

A Mechanistic Model for UO_2 Oxidation

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1. Introduction

In dry air, the oxidation of the uranium dioxide pellets can be described as a two-step process ($\text{UO}_2 \rightarrow \text{U}_4\text{O}_9/\text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8$). The principal oxidant is O_2 in air. The density of U_3O_8 is 23% less than that of UO_2 , which corresponds to a 36% net volume increase of oxidized pellets. As a result, the formation of U_3O_8 leads to fuel splitting. This volume change by oxidation effects heavily on safety management of long-time storage and disposal of spent fuel and wholesomeness of fuel.

Oxidation kinetics of spent fuel is essential to evaluate long time wholesomeness maintenance when dry storage of spent fuel be degraded.

In this study, We analyze oxidation kinetics of UO_2 and establish a mechanistic model at 300°C, 400°C, 500°C.

2. Methods and Results

Cox et al.[1] recognized that their experimental results on UO_2 oxidation could be interpreted in terms of a surface-reaction controlled process. They showed that the oxidation kinetics could be adequately described by a phenomenological rate law originally proposed by Carter and Lay for the oxidation of UO_2 in CO/CO_2 gas mixtures.[2]

The purpose of the present work is to broaden the scope of existing mechanistic interpretations to provide fuel oxidation kinetics in air.

Kang measured oxidation rate of UO_2 pellet in air [3] and these data were analyzed.

2.1 Phenomenological model

A phenomenological description of oxidation of UO_2 [1,4] can be following.

$$\left(\frac{\rho_U V}{S}\right) \dot{x} = k_{\text{phen}} (x_{\text{eq}} - x) \quad (1)$$

$$\dot{x} = k(x_{\text{eq}} - x)t^n \quad (2)$$

where the dot means to the time derivative. ρ_U is the molar density of uranium in UO_2 . And S/V is the surface-to-volume ratio of the specimen. k_{phen} is a rate constant. x_{eq} is equilibrium stoichiometry of U_3O_8 and k is $k_{\text{phen}} S/\rho_U V$.

$$x = x_{\text{eq}}(1 - e^{-kt}) \quad (3)$$

The experimental data showed in reasonable agreement with equilibrium predicted by Eq. (1). However, as shown in Figure, Eq. (1) cannot explain the overall result.

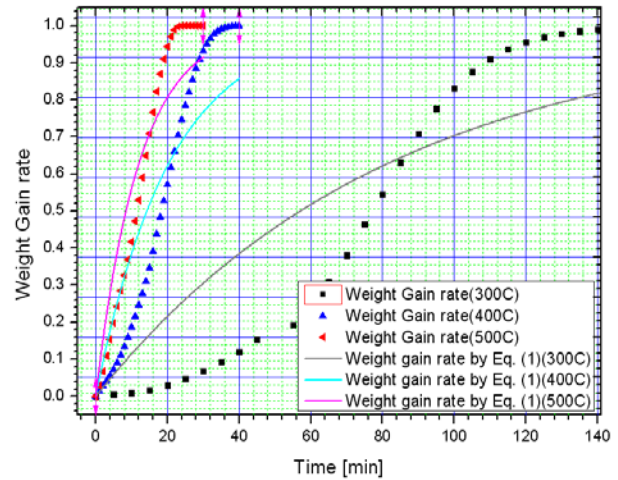


Figure 1. Comparison of experimental data and calculation data by Eq. (1)

This deficiency of the phenomenological model is the reason to develop mechanistic models.

2.2 An extended UO_2 oxidation model in air

An extended UO_2 oxidation model based on Eq. (1) was suggested.

The experimental oxidation curves of UO_2 are displayed sigmoidal reaction kinetics. In order to simulate this sigmoidal reaction kinetics, we added t^n for the right side of Eq. (1).

$$\left(\frac{\rho_U V}{S}\right) \dot{x} = k_{\text{phen}} (x_{\text{eq}} - x)t^n \quad (4)$$

$$\dot{x} = k(x_{\text{eq}} - x)t^n \quad (5)$$

where x_{eq} is 8/3.

$$x = \frac{8}{3} - \frac{2}{3} e^{-\frac{k}{n+1}t^{n+1}} \quad (6)$$

The unknown quantity, n was obtained by Eq. (7).

$$\dot{x} = (1 - x)t^n \quad (7)$$

$$x = 1 - e^{-\frac{t^{n+1}}{n+1}} \quad (8)$$

Eq. (7) is a simple transformation of Eq. (5) to find n value.

Table 1 shows the best fitting values of n. As the temperature increases, the n value decreases.

Table 1. The values of n at 300°C, 400°C, 500°C

Temperature(°C)	300	400	500
n	2.5	1.4	0.6

By using n value, k was obtained by Eq. (6). As the temperature increases, the k value increases.

Table 2 shows the values of k according to the temperature.

Table 2. The values of k at 300°C, 400°C, 500°C

Temperature(°C)	300	400	500
k	6.1E-7	3.2E-3	2.55E-2

Using calculated value n and k, we compared with value of x from Eq. (6) and experimental data. (Fig.2)

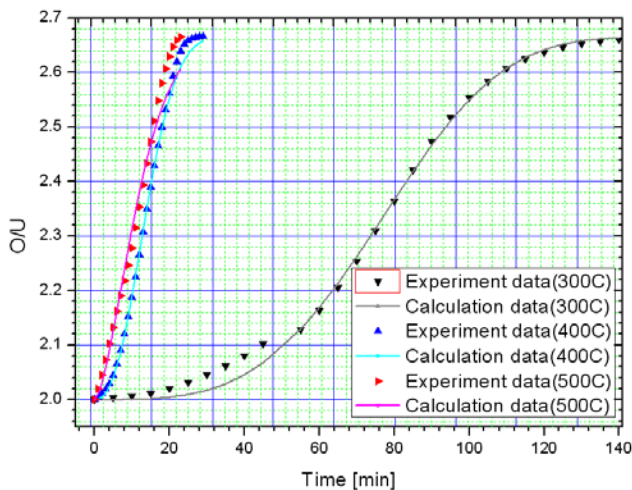


Figure 2. Comparison of experimental data and calculation data by Eq. (6)

The average error was less than 1% and the maximum error was 2.5 %.

Consequently, Eq. (6) simulates experimental data well.

3. Conclusions

The oxidation kinetics of UO_2 be analyzed and the mechanistic model established at 300°C, 400°C, 500°C.

By oxidizing from UO_2 to U_3O_8 , the oxidation curves are displayed sigmoidal reaction kinetics.

The phenomenological model does not fit the data for UO_2 oxidation experiments in air, whereas the mechanistic model in this study does.

In the mechanistic model, as the temperature increases, the n value decreases and the k value increase.

The mechanistic model in this study may be useful in oxidation kinetics analysis of UO_2 because of its simplicity.

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