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Surface chemical behavior of triuranium octaoxide in the atmospheres of carbon monoxide and hydrogen

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Abstract

The surface chemical behavior of U_3O_8 has been studied by X-ray photoelectron spectroscopy (XPS), gas chromatography (GC) and thermodynamic calculations in reducing atmospheres. The surface of U_3O_8 is remarkably reduced in the atmospheres of CO and H_2. The effect of the oxide reduction is more obvious at higher temperatures and the oxygen content in the oxide is decreased with increasing exposure to the gases. The influence of H_2 is less than that of CO. It is also shown that the oxide surface layer is resistant to further hydriding as there does not exist any hydriding reaction for U_3O_8 in a H_2 atmosphere. Results of GC investigations and thermodynamic calculations are in good agreement with the above conclusions. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The corrosion of uranium by atmospheric gases and water vapor is an important engineering problem and has received considerable attention. Many studies in the past were focused on the field of oxidation of uranium and oxides in air, O_2, H_2O (v) and O_2/H_2O (v) mixtures [1,2]. Although significant progress has been made, there are still many details of the oxidation process that have been not fully investigated or not well understood. In particular, the effect of carbon monoxide on the oxygen-, water vapor- and hydrogen- uranium reactions are unknown. The surface of uranium metal may have a resistance to further corrosion in the gas atmosphere which contains carbon monoxide as the strong interaction between carbon and uranium would be expected to effect significantly the adsorption of different gases on uranium and its subsequent oxidation [3].

There are some scattered papers which involve the surface reactions of uranium and its alloys with CO and H_2 [4–10]. We considered that the main compounds of uranium are oxides (for example UO_2, UO_3 and U_3O_8, etc.) in natural environment due to the humidity. So, it was thought worthwhile to carry out systematic surface chemical studies of uranium oxide in CO and H_2 atmospheres. The result is very important not only for exploring the atmospheric environment which is beneficial for uranium metal that has resistance to further corrosion, but also for providing an available experimental research method for further similar studies of uranium metal in the same atmospheres.

The previous reports on uranium oxides were focused on structure and valence studies using XPS [11,12]. In this paper, detailed XPS and GC measurements as well as thermodynamic calculations of U_3O_8 in CO and H_2 atmospheres are performed.

2. Experimental

2.1. Reagents and apparatus

U_3O_8, 99.945% purity, was a product of State 404 Factory of China. The test coupon was a pellet ($\Phi = 8.2$ mm, $h = 1$ mm) pressed from powder. The CO and H_2 used in these experiments were of 99.99% and 99.999% purity, respectively, and were products of Southwest Academy of Chemical Engineering of China.

The spectrometer used in this work was the Kratos XSAM 800. X-ray photoelectron spectra were produced

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using Al K α radiation. The routine anode power was 325 W and the spectrometer was run in the fixed analyzer transmission mode which gave a Ag $3d_{5/2}$ peak with full width at half maximum (FWHM) of 1 eV. The base pressure of the sample treatment chamber (STC) was 5.0×10^{-6} Pa and sample analysis chamber (SAC) was 5.0×10^{-8} Pa. The sample temperature was measured with a thermocouple attached to the side of a thin coupon cap. The spectrometer energy scale was calibrated using the binding energy of adventitious carbon to be 285.0 eV for the C 1s peak.

2.2. XPS analytical procedure of the surface reaction of U_3O_8 in CO and H_2 atmospheres

U_3O_8 spectra were measured in a copper holder and recorded in the SAC. Surface reactions were performed in atmospheres of CO and H_2 in the STC. Dry CO was dynamically flowed through the system at a pressure of 6.6 mPa for about 45 h at room temperature. Dry H_2 was statically flowed through the system at a pressure of 50 Pa for about 40 h at temperatures of 25°C, 80°C and 200°C, respectively. The data were collected in a multichannel analyzer and transferred to a computer system for storage and analysis.

2.3. GC analytical procedure of the surface reaction of U_3O_8 in CO atmosphere

A known amount of the U_3O_8 pellet was put into the glass testing bottle of which the volume had been accurately determined. The testing bottle was linked up with the vacuum apparatus system together with the blank bottle and then was evacuated to 0.64 Pa. CO was exposed to the system and stored statically. The gaseous components in different reaction times were analyzed by HP PE 9000 gas chromatography.

3. Results and discussion

3.1. XPS study on surface reaction of U_3O_8 in CO atmosphere

U_3O_8 is a mixed valence compound in which the metal is present in two formal oxidation states. An intensity analysis of the composite U 4f photoelectron spectrum of U_3O_8 indicates that the compound should be written as $U_2^{VI}\ U_{n-2}^{IV}\ O_{2n+2}$ [11]. As CO was dynamically flowed through the system for about 45 h which exposed up to 7.2×10^6 L (1 L = 1.33×10^{-4} Pa s), the U 4f signal changed the shape gradually with the low binding energy component slowly growing in intensity while its position also shifted to lower binding energies. There existed also a distinct wider shoulder to the low binding energy side of each of the U $4f_{7/2}$ and U $4f_{5/2}$ peaks. This indicates that the surface layer of U_3O_8 is partially reduced to UO_2 by CO, Fig. 1 shows the comparison of the U 4f photoelectron region for U_3O_8 after CO exposure up to 7.2×10^6 L. The equations of the U_3O_8–CO surface reaction are as follows:

$$2CO + U_3O_8 \rightarrow 2CO_2 + 3UO_2 \qquad (1)$$

$$CO + UO_3 \rightarrow CO_2 + UO_2. \qquad (2)$$

From the deconvolution spectrum of Fig. 2, we found that the content of UO_3 in U_3O_8 decreased and that of UO_2 increased with increasing exposure to CO. We also observed that the deconvoluted peak areas were in the ratio 1:1.58 according to Fig. 2. Compared with the original result of 1:1.9 for U_3O_8 [11], it showed that the content of UO_3 in U_3O_8 is decreased by 20%. Apart from UO_2 and UO_3 in the deconvoluted spectrum, there could exist a third peak of U $4f_{5/2}$ and U $4f_{7/2}$ which were 392.2 and 381.3 eV, respectively. The binding energy of the third deconvoluted peak was between that of

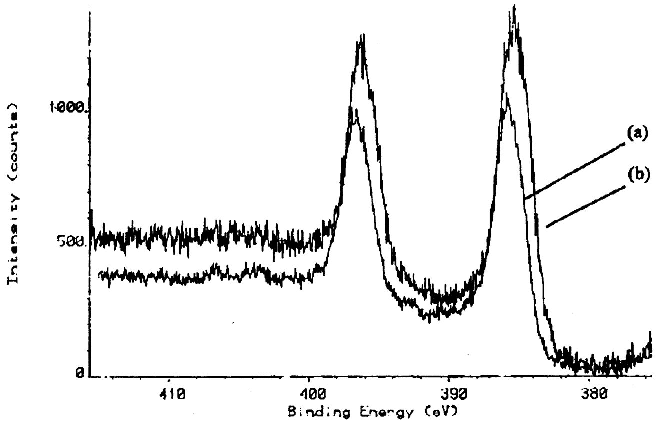

Fig. 1. Comparison of the U 4f photoelectron region of U_3O_8: (a) before and (b) after exposure to 7.2×10^6 L CO.

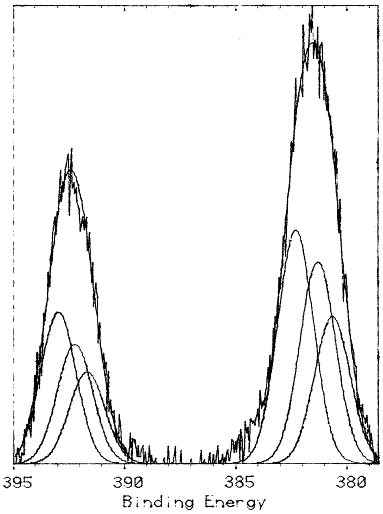

Fig. 2. Deconvolution of the U 4f photoelectron region of U_3O_8 after exposure to 7.2×10^6 L CO: 380.8 eV – U $4f_{7/2}$ for UO_2; 391.6 eV – U $4f_{5/2}$ for UO_2; 382.0 eV – U $4f_{7/2}$ for UO_3; 392.8 eV – $U4f_{5/2}$ for UO_3; 381.3 eV – $U4f_{7/2}$ for U_4O_{9-y} (UO_{2+x}); 392.2 eV – U $4f_{5/2}$ for U_4O_{9-y} (UO_{2+x}).

UO_3 (U $4f_{7/2}$, 381.9 eV) [13] and U_4O_9 (U $4f_{7/2}$, 380.8 eV) [14]. It may be an interim state, U_4O_{9-y} or UO_{2+x}. The intensity of the third peak in U_3O_8 increased with increasing exposure of carbon monoxide and the binding energy of the peak changed with increasing exposure of gas. Fig. 3 shows such change trade expressed above.

The effect of reduction by CO on the surface of U_3O_8 could be observed by the O 1s/U 4f intensity ratio. But it is difficult to carry out the quantification by simple use of the intensities of the XPS peaks since there exist some problems how to define the background of the measurements of the peak area, and the relative sensitivity factors are changed by changing the elements and spectrometers. The most practical solution at the present time is to compare the relative O 1s/U 4f intensity ratio by defining the background of the peak with the same as the method in the series experiments to overcome the systematic error. So, it is also important to recognize that the analysis of the O 1s/U 4f intensity ratio is dependent on the change of the oxygen content in the surface of U_3O_8. In the light of this investigation, we observed that the O 1s/U 4f intensity ratio decreased with increasing the CO exposure to the surface (see Fig. 4). After the CO exposure up to 7.2×10^6 L, the O 1s/U 4f intensity ratio showed that the oxygen content in the surface oxide is decreased by 11%. Obviously, there existed a difference of 9% compared with that of the oxygen content in the surface oxide which is decreased by 20% with method of deconvolution described above. The difference of 9% could be produced by the interim state (U_4O_{9-y} or UO_{2+x}) and confirmed the above assumption.

3.2. XPS study on the surface reaction of U_3O_8 in H_2 atmosphere

After U_3O_8 was stored statically in a H_2 atmosphere of 50 Pa at 200°C for about 40 h (the H_2 exposure was about 4.56×10^{10} L), there exists also a reduction on the surface of U_3O_8 according to the analysis of the XPS spectrum. Fig. 5 shows the comparison of the U 4f photoelectron region for U_3O_8 after exposure to H_2. This indicates obviously the position of the U 4f signal shifts to lower binding energies. But the shifting is smaller than that in CO atmosphere and the exposure to H_2 is much more than that to CO for the U_3O_8–CO reaction. The investigation indicates, although a reduction of U_3O_8 to UO_2 exists after exposure to H_2 for a long time, the effect of reduction by H_2 on the oxide

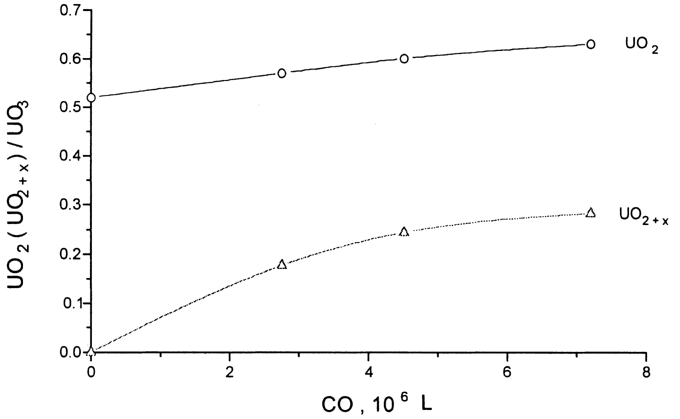

Fig. 3. Relative variation of UO_2 and U_4O_{9-y} (UO_{2+x}) in U_3O_8 with CO exposure at room temperature.

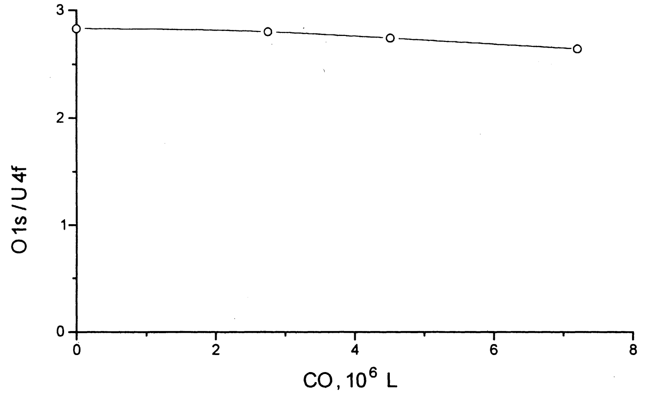

Fig. 4. Variation of the O 1s/U 4f intensity ratio of U_3O_8 with CO exposure at room temperature.

surface is obviously less than CO. The equations of the U_3O_8–H_2 surface reaction are the following:

$$2H_2 + U_3O_8 \rightarrow 3UO_2 + 2H_2O \quad (3)$$

$$H_2 + UO_3 \rightarrow UO_2 + H_2O. \quad (4)$$

The content of UO_3 in U_3O_8 is decreased and that of UO_2 is increased gradually with increasing the H_2 exposure, the same as the U_3O_8–CO surface reaction. It can be confirmed from the deconvoluted spectrum that the content of UO_2 is increased with increasing the H_2 exposure and at higher temperatures. There also existed a third peak of an interim state apart from UO_2 and UO_3 in the deconvoluted spectrum which were U $4f_{5/2}$ and U $4f_{7/2}$ with 392.2 and 381.3 eV, respectively, in U_4O_{9-y} or UO_{2+x}. The content of third peak in U_3O_8 increased with increasing the CO exposure, and the binding energy of the peak changed with increasing the exposure of the gas also. But the content of the interim state produced by the surface reaction of U_3O_8–H_2 is less than that of the surface reaction of U_3O_8–CO. Fig. 6 could express clearly the changing trade of UO_2, UO_3, $U_4O_{9-y}(UO_{2+x})$ in U_3O_8 with the H_2 exposure and temperature.

The effect of reduction by H_2 on the surface of U_3O_8 also could be observed by the change of the O 1s/U 4f intensity ratio. In the light of the analysis from Fig. 7, we observed that the O 1s/U 4f intensity ratio increased with increasing the exposure of H_2 and increased more with higher temperatures. But the increasing trade of the O 1s/U 4f intensity ratio for the U_3O_8–H_2 surface reaction is less than that of the U_3O_8–CO surface reaction. After CO exposure up to 4.8 × 10^{10} L (25°C), 5.1 × 10^{10} L (80°C) and 4.56 × 10^{10} L (200°C), respectively, the O

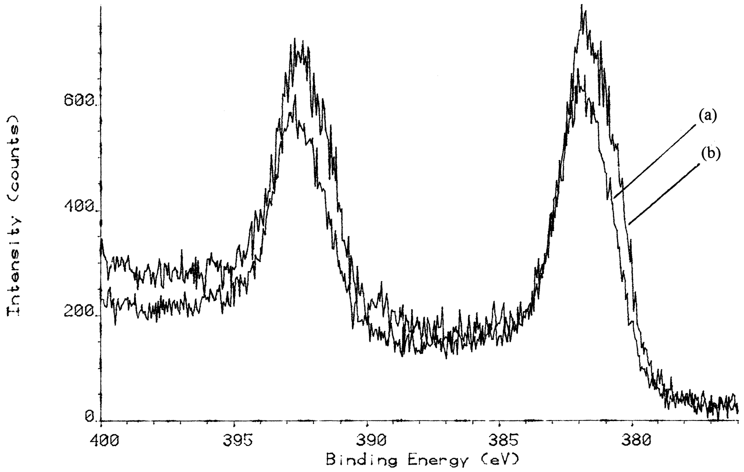

Fig. 5. Comparison of the U 4f photoelectron region of U_3O_8 at 200°C: (a) before and (b) after exposure to 4.56 × 10^{10} L H_2.

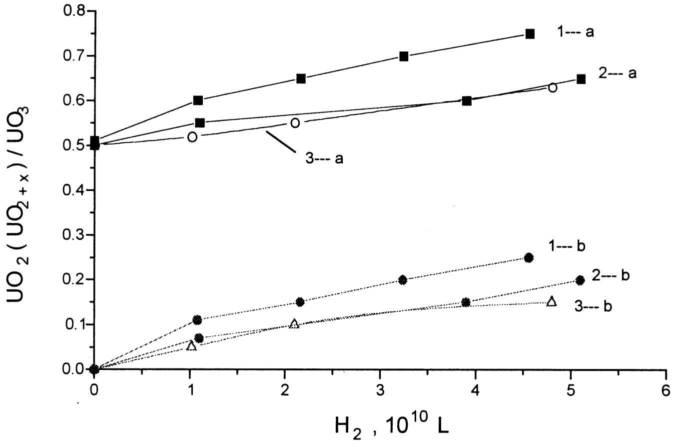

Fig. 6. Relative variation of UO_2 and U_4O_{9-y} (UO_{2+x}) in U_3O_8 with H_2 exposure. 1–200°C; 2–80°C; 3–25°C; a – UO_2/UO_3; b – UO_{2+x}/UO_3.

1s/U 4f intensity ratio shows that the oxygen content in the surface oxide is decreased by 10%, 16% and 20%, respectively.

3.3. GC analysis on the surface reaction of U_3O_8 in CO atmosphere

It has been deduced from the investigations using XPS that the surface of U_3O_8 is reduced remarkably in CO atmospheres and the effect of reduction on the oxide is more obvious at higher temperatures and increasing the exposure of gas. But the difference of the gaseous component in the STC cannot be observed due to the lack of an available instrument such as a quadrupole mass spectrometer in real-time. In order to judge and confirm the possibility for the U_3O_8–CO surface reaction, the content of CO_2 in the system produced by the U_3O_8–CO surface reaction for 1–8 days has been determined using GC, and the results are illustrated in Fig. 8. It is obvious that the content of CO_2 is increased with increasing the storage times and the results are entirely consistent with above XPS investigation.

Meanwhile, we also observed that there had been a small change of the content of CO_2 in the reaction system. In sharp contrast with this result, there was a large change of the content of UO_2 and UO_3 in the U_3O_8–CO surface reaction which was analyzed using XPS and it may be due to the difference of the method of the surface analysis and others. But results and conclusions by two methods above (XPS and GC analysis) are well in agreement. Fig. 9 is a GC spectrum of CO_2 for the U_3O_8–CO surface reaction.

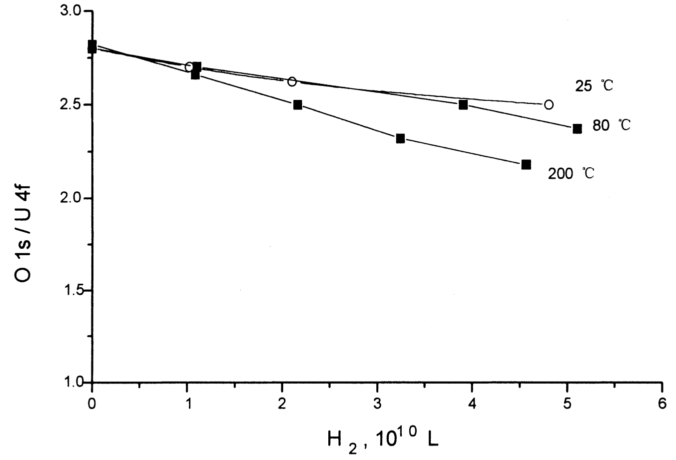

Fig. 7. Variation of the O 1s/U 4f intensity ratio of U_3O_8 with H_2 exposure.

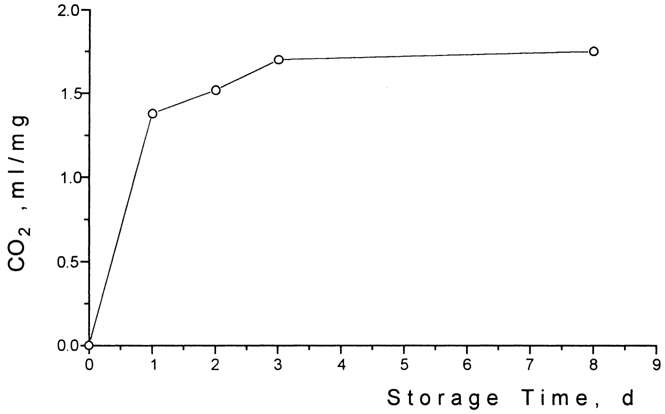

Fig. 8. Variation of CO_2 of the U_3O_8–CO surface reaction with storage time.

3.4. *Thermodynamic calculations on the surface reactions of U_3O_8–CO/U_3O_8–H_2*

The basic equations for thermodynamic calculations are very common to the following reaction:

$$3\mathrm{U(s)} + 2\mathrm{CO(g)} \rightarrow 2\mathrm{UC(s)} + \mathrm{UO_2(s)}. \tag{5}$$

The related changes of enthalpy, entropy and Gibbs energy of reaction are denoted by $\Delta_r H^o$, $\Delta_r S^o$ and $\Delta_r G^o$. The related $\Delta_r H$ $\Delta_r S$ and $\Delta_r G$ are written as

$$\begin{aligned}\Delta_r H^o &= \Delta_r H^o_{298} + \int_{298}^{T} \Delta C_p \,\mathrm{d}T = \Delta_r H^o_{298} \\ &\quad + \Delta a T + \frac{1}{2}\Delta b \times 10^{-3} T^2 - \Delta a \times 298 \\ &\quad - \frac{1}{2}\Delta b \times 10^{-3} \times 298^2,\end{aligned} \tag{6}$$

$$\begin{aligned}\Delta_r S^o &= \Delta_r S^o_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} \mathrm{d}T = \Delta_r S^o_{298} \\ &\quad + \Delta a \ln T + \Delta b \times 10^{-3} T - \Delta a \ln 298 \\ &\quad - \Delta b \times 298 \times 10^{-3},\end{aligned} \tag{7}$$

$$\Delta_r G^o = \Delta_r H^o - T \Delta_r S^o, \tag{8}$$

$$\Delta C_p = \Delta a + \Delta b \times 10^{-3} T, \tag{9}$$

where a, b are constants characteristic of the given substance (see Table 1).

It is not difficult to carry out the study of the equilibrium of the system which is described above and its thermodynamic calculation according to the principles of thermodynamics. The related data for the thermodynamic calculations are given in Table 1, the results are summarized in Table 2.

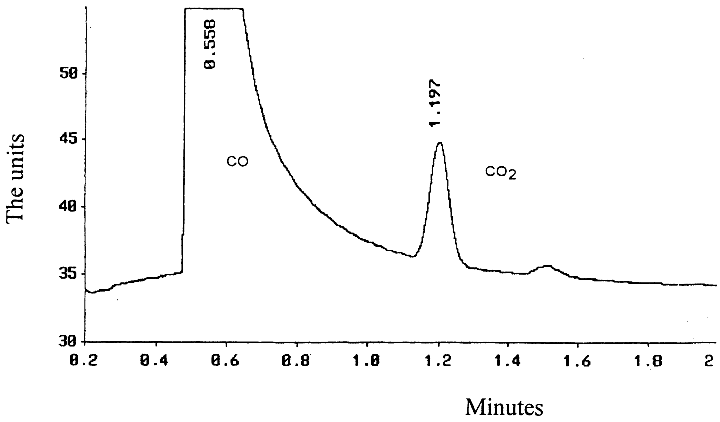

Fig. 9. GC spectrum of CO_2 of the U_3O_8–CO surface reaction.

Table 1
Related data for the thermodynamic calculations [15]

	$\Delta_r H^o_{298}$ (kJ mol^{-1})	S^o_{298} (J mol^{-1} K^{-1})	a	b
U (a)	0	50.24	2.6	8.95
UC (s)	−98.39	59.24	17.9	−3.7
UO_2 (s)	−1085.6	77.08	19.2	1.62
UO_3 (s)	−1224.6	96.17	22.1	2.64
UO (g)	20.93	(67.0)	(10.6)	(2.0)
U_3O_8 (s)	−3577.2	282.8	67.5	8.83
UH_3 (β)	−127.3	63.64	11.8	/
CO (g)	−110.6	198.0	6.60	1.2
CO_2 (g)	−393.8	213.8	7.7	5.3
H_2 (g)	0	130.7	6.62	0.81
H_2O (*l*)	−286.0	70.0	8.2	0.4

There are negative values of $\Delta_r G^o$ for the surface reactions of U_3O_8 in CO and H_2 atmospheres in Table 2. This indicates the possibility of a surface reaction and confirms the experimental result of the surface reduction discussed above. There are positive $\Delta_r G^o$ values for surface hydriding reactions of U_3O_8 in H_2 atmospheres. This means that there does not exist any surface hydriding reaction. It is true that the U 4f photoelectron region of UH_3 (of which the binding energy of U4f$_{7/2}$ is 378.5 eV [9]) cannot be observed in the surface reactions of U_3O_8 with H_2 using XPS. This indicates that there does not exist any hydriding reaction for uranium oxides in a H_2 atmosphere and the surface oxide layer has a resistance to further hydriding. But the H atom or H_2 molecule is very small. So, H_2 (molecule or H atom) can penetrate through the oxide layer into the metal/oxide interface and UH_3 is produced by the hydriding reaction. It is necessary to carry out further research on the mechanism of the hydriding reactions of uranium and its oxides due to the importance, practicability and complication of surface hydriding.

4. Conclusions

1. The surface of U_3O_8 is remarkably reduced in a CO atmosphere. The oxygen content in the surface oxide is decreased with increasing exposure to CO. After exposure to 7.2 × 10^6 L CO, the O 1s/U 4f intensity ratio shows that the oxygen content in the surface oxide is decreased by 11%. The GC investigation indicates that the CO_2 content is also increased with increasing storage times.
2. There exists also a reduction of the surface of U_3O_8 in a H_2 atmosphere. But the influence of H_2 is less than that of CO. The oxygen content in the oxide is decreased with increasing the H_2 exposure and the effect of reduction of the oxide is more obvious at higher temperatures. After CO exposure up to 4.8 × 10^{10}

Table 2
Variation of $\Delta_r H^o$, $\Delta_r G^o$ of the surface reaction of U_3O_8 with temperature in CO and H_2 atmospheres

Equations of surface reaction	Variation of $\Delta_r H^o$, $\Delta_r G^o$ with T	$\Delta_r G^o_{298}$(kJ mol^{-1})	$\Delta_r G^o_{510}$ (kJ mol^{-1})
$UO_3(s) + CO(g) \rightarrow UO_2(s) + CO_2(g)$	$\Delta_r H^o = -142520.2 - 7.54T + 6.45 \times 10^{-3}T^2$ $\Delta_r G^o = -142520.2 - 43.3T + 6.45 \times 10^{-3}T^2 + 7.54T \ln T$	−143.2	−142.3
$U_3O_8 (s) + 2CO(g) \rightarrow 3UO_2(s) + 2CO_2(g)$	$\Delta_r H^o = -237279.4 - 32.2T + 8.88 \times 10^{-3}T^2$ $\Delta_r G^o = -237279.4 - 190.6T - 8.83 \times 10^{-3}T^2 + 32.2T \ln T$	−240.1	−234.2
$U_3O_8(s) + 2H_2(g) \rightarrow 3UO_2(s) + 2H_2O(l)$	$\Delta_r H^o = -225674.1 - 83.65T - 13.42 \times 10^{-3}T^2$ $\Delta_r G^o = -225674.1 - 134.0T + 13.42 \times 10^{-3}T^2 + 83.65T \ln T$	−122.4	−245.6
$2U_3O_8(s) + 25H_2(g) \rightarrow 6UH_3 (s) + 16H_2O(l)$	$\Delta_r H^o = 971405.76 - 206.2T - 32.99 \times 10^{-3}T^2$ $\Delta_r G^o = 971405.76 - 235.4T + 32.99 \times 10^{-3}T^2 + 206.2T \ln T$	1254.3	1515.6

L (25°C), 5.1×10^{10} L (80°C) and 4.56×10^{10} L (200°C), respectively, the O 1s/U 4f intensity ratio shows that the oxygen content in the surface oxide is decreased by 10%, 16% and 20%, respectively.

3. The investigation shows that the surface oxide layer is resistant to further hydriding as there does not exist any hydriding reaction of U_3O_8 in a H_2 atmosphere. Results of GC investigations and thermodynamic calculations for the reactions of U_3O_8 in CO and H_2 atmospheres agree well with the conclusions made above.

Acknowledgements

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