Characterisation of uranium vacancies in hyper stoichiometric uranium dioxide

L.Desgranges[1], M.Gramont[2], C.Petot[2], G.Petot-Ervas[2], P.Ruello[3], B.Saadi[4]

1- CEA-Cadarache DEC/SA3C/L2EC Bat 316 13108 Saint-Paul lez Durance FRANCE

2- SPMS, Ecole Centrale Paris 92295 Chatenay-Malabry FRANCE

3- LPEC, Université du Maine 72085 Le Mans France

4- LESIM, Université de Annaba 23200 Annaba ALGERIA

Abstract : An experimental method, based on measurements of the expansion of a single crystal as a function of the PO_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 agreement with a theoretical modelling proposed by Matzke.

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 1000 and 1400°C, 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 Fm3m, like UO_2, with a decrease of the unit cell parameter as a function of x [1]. Willis proposed the existence of oxygen interstitial or clusters of oxygen interstitials 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 f defects in UO_{2+x}, an experimental method based on measurements of the expansion of a single crystal as a function of the PO_2 was used.

Experimental :

A 7 mm long UO_2 single crystal was set in Netzsch dilatometer and held at a constant temperature, ranging from 900 to 1300°C. In this configuration a 10,1 nm displacement induces a 1mV voltage variation of the detection system. The atmosphere inside the dilatometer was monitored in order to obtained various values of the oxygen partial pressure PO_2 using a zirconia made oxygen probe.

The PO_2 corresponding to the UO_2 stoichoimetry was determined in a previous study 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.

Results

The length increase of the single crystal as a function of the P_{O_2} for different temperatures is presented in figure 1. For each temperature, 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 less constant at each temperature.
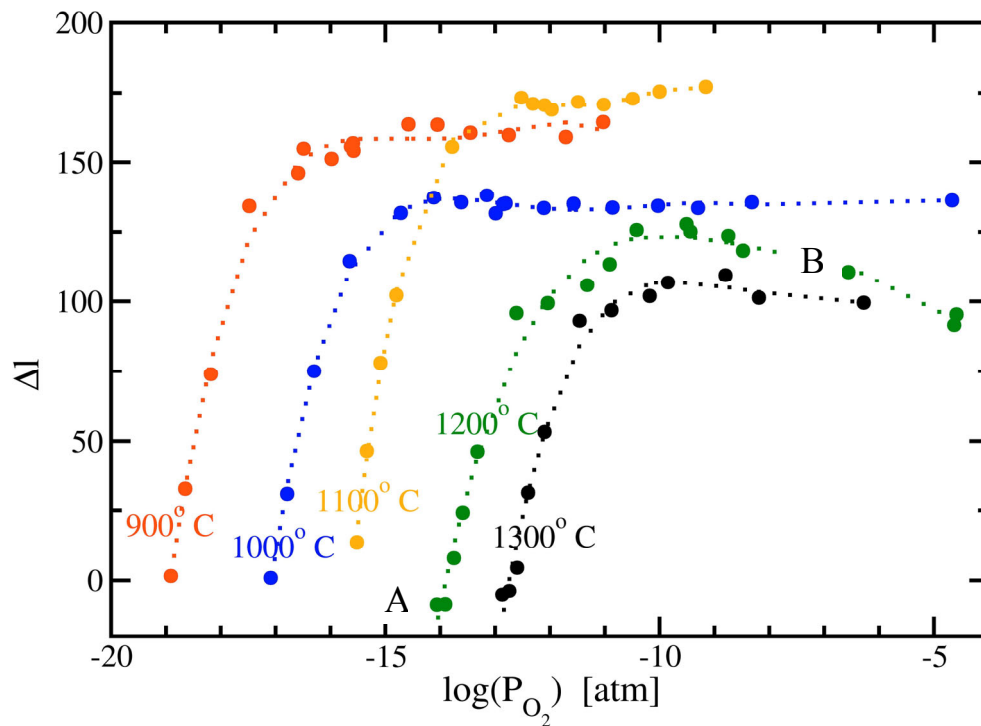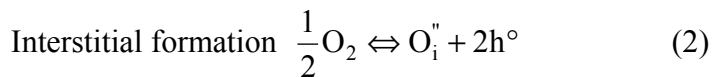

Figure 1 : *Expansion of a UO2 single crystal as function of PO2 at different temperatures. In order to obtain Δl in µm the scale has to be multiplied by 1.29.10^{-2}.*

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 hyperstoechiometry. 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 a internal swelling.

So it is possible to interpret the PO_2 driven expansion data as the sum of two contributions : one arising from the unit cell parameter decrease, the other resulting form the formation of new unit cells. This two contributions can be associated to two different point defects : oxygen interstitial and uranium vacancies. The formation of both defects is correlated to the incorporation of oxygen, which occurs when UO_2 stoichiometry is increased with increased PO_2. Their formation mechanism can be described with the following equations, using standard notation, :

New unit cell formation $\qquad O_2 \Leftrightarrow V_U'''' + 2O_O + 4h° \quad$ (1)

Interstitial formation $\quad \dfrac{1}{2}O_2 \Leftrightarrow O_i'' + 2h° \qquad\qquad$ (2)

According to equation (1), the new unit cell formation results only in a uranium vacancy formation. According to equation (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 figure 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.

The calculation is performed for the results obtained at T=1200°C. The point A, PO_2 equal to 10^{-14} atm, corresponds to stoechiometric UO_2. The point B, PO_2 equal to $10^{-6,56}$ atm, will be used for the calculation. Referring to thermodynamic data, B 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.

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 :

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

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 interstitial can be calculated with the following formulae :

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

$$\text{Concentration of oxygen interstitial} = \frac{n(u)x - 8\Delta N}{a^2 l} \quad (5)$$

Where $n(u)$ is the number of uranium atoms.

A numerical application of 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 interstitial equal to $1.4.10^{21}$ cm^{-3}.

Discussion:

The consistency of this evaluation of the point defect concentrations has been checked with the calculation of the electrical carrier concentration induced by the point defect formation and with the comparison with its actual value determined experimentally.

a) Assuming that uranium vacancies are ionised 4 times and that oxygen interstitial are ionised 2 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 ionisation number of U and O atom can be lower than 4 and 2 respectively, then the concentration of induced electrical carriers become less than the one proposed in a) and b).
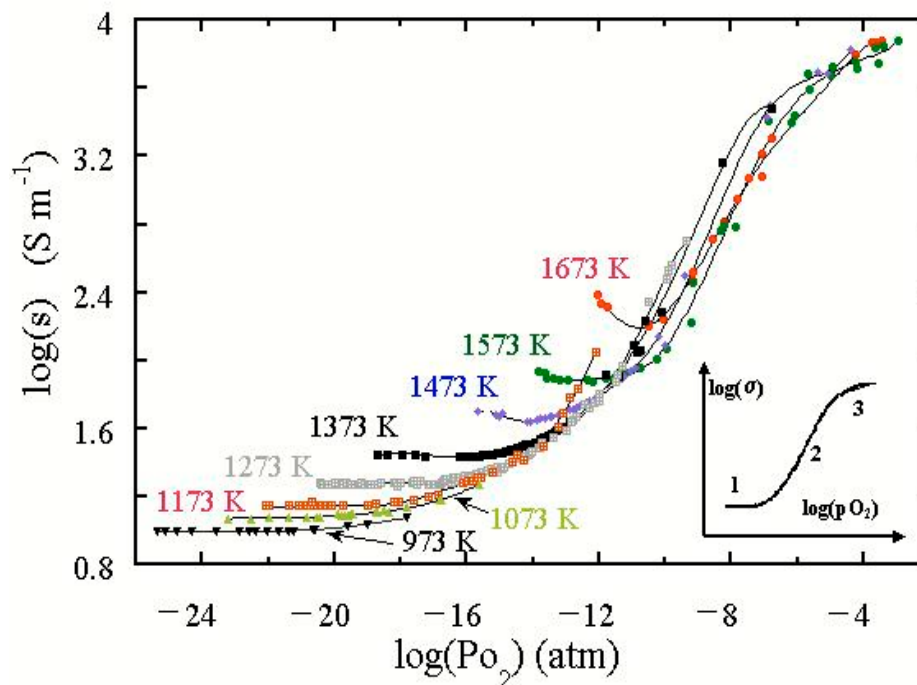

figure 2 : UO₂ electrical conductivity as a function of PO2 at different temperatures

d) The electrical conductivity of UO_2 as a function of PO_2 has been extensively studied in our laboratory [4]. The electrical conductivity of UO_2 as function of PO_2 is presented for several temperatures on figure 2. 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 PO_2. The creation of new carriers associated to the formation of point defects in UO_{2+x} can explain this conductivity increase. At 1200°C the increase of conductivity, between the points corresponding to A and B on figure 1, is equal to $\Delta\sigma = 0.824\ \Omega^{-1}.cm^{-1}$. Considering an electronic mobility of $3.7.10^{-2}\ cm^2V^{-1}s^{-1}$ at 1200°C the corresponding concentration of electrical carriers is around $1.4.10^{20}$ 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, Matzke [5] has developed a modelling predicting the concentration of the uranium vacancies as a function of x. According to these calculations the concentration of uranium vacancies increases rapidly from $UO_{2.00}$ to $UO_{2.05}$ and is more constant for x>0.05. These estimations are in qualitatively good agreement with our experimental results. A more quantitative analysis of our data is in progress in order to improve the comparison between our data and this modelling.

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 PO_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 consistent with the modelling proposed by Matzke .

References

1 M.Dodé, B.Touzelin, Revue de Chimie Minérale, 1972, **9**, 141-152

2 Willis B.T.M, Acta Cryst., 1978, **A34**, 88-90

3 T. R. G. Kutty, P. V. Hegde, K. B. Khan, U. Basak, S. N. Pillai, A. K. Sengupta, G. C. Jain, S. Majumdar, H. S. Kamath and D. S. C. Purushotham, Densification behaviour of UO_2 in six different atmospheres**, *Journal of Nuclear Materials, 2002, 305, 159-168*

4 P.Ruello, C.petot, G.Petot-Ervas, L.Desgranges, J. Am. Ceram. Soc in press

5 Matzke In proceedings Top. Meeting Proc. Intern. Conf. Fast Breeder Fuel Perform. , Monterey, Calif.1979, pp 202/13