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Characterisation of uranium vacancies in hyper stoichiometric uranium dioxide

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Abstract

An experimental method, based on measurements of the expansion of a single crystal as a function of the $p(O_2)$ was used to determine the concentration of uranium vacancies in hyperstoichiometric uranium dioxide. The results are consistent with the concentration of electrical carriers measured in the same conditions, they are also in qualitative agreement with a theoretical modelling proposed in the literature. However, an improved interpretation would require to take into account the clusters of oxygen interstitials and vacancies.

Keywords: UO_2; Defects; Chemical properties

In order to understand the behaviour of a given material, the knowledge of its actual point defects is a key point. In the case of hyper-stoichiometric uranium dioxide (UO_{2+x}), at temperature between 1173 and 1673 K, an apparent contradiction exists in the nature of the point defects associated to hyper-stoichiometry depending on the studied properties. On a crystallographic point of view, the crystalline structure of UO_{2+x} is $Fm\bar{3}m$, like UO_2, with a decrease of the unit cell parameter as a function of x.[1] Willis proposed the existence of oxygen intertitials or clusters of oxygen interstitials and vacancies to interpret the diffraction data.[2] On the another hand, the sintering speed of UO_2 is enhanced in an oxidising atmosphere, and some authors claim that it is due to an increase in the uranium vacancy concentration.[3] In order to get experimental data on the concentration of the two types of defects in UO_{2+x}, an experimental method based on measurements of the expansion of a single crystal as a function of the $p(O_2)$ was used.

1. Experimental

A 7 mm long UO_2 single crystal was set in Netzsch dilatometer and held at a constant temperature, ranging from 1173 to 1673 K. In this configuration a 10.1 nm displacement induces a 1 mV voltage variation of the detection system. The atmosphere inside the dilatometer was monitored in order to obtained various values of the oxygen partial pressure $p(O_2)$ using a zirconia made oxygen probe.

The $p(O_2)$ corresponding to the UO_2 stoichoimetry was determined in a previous study[4] and used as a starting point for the measurements at a given temperature. Then the PO_2 is increased step by step. At each step the expansion of the single crystal is measured.

2. Results

The length increase of the single crystal as a function of the $p(O_2)$ at 1473 K is presented in Fig. 1. The length of the single crystal first increases of about 1.5 μm just after leaving the stoichiometry. For larger $p(O_2)$, the crystal length is more or less constant at each temperature.

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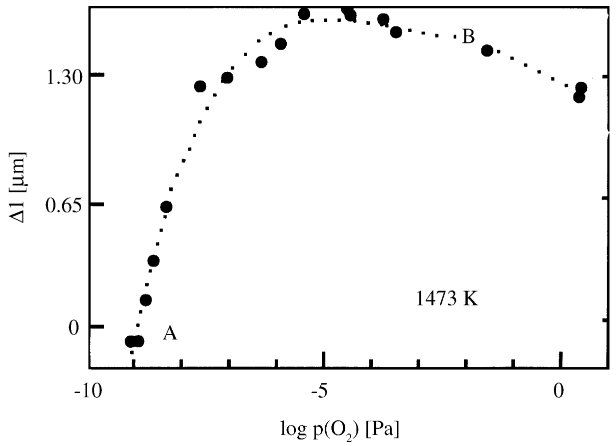

Fig. 1. Expansion of a UO_2 single crystal as function of $p(O_2)$ at 1473 K.

These results are clearly in contradiction with the length evolution deduced from the diffraction data of the literature. The unit cell parameter of UO_2 is indeed measured to decrease as a function of the hyperstoichiometry.[1] In order to interpret our expansion data, the evolution of the unit cell parameter is not enough and other mechanisms has to be considered. Because the sample is a single crystal, only the expansion induced by the formation of new unit cells can give a simple explanation of this behaviour. The formation of new unit cells has indeed a major impact on the total length of the sample because they create some empty volume inside the crystal resulting in an internal swelling.

So it is possible to interpret the $p(O_2)$ driven expansion data as the sum of two contributions: one arising from the unit cell parameter decrease, the other resulting of the formation of new unit cells. This two contributions can be associated to two different types of point defects: oxygen interstitials and uranium vacancies. The formation of both defects is correlated to the incorporation of oxygen, which occurs when UO_2 stoichiometry is increased with increasing $p(O_2)$. Their formation mechanism can be described with the following equations, using standard notation:

$$\text{New unit cell formation : } O_2 \Leftrightarrow V_U^{''''} + 2O_O + 4h^{\circ} \qquad (1)$$

$$\text{Interstitial formation : } \tfrac{1}{2}O_2 \Leftrightarrow O_i^{''} + 2h^{\circ} \qquad (2)$$

According to Eq. (1), the new unit cell formation results only in a uranium vacancy formation. According to Eq. (2) the oxygen interstitial formation would result in a decrease of the unit cell parameter, as it is described in the literature.[1]

These two types of defects have a different influence on the expansion of a UO_2 single crystal. It is then possible to calculate their respective concentration using the experimental data presented in Fig. 1. A simple calculation is presented to determine the concentration of oxygen interstitials and uranium vacancies for a given hyperstoichiometry, assuming that these concentrations are zero for the stoichiometric UO_2.

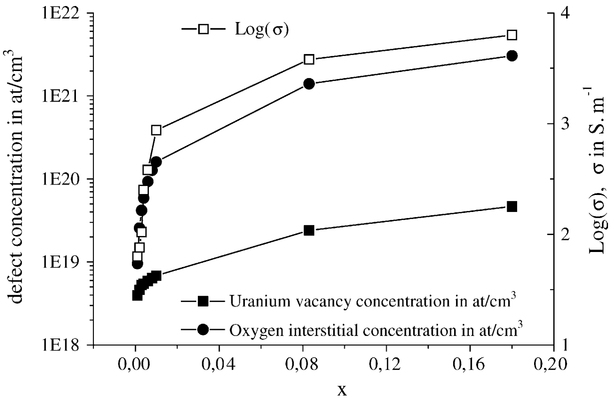

Fig. 2. Oxygen interstitial and uranium vacancy concentrations calculated from expansion data of Fig. 1 compared to UO_2 electrical conductivity as a function of x at 1473 K.

Knowing the length decrease due to the unit cell parameter evolution, it is then easy to deduce the number, ΔN, of created unit cells along an axis, from the experimental expansion Δl. It is equal to:

$$\Delta N = \frac{\Delta l + (L_0/a_0)(a_A - a_B)}{a} \qquad (3)$$

where L_0 is the initial length of the single crystal.

Taking into account a column of unit cells with a length equal to l, the length of the single crystal in B, the concentration of the uranium vacancies and the oxygen interstitials can be calculated with the following formulae:

$$\text{Concentration of uranium vacancies} = \frac{4\Delta N}{a^2 l} \qquad (4)$$

$$\text{Concentration of oxygen interstitials} = \frac{n(U)x - 8\Delta N}{a^2 l} \qquad (5)$$

where $n(U)$ is the number of uranium atoms.

The calculation is performed for the results obtained at $T = 1473$ K. The calculated concentration of oxygen interstitials and uranium vacancies is presented as a function of x in Fig. 2. The correspondence between the $p(O_2)$ values and the values of x was performed using the data of Ref. [6]

A numerical application is detailed for the points A and B of Fig. 1. The point A, $p(O_2)$ equal to 10^{-9} Pa, corresponds to stoechiometric UO_2. The point B, $p(O_2)$ equal to $10^{-1.56}$ Pa, corresponds to UO_{2+x} with $x = 0.083$. Referring to diffraction data[1] obtained at a similar temperature the unit cell parameter of UO_{2+x} is equal to $a_A = 5.54$ Å for $x = 0$ and to $a_B = 5.5355$ Å for $x = 0.083$. Using formulae (4) and (5) gives for point B a concentration of uranium vacancies equal to 2.4×10^{19} cm^{-3} and a concentration of oxygen interstitials equal to 1.4×10^{21} cm^{-3}.

3. Discussion

The consistency of this evaluation of the point defect concentrations has been checked with the calculation of the

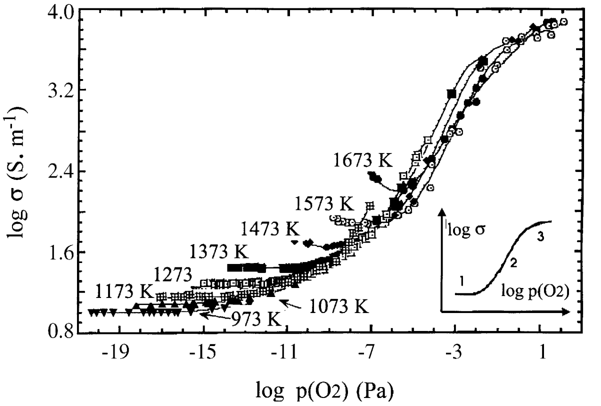

Fig. 3. UO_2 electrical conductivity as a function of $p(O_2)$ at different temperatures.[4]

electrical carrier concentration induced by the point defect formation and with the comparison with its actual value determined experimentally. The electrical conductivity of UO_{2+x} at 1473 K is represented as a function of x in Fig. 2 using data from.[4] The shape of this curve is very similar to the shape of the oxygen interstitial concentration given in Fig. 2, which is the main point defect for $x > 0.01$.

A more quantitative evaluation of the electrical carrier concentration at point B is proposed with different ionisation states of uranium vacancies and oxygen interstitials.

(a) Assuming that uranium vacancies are ionised four times and that oxygen interstitials are ionised two times, the concentration of induced electrical carriers should of the order of 3×10^{21} cm^{-3}.

(b) If the oxygen interstitials are not isolated and form clusters like $(2O_i^a, 2O_i^b, 2V_O^c)'$, then the concentration of induced electrical carriers should of the order of 8×10^{20} cm^{-3}.

(c) The electrical conductivity of UO_2 as function of $p(O_2)$ is presented for several temperatures in Fig. 3. For temperatures higher than 1373 K, the conductivity curves exhibit a minimum corresponding to the stoichiometric UO_2. The conductivity value associated to this minimum increases as function of temperature, which is interpreted as the contribution of intrinsic carriers whose concentration follows an Arrhenius law. On the right side of this minimum the electrical conductivity increases with increasing $p(O_2)$. The creation of new carriers associated to the formation of point defects in UO_{2+x} can explain this conductivity increase. At 1473 K the increase of conductivity, between the points corresponding to A and B in Fig. 1, is equal to $\Delta\sigma = 36.24\ \Omega^{-1}$ cm^{-1}. Considering an electronic mobility of 3.7×10^{-2} cm^2 V^{-1} s^{-1} at 1473 K the corresponding concentration of electrical carriers is around 6×10^{21} cm^{-3}.

The number of electrical carriers deduced from expansion measurements and calculated from electrical conductivity data are of the same range of magnitude. This represents a good agreement considering that many crude approximations have been made for these estimations.

On a theoretical point of view, a modelling predicting the concentration of the uranium vacancies as a function of x was developed taking into account four types of point defects.[5] The equilibrium constant for Schottky defects in uranium dioxide is given by $K_S = [V_U][V_O]^2$, the equilibrium constant for the Frenkel defects in uranium sublattice is given by $K_{FU} = [V_U][U_i]$ and similarly the equilibrium constant for the Frenkel defects in oxygen sublattice is given by $K_{FO} = [V_O][O_i]$. For the case of a large oxygen excess, it can be considered that $[O_i] = x$ which implies that $[V_U]$ is proportional to x^2. These estimations are only in qualitative agreement with our experimental results. For the case of large oxygen excess, the measured ΔL is nearly constant. Because the unit cell parameter decreases linearly with x,[1] the number of created unit cells, and hence, the concentration of uranium vacancies, varies as $\alpha + \beta x$, where α and β are constants.

This discrepancy can be explained by the nature of the point defects involved in the thermodynamic modelling. Willis demonstrated indeed that, for large excess of oxygen, oxygen interstitials were not isolated defects any more, but formed complex clusters. Including these clusters in the modelling would certainly improve its consistency with experimental data.

4. Conclusion

An original approach is proposed to determine the concentration of uranium vacancies in hyper-stoichiometric uranium dioxide using expansion measurement as a function of $p(O_2)$. The results obtained show that the concentration of oxygen interstitials is 100 times higher than the one of the uranium vacancies. The experimental evidence of cationic vacancies is consistent with the interpretation of the increase of sintering speed in oxidising atmosphere, and also qualitatively consistent with the modelling proposed in.[5] A new modelling including the clusters of oxygen interstitials and vacancies would improve the quantitative interpretation of point defects in hyperstoichiometric uranium dioxide.

References

1. Dodé, M. and Touzelin, B., Revue de Chimie Minérale. *Etude directe aux rayons X en atmosphère contrôlée des équilibres d'oxydation des oxydes d'uranium de 1150 à 1200 °C*, 1972, **9**, 141–152.
2. Willis, B. T. M., The defect structure of hyperstoichiometric uranium dioxide. *Acta Cryst.*, 1978, **A34**, 88–90.
3. Kutty, T. R. G., Hegde, P. V., Khan, K. B., Basak, U., Pillai, S. N., Sengupta, A. K., Jain, G. C., Majumdar, S., Kamath, H. S. and Purushotham, D. S. C., Densification behaviour of UO_2 in six different atmospheres. *J. Nucl. Mater.*, 2002, **305**, 159–168.

4. Ruello, P., Petot, C., Petot-Ervas, G. and Desgranges, L., Electrical conductivity and thermoelectric power of Uranium dioxide. *J. Am. Ceram. Soc.*, in press.
5. Matzke, Hj., In *Meeting Proceedings of International Conference on Fast Breeder Fuel Perform*, 1979, pp. 202–213.
6. Hagemarck, K. and Broli, M., Equilibrium oxide pressures over the nonstoichoimetric uranium oxide UO_{2+x} and U_3O_{8-z} at higher temperature. *J. Inorg. Nucl. Chem.*, 1966, **28**, 2837–2850.