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## **Oxidation behaviour of unirradiated sintered UO<sub>2</sub> pellets and powder at different oxygen partial pressures, above 350°C**

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**Key words:** *U3O8 ; kinetics ; oxygen partial pressure ; pseudo steady state ; rate-limiting step.*

### **Abstract**

The oxidation of sintered UO<sub>2</sub> pellets and powder into U<sub>3</sub>O<sub>8</sub> has been studied by thermogravimetry at 370°C, under controlled oxygen partial pressures (P<sub>O<sub>2</sub></sub> ranging from 2-40 kPa). Sigmoidal curves of oxidation weight gain were measured for both pellet and powder test samples. The rate of oxidation increased as the oxygen partial pressure increased. It has been shown, by simultaneous TG-DSC, that the reaction proceeds in a pseudo steady state. An experimental methodology based on temperature or P<sub>O<sub>2</sub></sub> jumps has shown that the assumption of a rate-limiting step is validated, and a mean value of activation energy for the formation of U<sub>3</sub>O<sub>8</sub> of 103 kJ.mol<sup>-1</sup> was estimated.

### **1. Introduction**

The oxidation of UO<sub>2</sub> into U<sub>3</sub>O<sub>8</sub> has been studied extensively for several years [1-3], because it is an important process in performance analysis for the dry storage and ultimate disposal of spent nuclear fuel. The formation of U<sub>3</sub>O<sub>8</sub> by oxidation of UO<sub>2</sub> corresponds to 36% increase in volume. This volume increase leads to further degradation of a defective fuel cladding and to the release of radioactive U<sub>3</sub>O<sub>8</sub> powder in the storage container. Also, the formation of U<sub>3</sub>O<sub>8</sub> increases significantly the surface area of the spent fuel from that of UO<sub>2</sub> pellet fragments. Consequently, detailed knowledge of the kinetics of the formation of U<sub>3</sub>O<sub>8</sub> is needed in order to define safe conditions of storage. For this reason, most studies previously reported focused on oxidation behaviour at rather low temperatures (200-300°C) [1, 4-13]. The purpose and background of our work is quite different. It consists of investigating the oxidation of sintered UO<sub>2</sub> pellets and powder at higher temperatures above 350°C. Information from these investigations will be used to optimise the calcination in air of recycled UO<sub>2</sub>, which is one of the industrial process steps to manufacture nuclear fuel.

It has been shown [1] that the oxidation of UO<sub>2</sub> is at least a two-step reaction, usually written as: UO<sub>2</sub> → U<sub>4</sub>O<sub>9</sub> / U<sub>3</sub>O<sub>7</sub> → U<sub>3</sub>O<sub>8</sub>.

With powders, the intermediate phases U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>7</sub> are more or less clearly observed up to about 200-250°C [4, 5, 9-11]; above 250°C, U<sub>3</sub>O<sub>8</sub> appears [1, 5, 11]. The reaction curves exhibit a first step with a continuously decreasing rate, corresponding to the U<sub>4</sub>O<sub>9</sub> / U<sub>3</sub>O<sub>7</sub> formation, then during the oxidation into U<sub>3</sub>O<sub>8</sub> they display a sigmoidal shape, often attributed to nucleation and growth behaviour and more generally to reaction area changes. Above 350°C, the intermediate phases U<sub>4</sub>O<sub>9</sub> / U<sub>3</sub>O<sub>7</sub> are generally not observed, the oxidation seems to proceed directly to U<sub>3</sub>O<sub>8</sub> [5, 11].

The temperatures leading to a significant oxidation of sintered UO<sub>2</sub> pellets are higher (about 300 – 350°C) and it seems that if only a thin layer of U<sub>3</sub>O<sub>7</sub> is formed on the surface of the pellets [12, 13], then the oxidation to U<sub>3</sub>O<sub>8</sub> proceeds according to only sigmoidal reaction curves. At higher temperatures (above 350°C), only U<sub>3</sub>O<sub>8</sub> is observed [14].

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Concerning the effect of oxygen pressure, there is no universal agreement in the case of  $U_4O_9$  /  $U_3O_7$  formation on powders [2, 9, 10]. The parabolic rate constant corresponding to the formation of  $U_3O_7$  has been measured at temperatures ranging from 130 to 200°C, and oxygen partial pressures varying between 0.003 and 101 kPa. A slight oxidation increasing effect is observed when  $P_{O_2} < 20$  kPa [9, 10], whereas it seems that there is no significant effect if  $P_{O_2} > 20$  kPa [9]. For sintered  $UO_2$  pellets, the influence of the oxygen partial pressure has been considered separately for the “induction” and “post-induction” (rapid and “linear” oxidation) periods of the sigmoidal curves. The literature [2] reports no effect on the induction period rates, but show that the oxidation rate in the “linear” part of the sigmoidal curves increases as  $P_{O_2}$  increases.

The sigmoidal curves are usually interpreted using the Avrami [15] or Johnson-Mehl [16] models. But these models assume that the nucleation occurs throughout the volume of the existing phase, rather than only at the surface of the grains. Thus, from a physico-chemical point of view, they are not appropriated to the oxidation of sintered  $UO_2$  pellets or powders (even though these models can be used to “approximate” closely the shape of the reaction curves).

Finally, despite the numerous studies dedicated to the formation of  $U_3O_8$ , this reaction is not yet fully understood. In particular, there is a wide range of reported values for the activation energy of  $U_3O_8$  formation [17]. These values depend on the method of data analysis used by the authors to estimate an activation energy; such as from the “linear part of the sigmoidal curves”, from the “maximum rate”, from the time necessary for “50% conversion to  $U_3O_8$ ”, etc... Thus, the literature data on the oxidation of  $UO_2$  at temperatures higher than 350°C is ambiguous. For this reason, we studied the oxidation of industrial sintered  $UO_2$  pellets and powder, at controlled oxygen partial pressure and temperature at 370°C. This is an approach we have used in previous oxidation studies [18-20]. With this approach, the validity of existing kinetic assumptions discussed in the literature can be experimentally determined. In particular:

- (i) the pseudo steady state assumption (which is necessary to assume the existence of a rate-limiting step) can be verified by measuring the reaction rate with two techniques (for example, simultaneous thermogravimetry and calorimetry [18-20]) : if the system proceeds in a pseudo steady state, the rates of weight gain and the heat flow should remain proportional during the whole reaction,
- (ii) the assumption of a rate-limiting step can be verified using a method based on temperature or pressure jumps [18-20]. When phase transformations in solids are modelled, the rate is usually written as:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

where  $\alpha$  is the fractional conversion,  $A$  is called the pre-exponential factor,  $E_a$  is the activation energy and  $f(\alpha)$  is an analytical function (which describes the evolution with time of the reaction area where the rate-limiting step of the phase transformation is located, it depends on the shape of the grains and the step controlling the growth [21, 22]).

Eq. (1) implies that the rate is controlled by a step following the Arrhenius law (which is not always the case, for example when an adsorption step is involved, following Langmuir isotherm). Eq. (1) also implies that the rate is fixed by the value of  $\alpha$  ( $f(\alpha)$ ), which may not be the case, particularly when nucleation and growth processes are in competition [23]. We propose a more general expression for the fractional conversion rate function, given in the following expression :

$$\frac{d\alpha}{dt} = \Phi(T, P_i) E(t) \quad (2)$$

in which  $\Phi$  is a rate per unit area ( $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ ), depends on the nature of the rate-limiting step (diffusion, interface reaction), may be a function of temperature  $T$  and of the partial pressures of the reacting gases  $P_i$ , but is independent of time.  $E(t)$  (in  $\text{m}^2\cdot\text{mol}^{-1}$ ) corresponds to the extent of the reaction zone where the rate-limiting step is spatially located. The interest of the general expression Eq. (2) is that it only assumes the existence of a rate-limiting step for the oxidation of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$ , but no additional explicit assumption is made concerning the nature and the localisation of this step (however, it is expressed in the  $E(t)$  function).

Once points i) and ii) have been validated experimentally, Eq. (2) can be used. Then the jump method, in which variations of  $T$  and  $P_i$  are made, is used to experimentally evaluate the variations in the function  $\Phi(T, P_i)$ . This testing method is very useful for identifying the rate-limiting step and verifying a conversion rate mechanism. It also makes it possible to determine experimentally whether the conversion rate is consistent with any of the possible  $f(\alpha)$  function choices available in the literature [23].

Thus, in this article we have tried to answer these questions, for the problem of oxidation of  $\text{UO}_2$  into  $\text{U}_3\text{O}_8$  at high temperature:

- \* Does the oxidation of  $\text{UO}_2$  into  $\text{U}_3\text{O}_8$  proceed in a pseudo steady state ?
- \* Is there a rate-limiting step ?
- \* If a rate-limiting step does exist, what is the influence of the oxygen partial pressure on the oxidation rate?
- \* Can we determine an activation energy for the formation of  $\text{U}_3\text{O}_8$ ?

## 2. Experimental

The test specimens were  $\text{UO}_2$  pellets and  $\text{UO}_2$  powder with large agglomerates, supplied by the industry Franco-Belge de Fabrication du Combustible (FBFC-FRAMATOME-ANP). The pellets were 8.2 mm in diameter and 1.9 mm in height. The mean  $\text{UO}_2$  grain size is about 10  $\mu\text{m}$ , as shown on the micrograph in Fig. 1. The agglomerated powder was prepared from the starting powder, by calcination at 1700°C under hydrogen during 4 hours (using the pellet sintering cycle). Its specific surface area, measured by nitrogen adsorption at 77 K (BET method), is 0.031  $\text{m}^2\cdot\text{g}^{-1}$ . It is constituted by agglomerates of about 100  $\mu\text{m}$  (Fig. 2a), in which the grain size varies between 2 and 10  $\mu\text{m}$  approximately (Fig. 2b).

The oxidation curves were obtained under isothermal and isobaric conditions with a symmetrical thermoanalyser SETARAM TG-DSC 111, under a flowing mixture of oxygen in helium. The flowrates of the gases are controlled by mass-flowmeters (Brooks 5850S), the total flowrate being 2  $\text{l}\cdot\text{h}^{-1}$ . The partial oxygen pressure could be controlled within the range of 2-40 kPa. The jump method tests with oxygen pressure changes were performed by changing quickly the calibrated oxygen flowmeter setpoint. The thermoanalyser software allows to control and record the temperature of the furnace. The signals corresponding to the weight gain and the heat flow are also recorded continuously. Some experiments have been carried out in a symmetrical thermobalance under static atmosphere (SETARAM MTB 10<sup>-8</sup>, the total pressure being the oxygen pressure fixed for the experiment). In that case, the temperature of the sample and the weight gain are recorded continuously.

In order to identify the phases formed during the oxidation of  $\text{UO}_2$  pellets and powder, XRD experiments were carried out on a Siemens D5000 diffractometer (Cu  $K_\alpha$  radiation, step:0.015°, step time: 5 seconds).

## 3. Results

### 3.1. Shape of the oxidation curves, effect of temperature

Fig. 3 shows kinetic curves giving the fractional conversion  $\alpha$  of sintered  $\text{UO}_2$  pellets versus time, at three different temperatures (260, 370, 500°C), and a partial oxygen

pressure of 20kPa. The fractional conversion is calculated from the weight gain ( $\Delta m(t)$ ), using the following equation :

$$\alpha = \frac{\Delta m(t)}{\Delta m(\text{theo})} \quad (3)$$

where  $\Delta m(\text{theo})$  is the theoretical weight gain corresponding to the total oxidation into  $\text{U}_3\text{O}_8$  (3.95%). No significant oxidation occurs at 260°C during the time investigated, a sigmoidal curve is observed at 370°C and the oxidation is very rapid at 500°C. In the results that follow, the experiments were mostly performed at 370°C, and a few experiments were at 600°C. The  $\text{U}_3\text{O}_8$  formed on the sintered  $\text{UO}_2$  pellets spalls from the surface as a powder. Its specific surface area (measured by nitrogen adsorption at 77 K according to the BET method) decreases when the oxidation temperature increases: it is equal to 0.8  $\text{m}^2.\text{g}^{-1}$  at 370°C, and 0.5  $\text{m}^2.\text{g}^{-1}$  at 600°C. The  $\text{U}_3\text{O}_8$  spallation particles have approximately the same size as the original  $\text{UO}_2$  grains, but have highly fractured microcracked features that are shown on the micrograph in Fig. 4. The possible oxide phases present in oxidized samples were studied by X-Ray diffraction. Prior to oxidation, only the  $\text{UO}_2$  phase was observed on sintered pellets and powder. A pellet partially oxidized up to a weight gain of 1.9% (theoretical weight gain corresponding to the oxidation into  $\text{U}_3\text{O}_7$ ) exhibits the diffraction peaks of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ : no  $\text{U}_3\text{O}_7$  is detected in this sample, or in a sample oxidized to a lower weight gain (1%). However, the quantity of  $\text{U}_3\text{O}_7$  that forms may be too small to be detected by XRD. In the following kinetic analysis, we will assume that the  $\text{UO}_2$  phase is transformed directly into a  $\text{U}_3\text{O}_8$  phase without any intermediate phases.

### 3.2. Effect of oxygen pressure

Fig. 5 shows  $\alpha(t)$  kinetic curves obtained at 370°C with sintered  $\text{UO}_2$  pellets (Fig. 5a) and powder (Fig. 5b): here, it is seen that the higher the oxygen partial pressure, then the higher the oxidation rate. However, the oxygen partial pressure influence is greater for lower pressures ( $P_{\text{O}_2} \leq 10$  kPa), and the oxygen partial pressure effect decreases between 10 and 20 kPa. In Fig. 6, it is seen that under the same conditions (370°C,  $P_{\text{O}_2} = 20$  kPa), the powder is fully oxidised more rapidly than a sintered pellet. This is a clear indication of the surface area dependence on the oxidation conversion rates of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$ .

### 3.3. Pseudo steady state assumption

Fig. 7a shows both the rate of weight gain ( $\frac{dm}{dt}$ ) and the heat flow ( $\frac{dQ}{dt}$ ) versus time at 370°C and 20 kPa of oxygen partial pressure, for a sintered pellet. The curves are superimposed during the whole reaction, which indicates that the reaction system is in a pseudo steady state. The data curves can be superimposed for experiments performed at different oxygen partial pressures, and with powdered samples. The constant ratio between the rate of weight gain and the heat flow is given by :

$$\frac{dQ}{dt} = \frac{\Delta H}{1/3 M_{\text{O}_2}} \frac{dm}{dt} \quad (4)$$

where  $M_{\text{O}_2}$  is the molar mass of oxygen, and  $\Delta H$  the enthalpy of the reaction (E1) :



Using the linear relationship (Eq. (4)) between  $\frac{dQ}{dt}$  and  $\frac{dm}{dt}$ , represented in Fig. 7b, it is possible to estimate the value of the enthalpy of the reaction (E1) for several isothermal and isobaric experiments. The result  $\Delta H = 101 \pm 2$   $\text{kJ}.\text{mol}^{-1}$ , is in close agreement with the value calculated using thermodynamic tables [24]:  $\Delta H_{\text{calc}} = 103$   $\text{kJ}.\text{mol}^{-1}$  at 370°C.

### 3.4. Rate-limiting step assumption

If a single rate-limiting step exists, Eq. (2) can be applied to describe the variations of the oxidation conversion rate with the intensive variables ( $T, P_i, \dots$ ) and time,  $t$ . In isobaric and isothermal conditions, the variations of the rate with time are given by  $E(t)$ , and  $\Phi(T, P_i)$  remains constant. A sudden change (jump) in temperature or partial pressure during an experiment will then lead to a change in  $\Phi$  only, while  $E(t)$  will remain approximately constant during the jump time interval (provided that the time interval necessary for the  $T$  or  $P_i$  change is short enough: in this case, it takes about 5 minutes, the whole experiment lasting 120 to 180 minutes (2 to 3 hours)). Thus the ratio of the rates

measured after (to the right) and before (to the left) of the jump is equal to  $\frac{\Phi_r}{\Phi_l}$  ( $E(t)$

dependence is eliminated in the ratio). Performing a series of similar jump experiments at

different reaction times, or equivalently values of  $\alpha$ , provides a set of  $\frac{\Phi_r}{\Phi_l}$  ratios, one for

each time. And if each of ratios  $\frac{\Phi_r}{\Phi_l}$  obtained from the series of experiments is equal, then

Eq. (2) is an acceptable model expression. This method, which we have named the “ $\Phi$ .E test”, has been successfully used in several previous experiments [18-20]. The results obtained with sintered pellets are indicated in Fig. 8. The sudden changes in temperature ranged from 360 to 390°C ( $P_{O_2} = 20$  kPa, Fig. 8a) and the sudden changes in oxygen pressure ranged from 2 to 20 kPa ( $T = 370^\circ\text{C}$ , Fig. 8b). Considering the experimental error bars, the ratio of the rates measured on both sides of the jumps remained approximately at a constant value, independent of the fractional conversion  $\alpha$ .

Consequently, it is concluded that the conversion rate model of Eq. (2) is validated. As the pseudo steady state assumption is also verified, the assumption of a single rate-limiting step for the  $U_3O_8$  growth mechanism is valid. This implies that the oxidation of  $UO_2$  to  $U_3O_8$ , at high temperatures (about 350°C), can be analysed with a model given by Eq. (2).

### 3.5. Variations of $\Phi$ with respect to partial oxygen pressure changes

The variations of  $\Phi$  with respect to a partial gas pressure  $P_i$  can easily be obtained by performing sudden changes, from  $P_0$  to  $P_i$ , at a given fractional conversion  $\alpha$ . At constant

temperature and using Eq. (2), the ratio of the rates are equal to  $\frac{\Phi(P_i)}{\Phi(P_0)}$  [18-20, 25]. A

series of experiments were carried out on sintered pellets at 370°C, with oxygen partial pressures varying from 2 kPa ( $P_0$ ) to 40 kPa after the jump. The variations of  $\Phi$  with  $P_{O_2}$  are shown in Fig. 9, for pressure jump experiments at two fractional conversions ( $\alpha = 0.2$  and  $\alpha = 0.5$ ). The data error bars overlap, which is in agreement with Eq. (2), and the increasing oxygen partial pressure experimental data show an increasing  $\Phi(P_{O_2})$  function for  $U_3O_8$  conversion.

### 3.6. Estimation of the activation energy for the formation of $U_3O_8$ .

Using the temperature jumps (from 360 to 390°C) made for the “ $\Phi$ .E” test data, it is possible to estimate an apparent Arrhenius activation energy for the formation of  $U_3O_8$ . Writing the  $\Phi$  function as:

$$\Phi(T, P_{O_2}) = A_0 \exp\left(-\frac{E_a}{RT}\right) f(P_{O_2}) \quad (5)$$

the ratio of the rates on both sides for only the temperature jump experiments is then:

$$\frac{\Phi(T_1, P_{O_2})}{\Phi(T_0, P_{O_2})} = \exp\left(-\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_0}\right)\right) \quad (6)$$

and thus

$$E_a = \frac{R T_0 T_1}{T_1 - T_0} \ln \left( \frac{\Phi(T_1, P_{O_2})}{\Phi(T_0, P_{O_2})} \right) \quad (7)$$

The values of  $E_a$  calculated from the temperature jump data made at different fractional conversions  $\alpha$  (see Fig. 8a) are provided in Table 1. The activation energy estimated values are in the range  $77-133 \pm 15 \text{ kJ.mol}^{-1}$ , and they depend somewhat on the value of  $\alpha$ . The mean value is  $103 \text{ kJ.mol}^{-1}$ , which is situated within an order of magnitude of the activation energy values reported in the literature data for pellets above  $300^\circ\text{C}$  [17]. It is worth noticing that the activation energy estimated in this work is obtained directly from experiments without any explicit analysis of the  $\alpha(t)$  curves; and the only assumption is that the Arrhenius law applies.

Conversely, if Arrhenius temperature kinetics are followed, then all data from the temperature jump experiments should provide the same estimated value for activation energy  $E_a$ , independently of the fractional conversion  $\alpha$ . This is approximately the case (considering the error bars on the temperature jumps).

#### 4. Conclusions

The oxidation of sintered  $\text{UO}_2$  pellets and powder to  $\text{U}_3\text{O}_8$  has been studied at  $370^\circ\text{C}$  under a controlled partial oxygen pressure,  $P_{O_2}$ . Sigmoidal curves have been obtained in both cases, and an increasing effect due to  $P_{O_2}$  was observed. It has been shown that the reaction proceeds in a pseudo steady state, and the assumption of a rate-limiting step has been validated using the jump method. Using temperature jump experiments, it has been verified that the oxidation rate for the formation of  $\text{U}_3\text{O}_8$  at high temperature ( $\sim 350^\circ\text{C}$ ) follows the Arrhenius law. A mean activation energy was estimated for the formation of  $\text{U}_3\text{O}_8$  of about  $103 \text{ kJ.mol}^{-1}$  at  $370^\circ\text{C}$ .

Further work is necessary to propose a mechanism involving elementary stages (oxygen adsorption, interface steps, diffusions) and  $\text{U}_3\text{O}_8$  point defects, in order to describe the conversion of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$ . Using the assumption of a rate-determining step, it would be possible to calculate theoretical laws for  $\Phi(P_{O_2})$ . Comparing these laws with the experimental results would lead to the determination of the rate-limiting step and to an interpretation of the variations of  $\Phi(P_{O_2})$ . Besides, the modelling of the sigmoidal shape of the kinetic curves  $\alpha(t)$  is under investigation.

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## Tables captations

*Table I: Values of the activation energy  $E_a$  of the formation of  $U_3O_8$ , obtained from temperature jump experiments (360 to 390°C) at different fractional conversions  $\alpha$ .*

Fractional conversion $\alpha$	0.1	0.1	0.1	0.2	0.2	0.3	0.3	0.5	0.6	0.7
	2	5	8	2	7	4	7	3		
$E_a$ (kJ.mol <sup>-1</sup> ) $\pm$ 15kJ.mol <sup>-1</sup>	110	133	109	109	109	89	87	115	77	98

## Figure captations

Fig. 1 : Micrograph of a fragment of a sintered  $UO_2$  pellet.

Fig. 2 : Micrograph of the  $UO_2$  powder (a) and magnification of one of the agglomerates (b).

Fig. 3 : Fractional conversion versus time for sintered  $UO_2$  pellets at an oxygen partial pressure of 20 kPa, at 260, 370 and 500°C.

Fig. 4 : Micrograph of the  $U_3O_8$  powder obtained by oxidation of a  $UO_2$  pellet (370°C,  $P_{O_2} = 20$  kPa).

Fig. 5 : Fractional conversion  $\alpha$  versus time for various oxygen pressures at 370°C, for  $UO_2$  pellets (a) and powder (b).

Fig. 6 : Fractional conversion  $\alpha$  versus time for a powder and a sintered pellet in the same conditions of oxidation ( $T = 370^\circ\text{C}$ ,  $P_{O_2} = 20$  kPa).

Fig. 7 : Rate of weight gain (--- dm/dt) and heat flow (— dQ/dt) versus time for a sintered  $UO_2$  pellet at 370°C in oxygen (20 kPa) (a), and dQ/dt versus dm/dt (b) to verify the linear relationship (Eq. (4)).

Fig. 8 : Ratios of the rate of weight gain before and after temperature jumps ( $P_{O_2} = 20$  kPa) (a) and oxygen pressure jumps ( $T = 370^\circ\text{C}$ ) (b).

Fig. 9 : Variations of  $\Phi$  with the partial oxygen pressure for a sintered pellet (jumps from  $P_{O_2} = 2$  kPa to  $P$ , for  $\alpha = 0.2$  and  $0.5$ ,  $T = 370^\circ\text{C}$ ).

## Figures captations

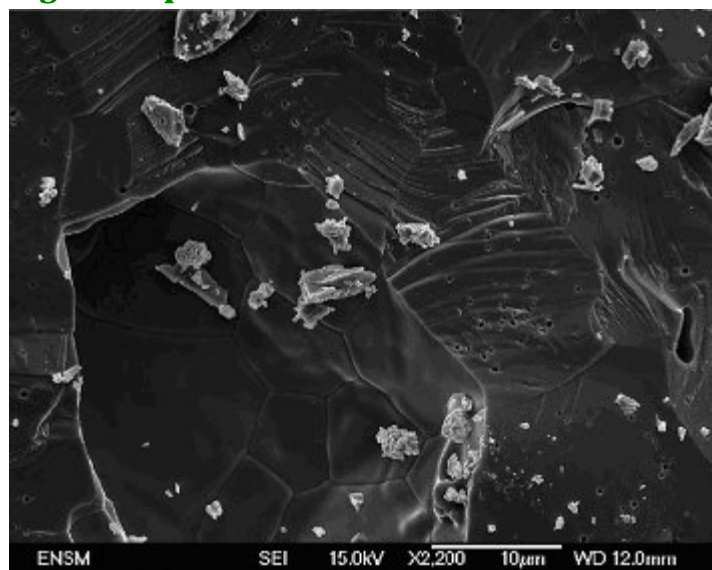


Figure 1

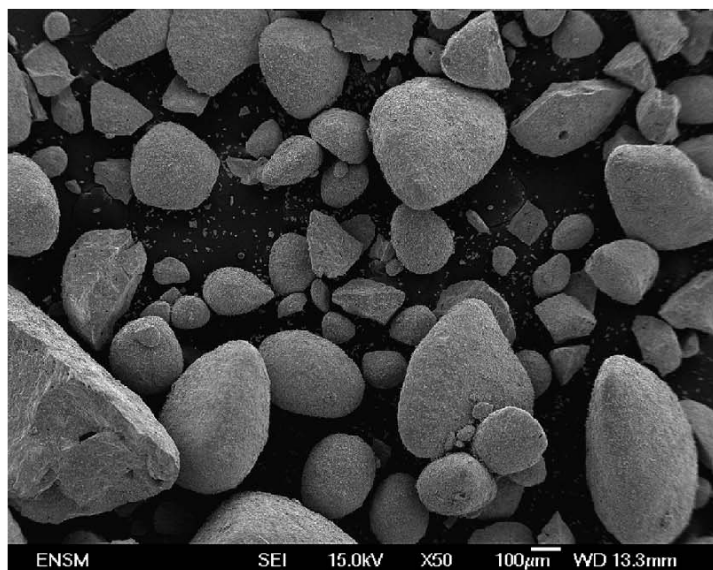


Figure 2a

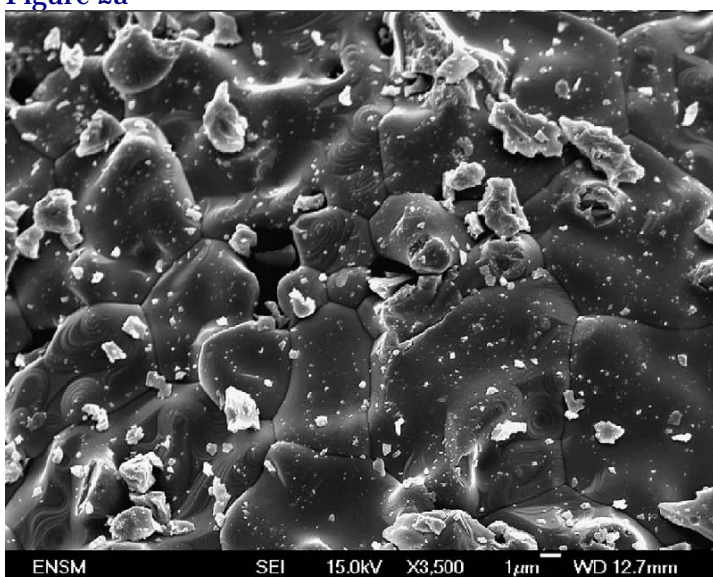


Figure 2b

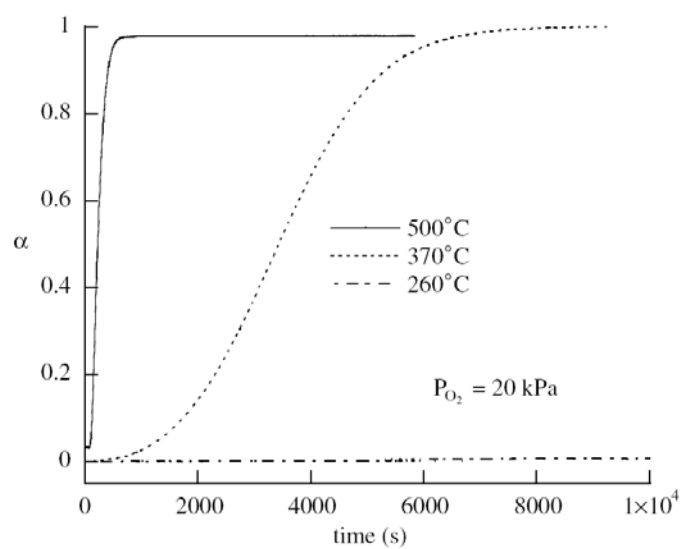
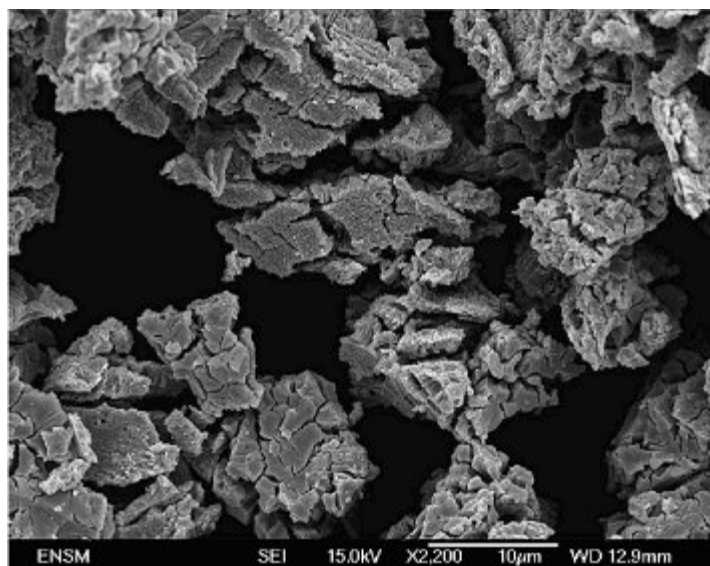
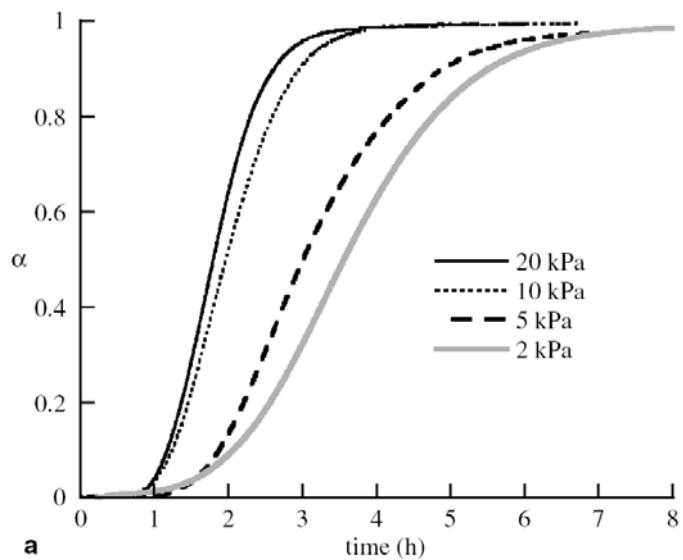


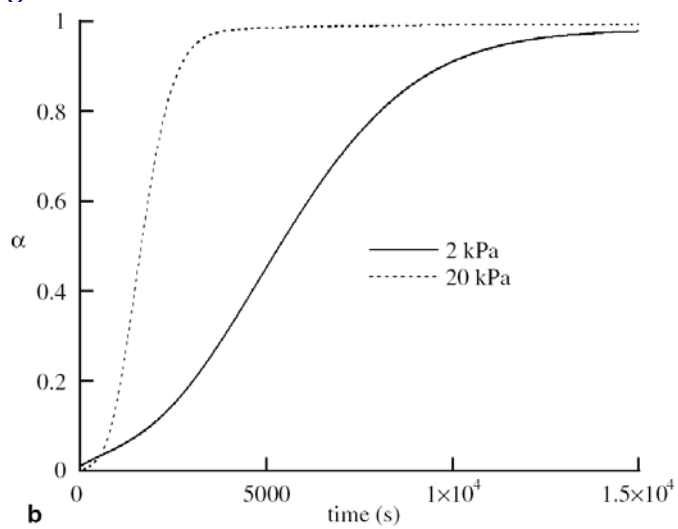
Figure 3



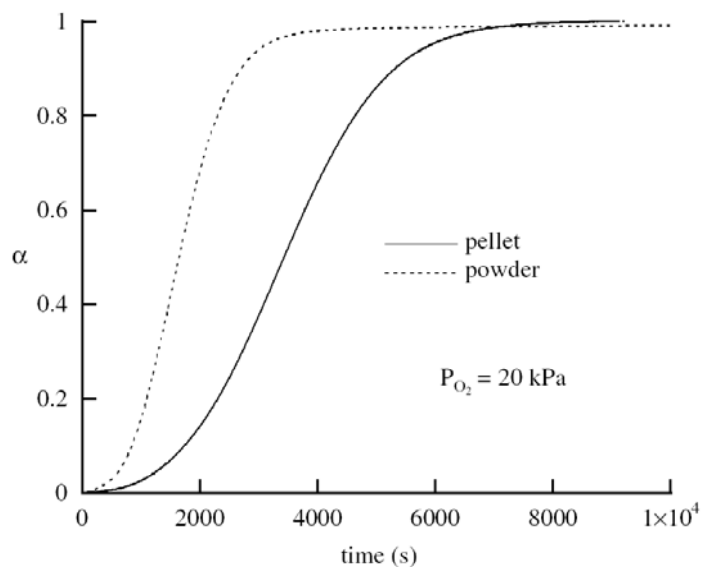
**Figure 4**



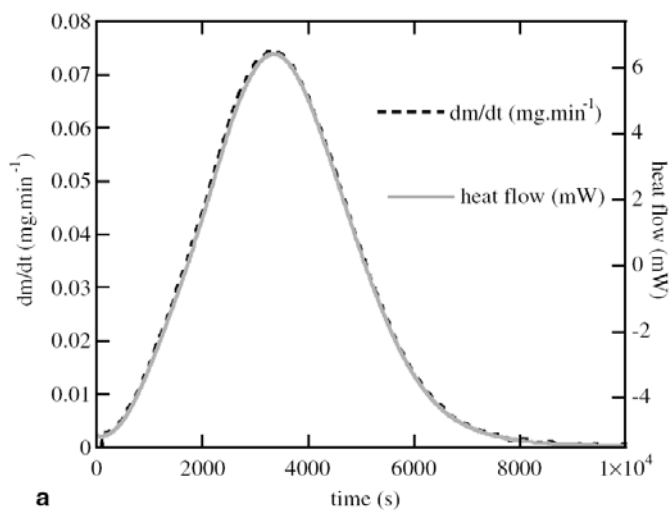
**Figure 5a**



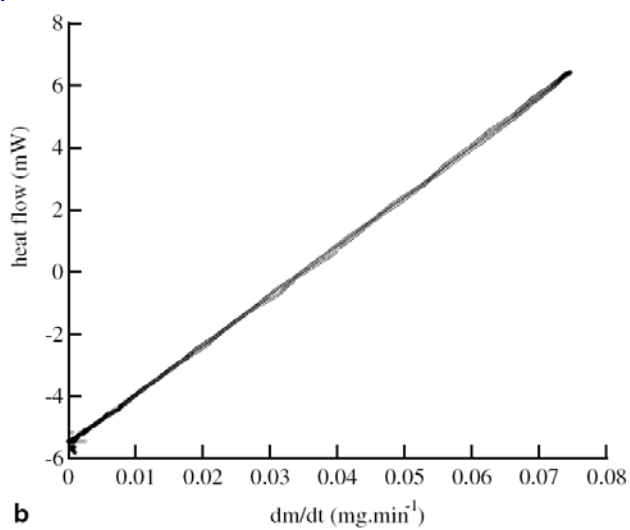
**Figure 5b**



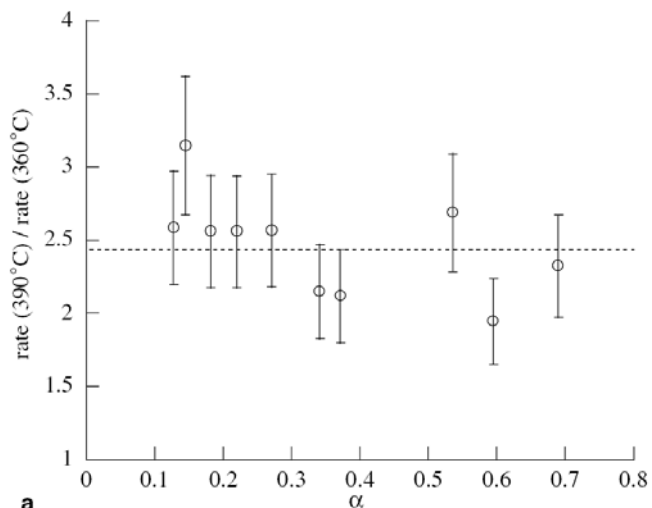
**Figure 6**



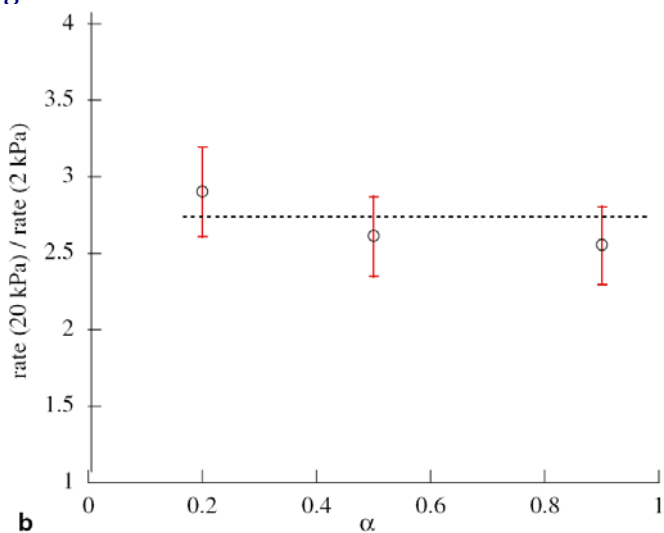
**Figure 7a**



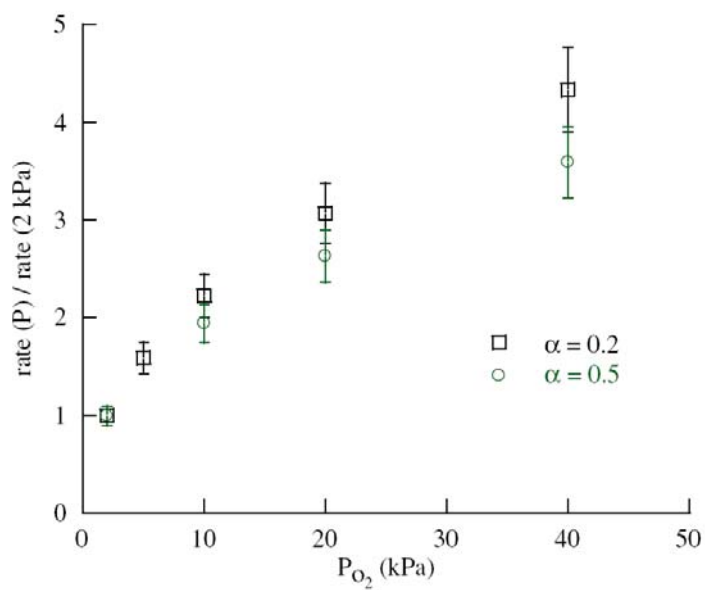
**Figure 7b**



**Figure 8a**



**Figure 8b**



**Figure 9**