

A surface-to-volume model of UO₂ oxidation in air at 573 - 723K

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1. Introduction

The mechanism of oxidation of uranium dioxide in the air condition can be described, $UO_2 \rightarrow U_4O_9/U_3O_7 \rightarrow U_3O_8$ [1].

The formation of U₃O₈ leads to an approximately 23% density decrease and a 36% volume increase [1]. The increased volume of U₃O₈ causes a safety problem of long-term storage. Because of the safety problem, more studies are required to estimate the behavior of a uranium oxidation.

In this study, a surface-to-volume model is suggested to describe the kinetic mechanism from UO₂ to U₃O₈. The purpose of this study is to describe the model of UO₂ oxidation mathematically.

2. Methods and Results

Many researches have been studied to figure out the mechanism of U₃O₈. The concept of nucleation and growth is used commonly to explain the mechanism from UO₂ to U₃O₈. It is agreeable to accept a sigmoidal curve to describe the formation of U₃O₈ [1].

Johnson-Mehl-Avrami model has been applied to express the sigmoidal curve of the reaction mechanism, nucleation and growth, mathematically [1,2,4]. However, Johnson-Mehl-Avrami model could not explain the effect of incubation time and cracking of uranium oxide [2].

A surface-to-volume model is suggested to consider the effect of incubation time and cracking.

2.1 Johnson-Mehl-Avrami model

$$\alpha = 1 - \exp(-K t^n) \quad (1)$$

The following expression is the Johnson-Mehl-Avrami equation. In the Eq. (1), K and n are determined empirically. α is a fraction from UO₂ to U₃O₈ and t is time [4].

Table 1: The values of K and n at 573, 623,673 and 723 K

	K	n
573 K	2.665E-8	1.7015
623 K	6.387E-7	1.7248
673 K	2.823E-6	1.7302
723 K	9.629E-5	1.3337

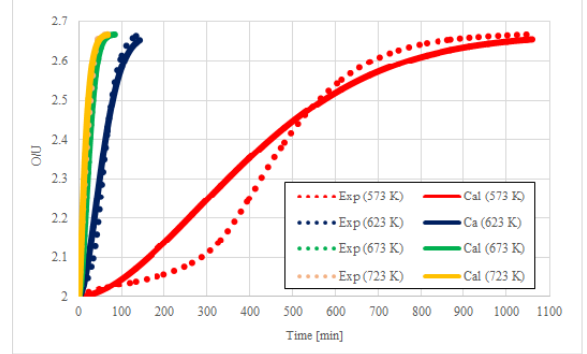


Fig. 1. Comparison of experimental data and calculation data by Eq. (1).

Maximum errors of 573, 623, 673 and 723 K are 6.53, 4.18, 0.49 and 2.83%. However, the model takes into account only the nucleation and growth without the effect of incubation time and cracking [2].

2.2 Phenomenological model

$$\dot{x} = \left(\frac{K_{phen} \cdot S(t)}{\rho_u \cdot V(t)} \right) \cdot (x_{eq} - x) \quad (2)$$

Eq. (2) is a phenomenological model. The dot is the time derivative of O/U. K_{phen} and ρ_u are a rate constant and molar density of uranium in UO₂ respectively. $S(t)/V(t)$ is the surface-to-volume ratio. x_{eq} is the equilibrium stoichiometry of U₃O₈ [3].

In the phenomenological model, the surface-to-volume ratio is constant. However, the surface-to-volume model proposes the change of the surface-to-volume ratio due to the incubation time and cracking [3].

2.3 A surface-to-volume model

$$\dot{x} = f(t) \cdot (x_{eq} - x) \quad (3)$$

where $f(t)$ is $(K_{phen} \cdot S(t)) / (\rho_u \cdot V(t))$

$$x(t, T) = x_{eq} + (x_0 - x_{eq}) e^{-\int f(t) dt} \quad (4)$$

x_0 is the initial stoichiometry of UO₂.

A surface-to-volume model, Eq. (3), is suggested using Eq. (2). The surface-to-volume ratio is used to derive the surface-to-volume model.

Some assumptions are given to derive the surface-to-volume model.

- Volume and surface increased exponentially.
- Volume and surface are time-dependent.
- Surface is affected by an increased volume.
- Incubation time and cracking affect the surface and volume constantly.

$$\frac{dV(t)}{dt} = \alpha \cdot (V(t) - a) \quad (5)$$

$$V(t) = (V_0 - a) \cdot e^{\alpha t} + a \quad (6)$$

Eq. (6) is given by integration of Eq. (5).

$$\frac{dS(t)}{dt} = \beta \cdot (V(t) - a) \quad (7)$$

$$S(t) = \frac{\beta}{\alpha} (V_0 - a) \cdot (e^{\alpha t} - 1) + S_0 \quad (8)$$

Eq. (8) is given by integration of Eq. (7). α and β are a volume growth rate and surface growth rate respectively [5]. a is a corrected value to explain the incubation time and cracking. V_0 and S_0 are an initial volume and surface.

$$f(t) = \left(\frac{K_{phen}}{\rho_u} \right) \left(\frac{\frac{\beta}{\alpha} (V_0 - a) \cdot (e^{\alpha t} - 1) + S_0}{(V_0 - a) \cdot e^{\alpha t} + a} \right) \quad (9)$$

$$f(t) = \left(\frac{K_{phen} \beta}{\rho_u \alpha} \right) \left(1 - \frac{\frac{1}{\alpha} (V_0 - \frac{\alpha}{\beta} S_0)}{1 + \left(\frac{V_0 - a}{a} \right) \cdot e^{\alpha t}} \right) \quad (10)$$

Eq. (10) is got by arrangement of Eq. (9).

$$A_1 = \left(\frac{K_{phen} \beta}{\rho_u \alpha} \right) \quad (11)$$

$$A_2 = \left(\frac{V_0 - a}{a} \right) \quad (12)$$

$$A_3 = \frac{1}{\alpha} \left(V_0 - \frac{\alpha}{\beta} S_0 \right) \quad (13)$$

$$f(t) = A_1 \left(1 - \frac{A_3}{1 + A_2 \cdot e^{\alpha t}} \right) \quad (14)$$

In order to organize Eq. (10) simply, unknown values are substituted with the constants like A_1, A_2 and A_3 . Eq. (14) is putted at Eq. (4) to derive the surface-to-volume model. In the Eq. (14), A_1, A_2, A_3 and α are determined empirically.

$$x(t, T) = \frac{8}{3} - \frac{2}{3} \left(\left(\frac{1 + A_2}{1 + A_2 e^{\alpha t}} \right) \frac{A_1 A_3}{\alpha} \cdot e^{A_1 (A_3 - 1) t} \right) \quad (15)$$

Eq. (15) is the surface-to-volume model to describe the sigmoidal curve of the reaction mechanism.

Table 2: The values of A_1, A_2, A_3 and α at 573, 623, 673 and 723 K

	A_1	A_2	A_3	α
573 K	1.95E-4	9.37E-3	1.00	1.70E-4
623 K	1.19E-3	1.98E-2	0.99	1.09E-3
673 K	2.60E-3	3.16E-2	0.99	2.59E-3
723 K	3.19E-3	5.80E-2	0.98	3.02E-3

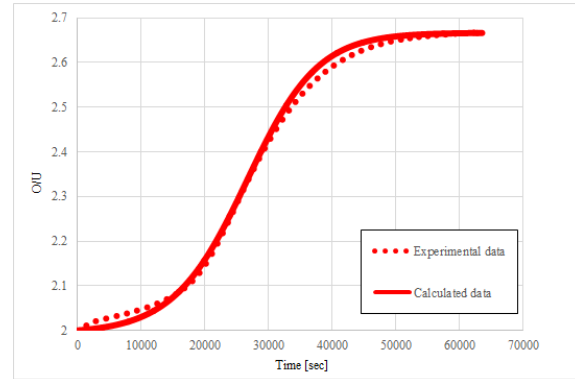


Fig. 2. Comparison of experimental data and calculation data at 573 K by Eq. (15).

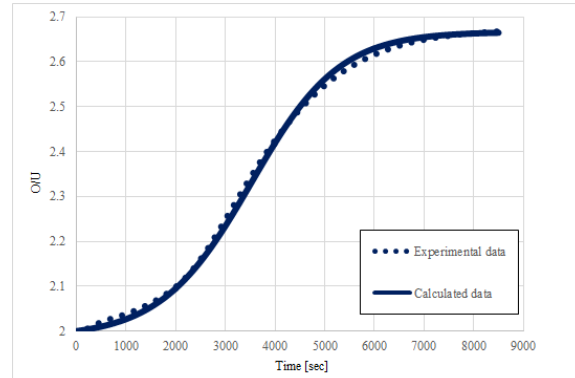


Fig. 3. Comparison of experimental data and calculation data at 623 K by Eq. (15).

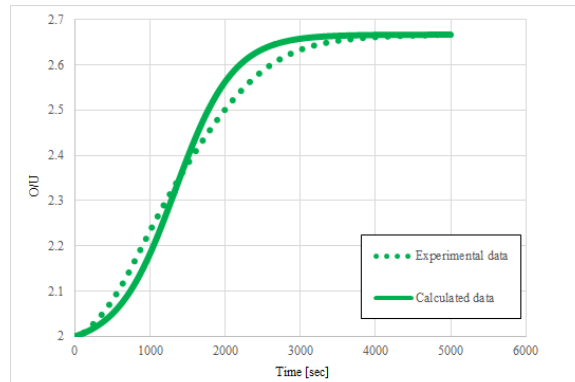


Fig. 4. Comparison of experimental data and calculation data at 673 K by Eq. (15).

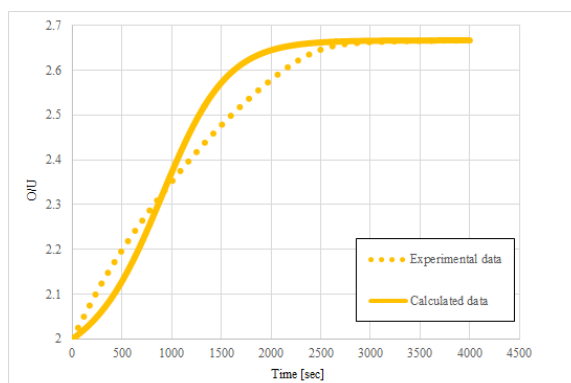


Fig. 5. Comparison of experimental data and calculation data at 723 K by Eq. (15).

Maximum errors of 573, 623, 673 and 723 K are 1.02, 0.67, 2.44 and 3.73%. The surface-to-volume model is matched well with the experimental data.

3. Conclusion

The Johnson-Mehl-Avrami model has widely been used to describe a sigmoidal curve of the reaction mechanism from UO_2 to U_3O_8 . However, the model takes into account nucleation and growth without the incubation time and cracking [1,2].

The surface-to-volume model describes the sigmoidal curve of the reaction mechanism with time-dependent surface-to-volume ratio.

The surface-to-volume model is correct as well as the Johnson-Mehl-Avrami model with the experimental data at 573, 623, 673 and 723 K.

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