Wettability of Liquid CsI on Polycrystalline UO_2

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Abstract

Our group has confirmed the high wettability of liquid caesium iodine (CsI) on the polycrystalline UO_2 solid surface. However, the mechanism of such high wettability has not been clarified. Here, the sessile drop tests were performed for liquid CsI on various solids including UO_2 to understand the origin of the high wettability of CsI against UO_2. On the solid surfaces of polycrystalline UO_2, yttria-stabilized zirconia (YSZ) (100) plane, and TiO_2 (100) plane, melted CsI spread immediately onto these solid surfaces with the contact angle nearly 0°. However, on the solid surface of MgO (100) plane, liquid CsI did not spread and the contact angle was measured to be 27°. One of the reasons of the high wettability of liquid CsI against UO_2 is the effect of common properties of solid surfaces of UO_2, YSZ, and TiO_2, such as the oxygen-defects formed at oxide solid surface.

1. Introduction

An understanding of the release behaviour of volatile fission products (FPs) from fuels contributes for analyzing a nuclear severe accident. Several groups had launched for gathering the information concerning to the release behaviour of various volatile FPs [1-4]. Our group has been focusing on the surface and interface effects for the release behaviour of caesium (Cs) and iodine (I). The fuel surface is supposed to be a migration path when FPs are released from fuels. Our group has confirmed that liquid caesium iodine (CsI) showed high wettability against polycrystalline UO_2 solid surface, where the contact angle formed between liquid CsI and UO_2 was measured to be virtually 0° [5]. However, the mechanism of this high wettability is not clarified. Deep understanding of the liquid CsI behaviour on polycrystalline UO_2 solid surface is beneficial to clarify the release behaviour of Cs and I from fuels. On the other hand, basically, the wetting phenomenon is determined by the interaction between solid surface and liquid [6]. From these back grounds, the present study focuses on the effects of the solid surface on the wettability of liquid CsI. On the various solid surfaces, the behaviour of liquid CsI was tested by a sessile drop test. The sessile drop test is one of the most common methods for wettability measurement and widely used for evaluating the solid-liquid interface energy [7].

2. Experimental

This study employed three types of single crystalline solid surfaces in addition to polycrystalline UO_2. Yttria-stabilized zirconia (YSZ) was selected because YSZ possesses the same crystal structure as UO_2. A rutile-type titanium dioxide (TiO_2) with a tetragonal structure and magnesium oxide (MgO) with the NaCl-type structure were selected from the view point of the crystal structure. The appearances of the samples, i.e., polycrystalline UO_2, single crystalline YSZ (100) plane (99.99% purity, Furuuchi Chemical Co.), single crystalline TiO_2 (100) plane (99.999% purity, Furuuchi Chemical Co.), single crystalline MgO (100) plane (99.9% purity, Furuuchi Chemical Co.), and CsI chunks (99.99% purity, Furuuchi Chemical Co.) are shown in Fig. 1. The surface of the polycrystalline UO_2 was polished by using a No. 2000 rough polishing sheet and a diamond polishing sheet.

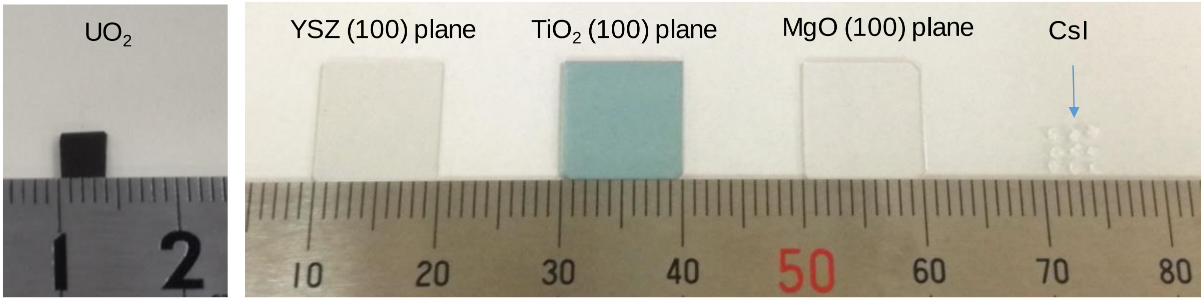

Fig. 1. Appearances of the samples used for the sessile drop test.

In the sessile drop test, the contact angle (θ) of a liquid droplet on a solid surface is directly measured. Generally, when no chemical reaction occurs between liquid and solid, the solid-liquid interface energy σ_{LS} can be calculated from Young's equation [8],

$$\sigma_S = \sigma_{LS} + \sigma_L \cos\theta \quad (1)$$

where σ_S and σ_L are the solid and liquid surface energies, respectively. The schematic image and the balance of Young's equation is shown in Fig. 2.

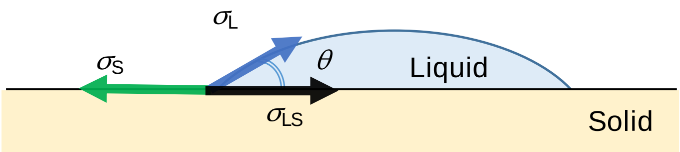

Fig. 2. Schematic image of the sessile drop test and the balance of Young's equation.

We used a special infrared heating furnace for the sessile drop test. The details of the measurement system and conditions are reported in our previous paper [5].

3. Results and discussion

Figure 3 shows the x-ray diffraction (XRD) patterns of the polycrystalline UO_2 and CsI, together with the literature data [9, 10]. In the XRD pattern of UO_2, slight crystal orientation for the <111> direction was confirmed, but no peaks corresponding to impurities were observed. Similar to UO_2, the CsI sample has no impurities, which can be confirmed by the XRD pattern.

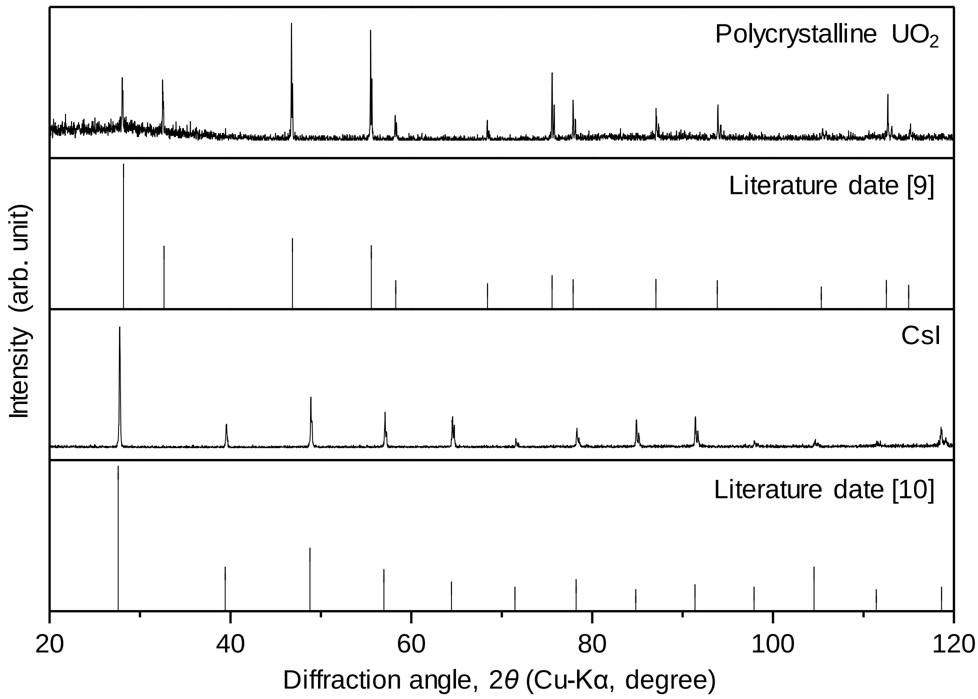

Fig. 3. XRD patterns of polycrystalline UO_2 and CsI used for the sessile drop test.

Figure 4 shows the XRD patterns of the single crystalline samples of YSZ (100) plane, TiO_2 (100) plane, and MgO (100) plane, together with the literature date [11-13]. The XRD patterns well agreed with the literature data for all solid samples.

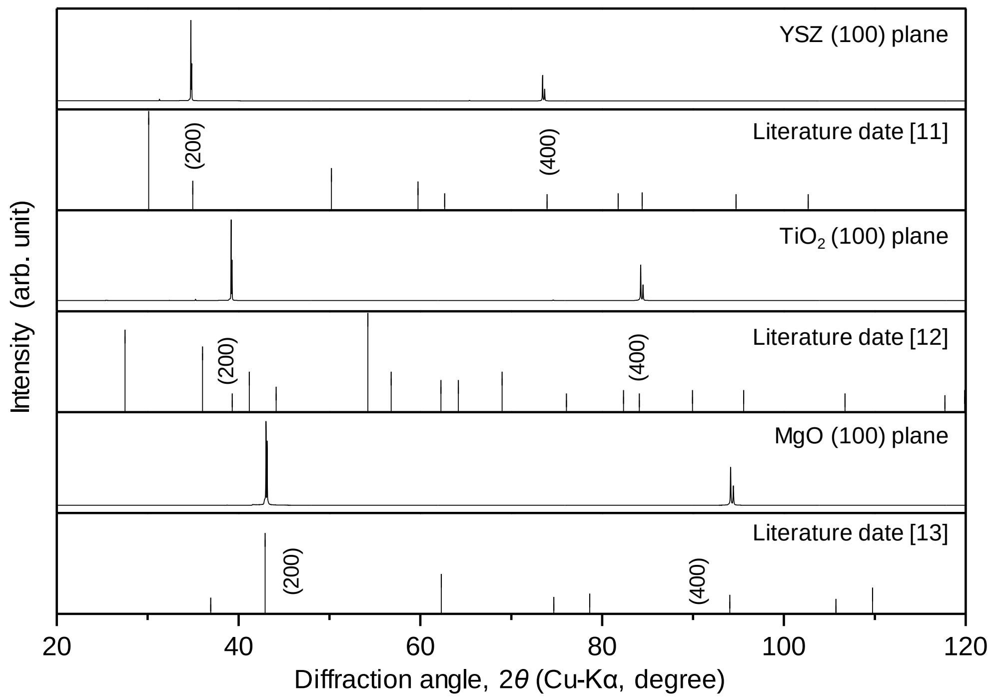

Fig. 4. XRD patterns of solid surface samples used for the sessile drop test.

Figure 5 shows the appearance of the melting behaviour of CsI on various solid samples. On the polycrystalline UO_2, after reaching the melting temperature, CsI melted fully within 30 seconds and the liquid CsI showed high wettability like the contact angle was measured to be virtually 0°. Similar to the case of polycrystalline UO_2, on the single crystalline YSZ (100) plane and TiO_2 (100) plane, liquid CsI showed high wettability with the contact angle nearly 0°. However, on the single crystalline MgO (100) plane, liquid CsI showed lower wettability than those on other solid samples. The contact angle between liquid CsI and MgO (100) plane was measured to be 27°.

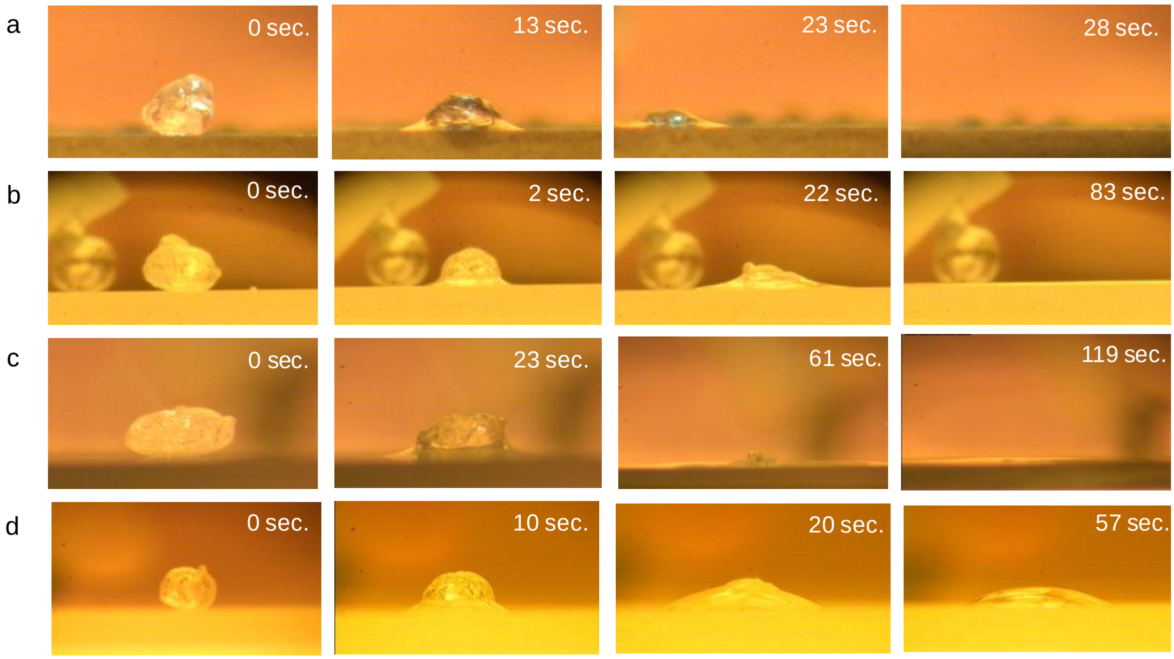

Fig. 5. Melting behaviour of CsI on various solid samples. (a) polycrystalline UO_2, (b) YSZ (100) plane, (c) TiO_2 (100) plane, and (d) MgO (100) plane.

Based on eq. (1), the σ_{LS} between liquid CsI and various solid surfaces were calculated, where the literature data of σ_S for UO_2, YSZ, and MgO and σ_L for CsI were used [14-18]. Unfortunately, there are no literature date on the σ_S for TiO_2 (100) plane. The values of θ, σ_S, and σ_{LS} are summarized in Table 1.

Table 1. Contact angle θ and solid-liquid interface energy σ_{LS} obtained by the sessile drop test between liquid CsI and polycrystalline UO_2, YSZ (100) plane, TiO_2 (100) plane, and MgO (100) plane. The solid surface energy σ_S of UO_2, YSZ (100) plane, and MgO (100) plane were obtained from the literatures [14-17], while no reference date of σ_S for TiO_2 (100) plane are obtained. For the liquid surface energy of CsI, σ_L = 0.072 J/m^2 at the melting temperature [18] was used.

	θ deg.	σ_S J/m^2	σ_{LS} J/m^2
Polycrystalline UO_2	≒0	0.76 [14]	0.69
YSZ (100) plane	≒0	2.33 [15, 16]	2.25
TiO_2 (100) plane	≒0	-	-
MgO (100) plane	27	0.52 [17]	0.46

4. Summary

The most important finding obtained in the present study is that the wettability of liquid CsI on MgO is different from those on other solid surfaces. It has been reported that the wettability is very sensitive to the oxygen-defects at the oxide solid surface [19]. In case of UO_2, YSZ, and TiO_2, the existence of non-stoichiometric compounds have been reported [20-22], while the oxidation state of Mg is only 2+. This means that UO_2, YSZ, and TiO_2 have the oxygen-defects, while MgO has no such defects. This would be one of the reasons why liquid CsI shows such high wettability on UO_2, YSZ, and TiO_2, while does not show on MgO.

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