Improved Analytic Crackling Core Model for the Description of UO_2 Sphere and Pellet Oxidation

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1. Introduction

The oxidation behavior of UO_2 to U_3O_8 is especially characterized by sigmoid behavior and mainly modeled by nuclear-growth model. Crackling core Model(CCM) proposed by Park and Levenspiel was found to exhibit sigmoid behavior [1] and applied to the modeling of UO_2 oxidation [2]. However, the close description of the experimental data was not achieved. In this study, for the improved description of UO_2 oxidation, we propose an analytic CCM accounting for area expansion effect and evaluate the applicability of the model toward the description of UO_2 sphere and pellet oxidation.

2. Model development

In CCM, the overall conversion is obtained from individual grain conversion by integration

$$1 - X(t) = \frac{\int_0^R [1 - X_g(r,t)] r^2 dr}{\int_0^R r^2 dr} = \frac{3}{R^3} \int_0^R [1 - X_g(r,t)] r^2 dr \quad (1)$$

where $X(t)$ is overall conversion at give t time and R denotes the initial radius of UO_2 sphere or pellet. $X_g(r,t)$ refers to the conversion of grain at position r. In this study, UO_2 particle and grain are assumed to follow Shrinking Core Model(SCM) considering reaction rate as rate limiting step. Then the radius of UO_2 particle is related to the following equation

$$-\frac{d}{dt}\left(\frac{4}{3}\pi r^3 \rho_B\right) = 4\pi r^2 k_c C_A \quad (2)$$

where ρ_B refers to the density of solid and k_c to reaction constant. C_A indicates the concentration of gaseous species A in bulk phase. The time required for complete reduction of r to zero, τ_c, is defined by

$$\tau_c = \frac{\rho_B R}{k_c C_A} \quad (3)$$

Then the radius r is related to time by

$$\frac{r}{R} = Y = 1 - \frac{t_c}{\tau_c} \quad (4)$$

where t_c denotes the age of solid particle .

In original CCM, the non-porous surface of solid particle is considered to be transformed into porous surface through crackling of surface. This assumption implies that the reactive surface area becomes increased due to the newly formed porosity. In this study, the area expansion effect is included in eq (2) as follows

$$-\frac{d}{dt}\left(\frac{4}{3}\pi r^3 \rho_B\right) = \frac{4\pi r^2 k_c C_A}{\left(1 - \beta \frac{t}{\tau_c^*}\right)^2} \quad (5)$$

where β is area expansion coefficient and τ_c^* is related to $\tau_c(1\text{-}\beta)$. Then the radius r is newly obtained.

$$Y = \frac{1 - \frac{t_c}{\tau_c^*}}{1 - \beta \frac{t_c}{\tau_c^*}} \quad (6)$$

As grain reaction follows SCM, the conversion of grain is related to t_g, grain age, and τ_g, the conversion time of grain

$$\frac{t_g(r)}{\tau_g} = 1 - \left[\frac{1 - X_g(r,t)}{1 - X_i}\right]^{1/3} \quad (7)$$

where X_i refers to the conversion of intermediate. If w is defined by $\tau_c/\tau = \tau_c/(\tau_c+\tau_g)$ and $t_g = t - t_c$, the overall conversion in three steps is determined.

Initiation step : $t/\tau_c^* < 1\text{-}w$

$$1 - X(t) = Y_c^3 + 3\int_{Y_c}^1 [1 - X_g(Y,t)] Y^2 dY \quad (8)$$

Propagation step : 1-$w < t/\tau_c^* < w$

$$1 - X(t) = Y_c^3 + 3\int_{Y_c}^{Y_a}[1 - X_g(Y,t)]Y^2 dY \qquad (9)$$

Termination step : $w < t/\tau_c^* < 1$

$$1 - X(t) = 3\int_0^{Y_a}[1 - X_g(Y,t)]Y^2 dY \qquad (10)$$

where Y_a and Y_c is defined by

$$Y_c = \frac{1 - \frac{t_c}{w\tau_c^*}}{1 - \beta\frac{t_c}{w\tau_c^*}} \qquad Y_a = \frac{\frac{1}{w}\left(1 - \frac{t_c}{\tau_c^*}\right)}{1 - \beta - \frac{\beta}{w}\left(\frac{t_c}{\tau_c^*} - 1\right)} \qquad (11)$$

The unreacted conversion in eq (8)-(10) is formulated as follows-

$$1 - X_g(Y,t) = (1 - X_i)\left(1 - \frac{1}{1-w}\left(\frac{t}{\tau} - \left(\frac{1-Y}{1-\beta Y}\right)w\right)\right)^3 \qquad (12)$$

X_i is assumed to 0.375 implying that UO_2 is oxidized to U_3O_8 through the conversion to intermediate U_4O_9. As demonstrated in Fig. 1 and 2, the proposed model showed a good agreement with experimental conversion data of UO_2 sphere and pellet. The optimized parameters were τ_c^* = 683, w = 0.5 and β = 0.92 for UO_2 sphere and τ_c^* = 383, w = 0.8 and β = 0.94 for UO_2 pellet. The high value of β indicates that area expansion was significantly proceeded in the oxidation of both sphere and pellet.

3. Conclusions

In spite of its simplicity formulation, the improved CCM accounting for area expansion effect was found to closely describe the experimental behavior of UO_2 oxidation behavior. The overall performance of the model will be evaluated by correlating more experimental data.

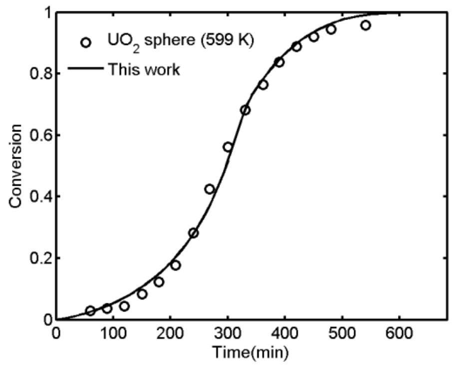

Fig. 1. Optimized conversion curves of UO_2 sphere in air atmosphere at 599 K.

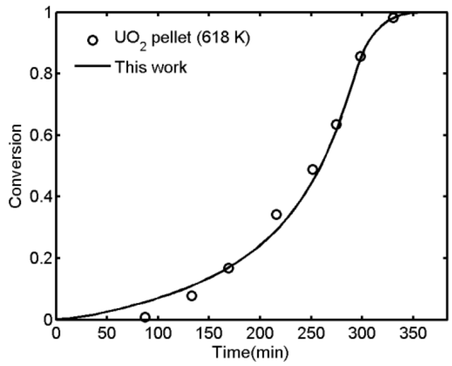

Fig. 2. Optimized conversion curves of UO_2 pellet in air atmosphere at 618 K.

ACKNOWLEDGEMENT

This work was supported by a grant (NRF-2017M2A8A5015075) from the Nuclear Research & Development Program of National Research Foundation (NRF) funded by the Ministry of Science ICT & Future Planning (MSIP), Republic of Korea.

REFERENCES

[1] J.Y. Park and O. Levenspiel, "The Crackling Core Model for the reaction of solid particles", Chem. Eng. Sci., 30, 1207-1214 (1975).

[2] J.H.Lee, S.C.Jeon, Y.H.Kim, S.J.Kang, K.Y.Lee, and G.I.Park "Modeling of Low-Temperature Voloxidation Processes based on Modified Shrinking Cylinder Model", Proc. of the KRS 2014 Spring Conference, 12(1), May 7-9, 2014, PyeongChang.