

EXPERIMENTAL STUDY AND KINETIC MODELLING OF THE REDUCTION OF U_3O_8 BY HYDROGEN IN NON ISOTHERMAL OR NON ISOBARIC CONDITIONS

S.Perrin, M.Pijolat, F.Valdivieso, M.Soustelle

LPMG CNRS URA 2021, Centre Spin,
Ecole Nationale Supérieure des Mines
158 cours Fauriel
42023 Saint-Etienne Cedex, France

The conventional analysis of the kinetics of solid state reactions in non isothermal conditions relies on identification of pre-established rate equations which fit the experimental data $\alpha(T) - d\alpha/dt(T)$. The use of these kinetic equations, which are based on the assumption of the control of growth by internal interface step or diffusion, and on the Arrhenius law, makes the analysis restrictive and inappropriate to complex transformations such as nucleation-growth reactions or successive reactions. The aim of this work is to develop a new approach to the kinetic modelling in non isothermal or/and non isobaric conditions, based on the effective kinetic analysis of the transformation. The reaction under study is the reduction of U_3O_8 into UO_2 by hydrogen.

The kinetics of reaction and the changes in the powdered samples of U_3O_8 are followed using thermogravimetry, calorimetry, microscopy and X-ray diffraction.

It is found from isothermal and isobaric experiments that the overall transformation proceeds through three successive reactions: (1) the oxygen stoichiometry of U_3O_8 is changed into U_3O_{8-x} ($x \approx 0.2$), (2) the transformation of U_3O_{8-x} into U_4O_9 , (3) the reduction of U_4O_9 into UO_2 (Fig. 1).

The non isothermal and non isobaric experiments have been performed in a symmetrical thermobalance in the range 350°C-600°C and 1-5kPa of hydrogen in helium. The experimental rate was obtained as a function of time while temperature (T) or hydrogen pressure (P) variation was continuously monitored (Fig. 2).

A kinetic model is proposed which takes into account the three successive reactions. The particles are assumed to be spherical. The rate is calculated using the areic reactivity ($\text{mol.m}^{-2}.\text{s}^{-1}$) of each reaction, noted ϕ_1 , ϕ_2 and ϕ_3 , whose variations with T and P are obtained from preliminary isothermal and isobaric experiments. Reaction (1) is controlled by a surface reaction step. In reaction (2) the rate limiting step for the inward growth of U_4O_9 is the reactive desorption of water at the surface of the particles. In reaction (3), a similar rate limiting step is assumed for the growth of UO_2 from U_4O_9 . Moreover, the calculation of the resulting rate takes into account the particle size distribution of the powder.

Using the appropriate equations of ϕ_1 , ϕ_2 and ϕ_3 versus T or P, the calculated resulting rate fits very well the experimental one, as shown in the example of Figure 3. Similar good agreement was obtained in the case of a continuous variation in hydrogen pressure from 0 to 3 kPa, at a constant temperature.

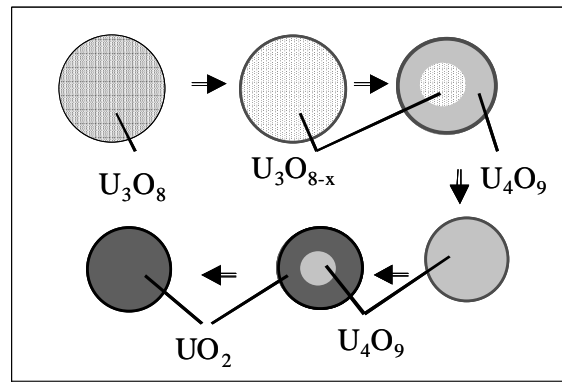


Fig.2. Schematic representation of a particle during the reduction of U_3O_8 by hydrogen, according to the kinetic model.

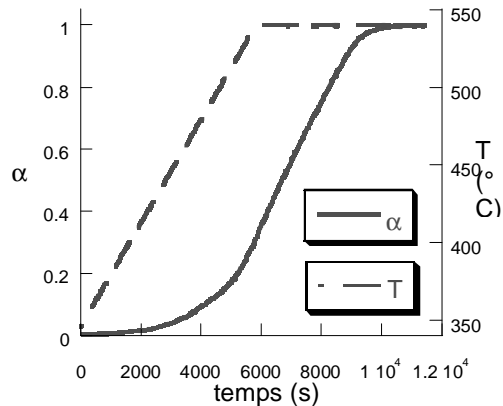


Fig.2. Experimental curve $\alpha(t)$ for a rate of temperature increase of $2^\circ\text{C}.\text{min}^{-1}$ and a hydrogen pressure of 3 kPa.

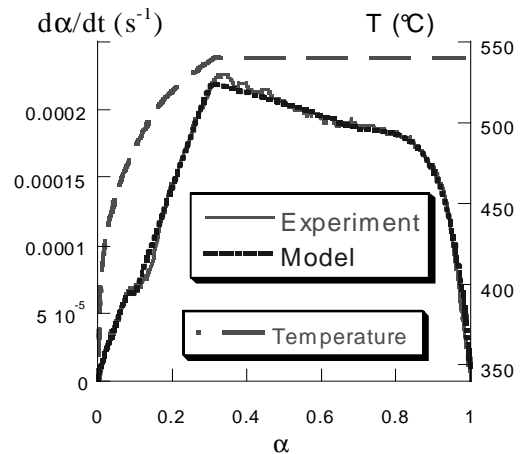


Fig.3. Calculated and experimental curves (rate of temperature increase of $2^\circ\text{C}.\text{min}^{-1}$ and $P_{H_2} = 3 \text{ kPa}$).