradiation on the work function of solid materials, and found that significant drop in the work function of metals and oxides occur on hydrogen ion beam irradiation.[25]

Although thermochemical evaluation of ceramic breeder may be possible by means of high temperature mass spectrometry alone, some properties are characteristics of material and / or environment to which it belongs. Without microscopic characterization of materials in use, macroscopic predictions can vary by orders of magnitude as shown in the case of Li_4SiO_4, see **Fig.4**.

As is clear from the present study, application of two independent experimental techniques can provide valuable information on the thermochemical behavior of Li ceramics, both from macroscopic and microscopic standpoints. According to the results of vapor pressure measurements on various Li-bearing ceramics, the vaporization behavior was observed to be dependent on the oxygen potential in the cases of Li_4SiO_4 and Li_2ZrO_3. This observation led the authors to assume an existence of oxygen-deficient surface layer in these ceramics. In order to further investigate the thermochemical behavior of Li-bearing ceramics, a high temperature Kelvin probe was employed. The work function changes of Li_4SiO_4 (973 K) and Li_2ZrO_3 (943 K) were measured. The work function change of oxygen vacancies formation / annihilation was observed, followed by the change due to adsorption / desorption. In the case of Li_2TiO_3 (933 K) and Li_2O (823 K), where a single step of the work function change, due to adsorption / desorption, was observed. These results support the authors' interpretation of the results of the high temperature mass spectrometry described above, indicating possible relevance between macroscopic and microscopic behaviors of hydrogen at the surface of ceramic breeders.

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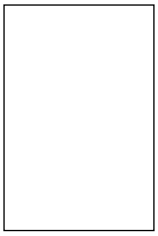
要　旨

高温質量分析計のクヌーセンセルの底部中央に小孔を穿ち，そこに白金細管を溶接し，毛細管を介して外部ガス貯めに結合させることにより，固体－気体反応を直接的に観測しうる実験体系を作製した。この言わゆる雰囲気制御型高温質量分析計（ACHTMS）の性能を詳細に調べ，クヌーセンセル内ガス圧に及ぼすガス分子量／原子量，セル温度等の影響を明確にした。本システムを用いることにより，核融合炉ブランケット増殖材，Li_2O，Li_4SiO_4，Li_2TiO_3，Li_2ZrO_3，$LiAlO_2$について，スイープガス中の添加水素によるリチウム蒸発損失増加量を評価し，特にLi_4SiO_4やLi_2ZrO_3では，雰囲気の酸素ポテンシャルにより蒸気圧が強く影響されることを明らかにするなどの成果を挙げた。さらに，強い放射性能を持つ核分裂生成物（FP）であるCs，Sr，BaとUO_2との各複合酸化物からのこれらFPの蒸発に対する水蒸気／水素添加効果を測定し，軽水型原子炉の事故時におけるこれらFPの蒸発挙動について化学種毎に特異性を有するなどを明らかにし過酷事故解析に寄与した。また，高温ケルビン計による仕事関数測定から，固体の雰囲気ガスとの相互作用，特に欠陥生成消滅，ガス吸脱着などをその場的に観測しうることを明らかにした。特に，安定化ZrO_2，Li_4SiO_4，Li_2ZrO_3などでは酸素空孔生成に基づく仕事関数の低下が，またLi_2TiO_3などではガスの吸着による仕事関数の低下が観測されること，さらにそれらは時定数の違いから明瞭に識別しうることなどを見出した。本手法により求まるミクロな挙動と，ACHTMSにより求まるマクロな挙動を結び合わせることにより，固体－気体反応の本質に迫る新たな解明が可能になるものと期待される。



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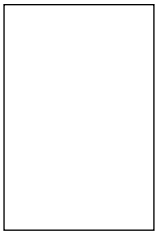
研究テーマ：核燃料，原子力材料，核融合材料に関する研究
趣味：クラシック音楽，自然・歴史の探勝・探索，ゴルフ



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研究テーマ：核融合炉プラズマー材料相互作用，表面分析による界面現象解明
趣味：古典音楽鑑賞，読書