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OXYGEN POTENTIAL, ELECTRICAL CONDUCTIVITY AND DEFECT STRUCTURE OF TITANIUM-DOPED URANIUM DIOXIDE

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The oxygen potential of $(U_{0.993}Ti_{0.007})O_{2+x}$ was measured by means of thermogravimetry in the range of $1173 \leqq T/K \leqq 1373$ and $10^{-16} \leqq P_{O_2}/Pa \leqq 10^{-4}$, and the electrical conductivity by the four inserted wires method in the range from 10^{-15} to 10^{-6}Pa at 1173 K. Both the oxygen potential and the electrical conductivity of UO_{2+x} were decreased by doping with titanium ions, which can not be interpreted by the substitutional model, but may be explained by assuming the Ti^{4+} interstitials as the predominant defect. From the oxygen partial pressure dependence of the compositional deviation from stoichiometry and that of the electrical conductivity for $(U_{0.993}Ti_{0.007})O_{2+x}$, the defect structure was discussed with the complex defect model consisting of interstitial titanium ions, oxygen vacancies and two kinds of interstitial oxygens.

1. Introduction

It is well known that a relatively small addition of titania in UO_{2+x} increases the grain size of UO_2 remarkably [1–3]. This may lead to the possibility of reducing the release of fission gas from fuel due to the long diffusion length [4]. It is also shown that the doping of titania in UO_{2+x} increases not only the rate of densification and the final bulk density [1–3,5,6], but also the diffusion coefficients of uranium [7] and ^{133}Xe [8] in UO_{2+x}. These doping effects of titania into UO_{2+x} may be understood from the fundamental knowledge based on defect structure which can be discussed with the oxygen partial pressure dependence of the compositional deviation from stoichiometry and that of the electrical conductivity.

The oxygen potential and electrical conductivity of UO_{2+x} doped with various cations (lanthanum [9], niobium [10], thorium [11,12], chromium [13], yttrium [14], magnesium [15], gadolinium [16,17], and zirconium [18]) have been extensively studied. It was generally concluded that the oxygen potential and the electrical conductivity of UO_{2+x} are increased (or decreased) by doping with lower (or higher) valent cations [19]. These facts are explained from the valence control rule, assuming that these dopant cations are present as the substitutionals for uranium ions. However, the oxygen potential and the electrical conductivity of UO_{2+x} doped with titanium have not been measured yet.

In this study, the oxygen potential of $(U_{0.993}Ti_{0.007})O_{2+x}$ was measured by means of thermogravimetry in the range of $1173 \leqq T/K \leqq 1373$ and $10^{-16} \leqq P_{O_2}/Pa \leqq 10^{-4}$, and the electrical conductivity was also measured using the four inserted wires method in the range from 10^{-15} to 10^{-6} Pa at 1173 K to check whether the valence control rule can hold or not. From the oxygen partial pressure dependence of the compositional deviation from stoichiometry (x) and that of the electrical conductivity (σ), the defect structure of $U_{0.993}Ti_{0.007}O_{2+x}$ was discussed.

2. Experimental

The powder samples of $(U_{0.993}Ti_{0.007})O_2$ for thermogravimetric study and electrical conductivity measurement were prepared by mixing titanium metal powder (99.99% purity), U_3O_8 powder and stoichiometric $UO_{2.000}$ powder in an appropriate ratio. The stoichiometric $UO_{2.000}$ power was obtained by reducing U_3O_8 powder in dried hydrogen gas at 1273K for 48 h. The U_3O_8 was prepared by precipitating ammonium diuranate from uranyl nitrate solution purified by TBP (tributyl phosphate) extraction, then by calcining it at 1023 K for 48 h in air. The mixture of titanium metal powder, U_3O_8 and $UO_{2.000}$ powders was mixed in an agate mortar and pressed into pellets. The pellets were

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heated in an evacuated and sealed quartz tube at 1323 K for 576 h, and then pulverized into powder form, which was used for thermogravimetry.

The pellet of $(U_{0.993}Ti_{0.007})O_2$ for the electrical conductivity measurement was prepared as follows: the mixture of titanium powder, U_3O_8 and $UO_{2.000}$ powders was pressed in a circular die of 10 mm in diameter at about 400 MPa. Four holes of 0.5 mm in diameter were drilled in a line and a platinum wire of 0.5 mm in diameter was inserted into each hole of the pellet as an electrode. The pellet with platinum electrodes was sintered in an evacuated and sealed quartz tube at 1323 K for 576 h, taken out from the quartz tube and annealed again in hydrogen at 1523 K for 2 h. X-ray diffraction analysis indicated that each powder or pellet sample was of single phase with fluorite structure.

The thermogravimetric study was performed with a Cahn 1000 electronic microbalance. The quartz crucible containing about 500 mg of sample powder was suspended with a quartz string in the hot zone of the furnace. The peak to peak noise of the thermobalance was about 10 μg, due mainly to gas turbulence.

The electrical conductivity measurement was carried out by means of the conventional four inserted wires method as described in an earlier paper [20].

The oxygen partial pressure was controlled by mixing hydrogen and carbon dioxide gases. The sample was equilibrated with the mixed gas for 24 to 72 h, depending on the temperature and oxygen partial pressure.

3. Results and discussion

3.1. Oxygen potentials

The O/M (M = Ti + U) ratios of $(U_{0.993}Ti_{0.007})O_{2+x}$ in the temperature range from 1173 to 1373 K obtained in this study are shown as a function of oxygen partial pressure in fig. 1. It can be seen in the figure that the O/M ratio at 1173 K increases with increasing oxygen partial pressure, and its value becomes nearly constant (O/M = 2.03) in the oxygen partial pressure range from 10^{-9} to 10^{-6} Pa. Similar behavior is also observed at 1373 K. The O/M ratio at 1373 K becomes nearly constant in the oxygen partial pressure range above around 10^{-6} Pa. A similar tendency can be seen at 1282 K in the figure. The dependence of the oxygen partial pressure on the O/M ratio at 1318 K probably shows similar behavior with that at temperatures of 1173 and 1373 K, judging from an intermediate temperature between 1173 and 1373 K.

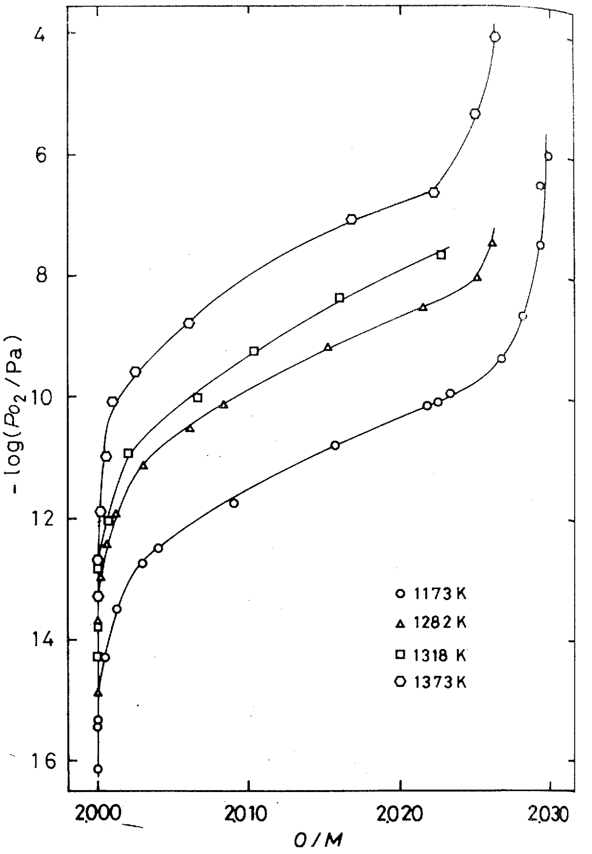
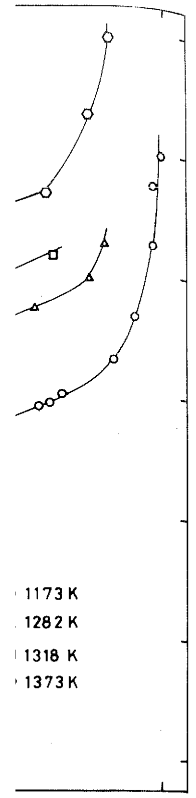


Fig. 1. The O/M (M = Ti + U) ratios of $(U_{0.993}Ti_{0.007})O_{2+x}$ as a function of oxygen partial pressure in the temperature range from 1173 to 1373 K.

Fig. 2 shows the oxygen potential ($\Delta\bar{G}_{O_2} = RT \ln P_{O_2}$) of $(U_{0.993}Ti_{0.007})O_{2+x}$ at 1282 K obtained in this study as a function of the O/M ratio together with the previous result of pure UO_{2+x} [12]. In the previous paper [19], the effect of aliovalent cations doped substitutionally in UO_{2+x} on the $\Delta\bar{G}_{O_2}$ values is generally explained by the following valence control rule. The $\Delta\bar{G}_{O_2}$ values are increased (or decreased) by doping with cations of lower valency such as La^{3+}[9], Mg^{2+}[15] and Gd^{3+}[16] (or higher valency such as Nb^{5+}[10] and Cr^{6+}[13]), since the oxidation state of the remaining uranium ions is increased (or decreased) by the substitution of lower (or higher) valent cations than the uranium ions. However, the valence control rule based on the substitutional model mentioned above is not likely to be applicable to the case of Ti-doping, because the $\Delta\bar{G}_{O_2}$ value of UO_{2+x} doped with Ti ion (tetravalency) is lower than that of pure UO_{2+x}. Since the ionic radius



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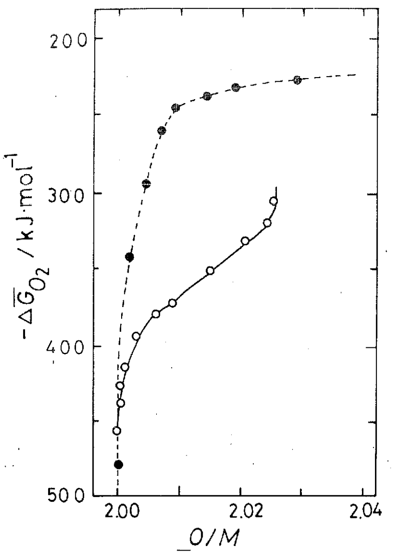

Fig. 2. Oxygen potential ($\Delta \bar{G}_{O_2}$) versus oxygen-to-metal ratio for $(U_{0.993}Ti_{0.007})O_{2+x}$(○) in this work, together with the previous results [12] of pure UO_{2+x} (●) at 1282 K.

of Ti^{4+} (68 pm) is smaller than that of the interstitial sites (about 100 pm) in the UO_2 lattice, titanium cations may enter the UO_2 lattice interstitially instead of substitutionally for uranium ions. The lower $\Delta \bar{G}_{O_2}$ value of UO_{2+x} doped with titanium observed in this study may be explained from the decrease in the oxidation state of the remaining uranium ions, since the interstitial titanium ions doped in UO_{2+x} impart an effective positive charge to the lattice.

The enhanced diffusions of uranium [7] and ^{133}Xe [8] in UO_{2+x} doped with TiO_2 were also interpreted by the increase of the concentration of the uranium vacancy, assuming Ti interstitials instead of the substitutional Ti ions for uranium ions. The Ti^{4+} interstitials are able to increase the concentration of oxygen interstitials and decrease the concentration of oxygen vacancies through Frenkel defect equilibrium, thereby increasing the concentration of the uranium vacancies through Schottky defect equilibrium. The increase of the concentrations of uranium vacancies is expected to cause the increase of self-diffusion coefficients of uranium as well as ^{133}Xe in Ti-doped UO_{2+x}.

3.2. Electrical conductivity measurement

The electrical conductivity of $(U_{0.993}Ti_{0.007})O_2$ at 1173 K obtained in this study is shown in fig. 3 as a function of the oxygen partial pressure together with the previous result of pure UO_{2+x} at 1282 and 1373 K [9]. It can be seen from the figure that the electrical conductivity of $(U_{0.993}Ti_{0.007})O_{2+x}$ is nearly independent of the oxygen partial pressure in the range of relatively higher and lower oxygen partial pressures, and increases with increasing oxygen partial pressure in the range of intermediate oxygen partial pressure. The oxygen partial pressure dependence of the electrical conductivity for $(U_{0.993}Ti_{0.007})O_{2+x}$ will be discussed in the following section concerning defect structure. It can also be seen in the figure that at lower oxygen partial pressures the electrical conductivity of $(U_{0.993}Ti_{0.007})O_{2+x}$ is lower than that of pure UO_{2+x}, even if we consider the temperature dependence of the electrical conductivity of pure UO_{2+x}.

The effect of aliovalent cations doped substitutionally in UO_{2+x} on the electrical conductivity is also generally explained by the valence control rule [19]: the electrical conductivity of UO_{2+x} is increased by doping with cations of lower valency (Y^{3+} [14] and Gd^{3+} [17]) than uranium ions, since the lower valent cations substituted for uranium ions can act effectively as hole donors. Conversely, the electrical conductivity of UO_{2+x} is decreased by doping with cations of higher valency (Nb^{5+} [10] and Cr^{6+} [13]) than the uranium ions which act effectively as electron donors.

However, the lower electrical conductivity of UO_{2+x} doped with Ti ions than that of pure UO_{2+x} at lower oxygen partial pressures cannot be interpreted by the substitutional model, but may be explained by assuming the presence of Ti interstitials as in the case of the effect

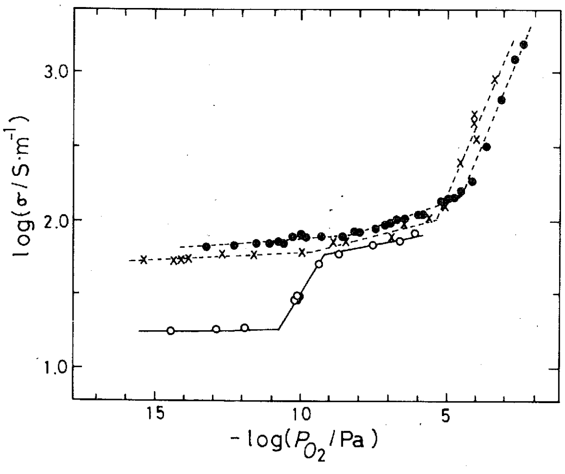

Fig. 3. Oxygen partial pressure dependence of the electrical conductivity for $(U_{0.993}Ti_{0.007})O_{2+x}$ at 1173 K (○) in this study, together with the previous result [9] of pure UO_{2+x} at 1282 (×) and 1373 K (●).

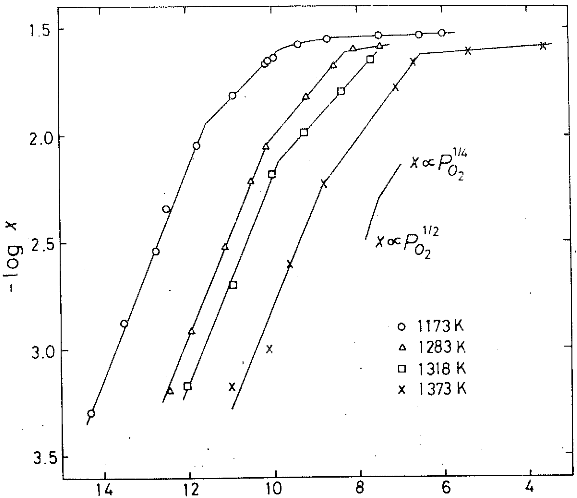

Fig. 4. Oxygen partial pressure dependence of x for $(U_{0.993}Ti_{0.007})O_{2+x}$ in the temperature range from 1173 to 1373 K.

of doping on the oxygen potential. Since the interstitial Ti ions can act effectively as electron donors, the electrical conductivity of $(U_{0.993}Ti_{0.007})O_{2+x}$ is decreased by doping with titanium.

3.3. Defect structure

The oxygen partial pressure (P_{O_2}) dependence of the departure from stoichiometric composition (x) and that of the electrical conductivity (σ) for $MO_{2\pm x}$ are usually expressed as $x \propto P_{O_2}^{1/n}$ and $\sigma \propto P_{O_2}^{1/n'}$, respectively. The defect structure can be discussed from the values of n or n'.

The oxygen partial pressure dependences of x for $(U_{0.993}Ti_{0.007})O_{2+x}$ in the temperature range from 1173 to 1373 K are shown in fig. 4. It can be seen in the figure that the values of n change as 2, 4 and ∞ in turn from the lower oxygen partial pressure. Similarly, the values of n' also change as ∞, 4 and ∞ in turn from the lower oxygen partial pressure as seen from fig. 3.

Based on the experimental values of n and n', the defect structure of pure UO_{2+x} [12] has been explained

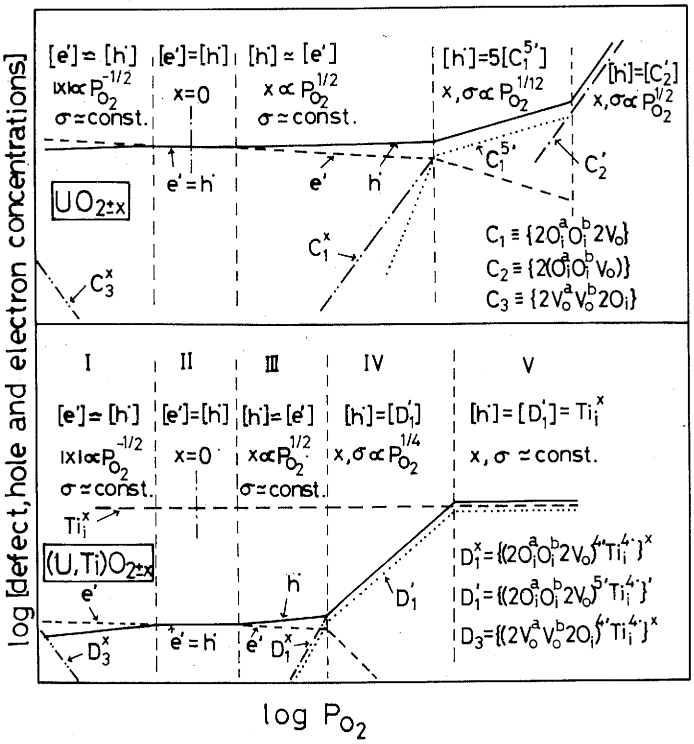

Fig. 5. Schematic representation of the relationship between the relative concentration of defects and P_{O_2} for pure $UO_{2\pm x}$ [12] and $(U,Ti)O_{2\pm x}$ in this study. The equations indicate the conditions for electroneutrality and the dependences of x and σ on P_{O_2}.

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by considering the presence of the complex defect $\{2(O_i^aO_i^bV_O)\}^{m'}$ or $\{2O_i^aO_i^b2V_O\}^{m'}$ or $\{2V_O^aV_O^b2O_i\}^{m'}$ (m' is the charge of the complex defect) consisting of oxygen vacancies (V_O) at the normal lattice sites and two kinds of interstitial oxygen (O_i^a and O_i^b) together with some electroneutrality conditions between the concentrations of holes and complex defects (or electrons) as shown schematically in fig. 5. In the case of $(U,Ti)O_{2+x}$, the interstitial model rather than the substitutional one seems to be appropriate as mentioned above. Using the Kröger–Vink notation [21], the following reaction can be assumed:

$$Ti_i^x + \tfrac{1}{2}O_2(g) + 2V_i^a + V_i^b + 2O_O = \left\{\left(2O_i^aO_i^b2V_O\right)^{m'}Ti_i^{4\bullet}\right\}^{q'} + qh^{\bullet}, \tag{1}$$

where Ti_i^x is the neutral titanium in the interstitial position produced by doping, $h^{\bullet}$ is a hole and q' is the charge of the complex defect $\{(2O_i^aO_i^b2V_O)^{m'}Ti_i^{4\bullet}\}^{q'}$ which consists of $(2O_i^aO_i^b2V_O)^{m'}$ and $Ti_i^{4\bullet}$. The dependences $n = 2$ and $n' = \infty$ observed for x and σ, respectively, in the relatively lower oxygen partial pressure region can be interpreted from eq. (1) by assigning the value $m = 4$ and $q = 0$ and by using the electrical neutrality condition $[e'] \simeq [h^{\bullet}] \simeq$ constant, since the intrinsic electronic defect is larger than the complex defect at nearly stoichiometric composition. The dependences of x and σ upon P_{O_2}, $n = n' = 4$, in the intermediate oxygen partial pressure region can be interpreted from eq. (1) by assuming $m = 5$ and $q = 1$. In the relatively higher oxygen partial pressure regions, the electroneutrality condition can be expressed as

$$[Ti_i^x] = \left[\left(2O_i^aO_i^b2V_O\right)^{5'}Ti_i^{4\bullet}\right]' = [h^{\bullet}] = \text{constant}. \tag{2}$$

The oxygen partial pressure dependence $n = n' = \infty$ is explained by using eqs. (1) and (2). In this range of relatively higher oxygen partial pressures, the electrical conductivity of $(U_{0.993}Ti_{0.007})O_{2+x}$ nearly equals to that of pure UO_{2+x} as seen in fig. 3. This fact may be explained by the following: at higher oxygen partial pressures, the predominant defect for $(U_{0.993}Ti_{0.007})O_{2+x}$ is thought to be the same as that for UO_{2+x}, since the doped titanium concentration (0.007) is smaller than the defect concentration ($x \simeq 0.012$ at $P_{O_2} = 10^{-5}$ Pa) due to the nonstoichiometry of pure UO_{2+x} [12]. Hence, the electrical conductivity of $(U_{0.993}Ti_{0.007})O_{2+x}$ in the range of relatively higher oxygen partial pressures approaches that of pure UO_{2+x}. The results mentioned above are summarized in table 1.

The relationship between the relative concentration of the predominant defect and log P_{O_2} for $(U,Ti)O_{2\pm x}$ is shown schematically in fig. 5, where the electroneutrality condition and the dependences of x and σ on P_{O_2} are also expressed for each region. The defect structures of hyperstoichiometric $(U,Ti)O_{2+x}$ (from regions III to V in fig. 5) have already been discussed. In the figure, neutral and singly negative charged complex defects, $\{(2O_i^aO_i^b2V_O)^{4'}Ti_i^{4\bullet}\}^x$ and $\{(2O_i^aO_i^b2V_O)^{5'}Ti_i^{4\bullet}\}'$ in eqs. (1) and (2) are written for short as D_1^x and D_1', respectively.

As for the defect structure of hypostoichiometric $(U,Ti)O_{2-x}$ (region I in fig. 5), the complex defect $\{(2V_O^aV_O^b2O_i)^{4'}Ti_i^{4\bullet}\}^x \equiv D_3^x$ is assumed, although experimental work was not carried out. The formation of $\{(2V_O^aV_O^b2O_i)^{4'}Ti^{4\bullet}\}^x$ is given by the reaction:

$$Ti_i^x + 2O_O^a + O_O^b + 2V_i = \left\{\left(2V_O^aV_O^b2O_i\right)^{4'}Ti_i^{4\bullet}\right\}^x + \tfrac{1}{2}O_2(g). \tag{3}$$

The dependence of x and σ on P_{O_2}, $n = -2$ and $n' = \infty$ can be derived from eq. (3) by using the electrical neutrality condition $[e'] \simeq [h^{\bullet}] \simeq$ constant.

4. Conclusions

The oxygen potential of $(U_{0.993}Ti_{0.007})O_{2+x}$ was measured by means of thermogravimetry in the range of $1173 \leqq T/K \leqq 1373$ and $10^{-16} \leqq P_{O_2}/Pa \leqq 10^{-4}$, and the electrical conductivity by the four inserted wires method in the range from 10^{-15} to 10^{-6} Pa at 1173 K.

Table 1.
Defect structure for $(U,Ti)O_{2+x}$

P_{O_2} region	$x \propto P_{O_2}^{1/n}$ n value	$\sigma \propto P_{O_2}^{1/n'}$ n' value	Defect model	Neutrality conditions
High	Very large	Very large	$[\{2O_i^aO_i^b2V_O)^{5'}Ti_i^{4\bullet}\}']$	$[h^{\bullet}] = [\{(2O_i^aO_i^b2V_O)^{5'}Ti_i^{4\bullet}\}'] = [Ti_i^x]$
Intermediate	4	4	$[\{2O_i^aO_i^b2V_O)^{5'}Ti_i^{4\bullet}\}']$	$[h^{\bullet}] = [\{(2O_i^aO_i^b2V_O)^{5'}Ti_i^{4\bullet}\}']$
Low	2	Very large	$[\{2O_i^aO_i^b2V_O)^{4'}Ti_i^{4\bullet}\}^x]$	$[h^{\bullet}] \simeq [e']$

The conclusions obtained in this study are summarized as follows:

(1) The oxygen potential of UO_{2+x} was decreased by doping with titanium ions, which cannot be interpreted by the valence control rule based on the substitutional model, but may be explained by assuming that the Ti^{4+} interstitials are the predominant defect.

(2) The lower electrical conductivity of UO_{2+x} doped with titanium ions than that of pure UO_{2+x} at lower oxygen potentials may also be explained by assuming the Ti^{4+} interstitial model instead of the substitutional one.

(3) From the oxygen partial pressure dependence of the compositional deviation from stoichiometry and that of the electrical conductivity for $(U_{0.993}Ti_{0.007})O_{2+x}$, the defect structure was discussed with the complex defect model consisting of interstitial titanium ions, oxygen vacancies and two kinds of interstitial oxygens. The singly negative charged complex defect $\{(2O_i^aO_i^b2V_O)^{5\prime}Ti_i^{4\cdot}\}^\prime$ was proposed as the predominant defect in the relatively higher and intermediate oxygen partial pressure regions, and neutral defect $\{(2O_i^aO_i^b2V_O)^{4\prime}Ti_i^{4\cdot}\}^x$ in the relatively lower oxygen partial pressure region.

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