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Studies on the dissolution kinetics of ceramic uranium dioxide particles in nitric acid by microwave heating

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Abstract

The kinetics of dissolution of uranium dioxide particles in 4–8 M (M = mol/L) nitric acid by microwave heating has been studied. It is supposed that the UO_2 particles dissolve homogeneously in the form of spherical particles. The dissolution process can be dealt with the well-known shrinking core model. The results show that under the 600 W microwave field, the dissolution of UO_2 particles is controlled by the product layer diffusion at the temperature of 90–110 °C. The average activation energy for the dissolution of UO_2 particles in 4–8 M nitric acid was calculated to be 73.2 ± 1.8 kJ/mol from Arrhenius plots.

PACS: 81.05.Je; 82.30.Lp; 78.70.Gq

1. Introduction

Some studies on the dissolution of UO_2 particles or powders have been reported. Taylor and his co-workers [1] studied the dissolution of sintered UO_2 particles in HNO_3 at various temperatures by the conventional heating. For unstirred dissolution rates below 4 mg cm^{-2} min^{-1} at temperatures below 95 °C, the experimental activation energies are about 15 kcal mol^{-1} which lies in the range exhibited by catalyzed and heterogeneous chemical reactions; and at the higher dissolution rates near the boiling point, the activation energies fall to between 2 and 5 kcal mol^{-1} which may be compared with the value of 4 kcal mol^{-1} for the energy of diffusion. Ikeda et al. [2] studied the dissolution kinetics of the UO_2 powders by conventional heating and found that the dissolution rate depended on the 2.3 power of $[NO_3^-]_T$ in 4–8 M (M = mol/L) HNO_3 solutions. The dissolution rate constant ϕ in mol cm^{-2} min^{-1} was expressed as $\phi = (k_a + k_b[HNO_2])[NO_3^-]_T^{2.3}$. The activation energies for k_a and k_b are 79.5 ± 6.7 and 36.8 ± 2.9 kJ/mol, respectively.

On the other hand, the applications of microwave energy in mineral processing were widely investigated after 1970. Microwave-assisted leaching has been studied to improve the yield of extracted metal and reduce the process time. The unique microwave heating advantages such as short processing time, direct, selective and volumetric heating, and a more controllable heating process [3] are the main driver for potential implementation in metal extraction.

In order to explore a new concept of head-end process for the treatment of spent fuel from high temperature gas-cooling reactor (HTGR), the dissolution of UO_2 particles in the nitric acid solution by microwave heating is considered because the microwave energy can give a selective and rapid volumetric heating. In this paper, the dissolution of the UO_2 particles in nitric acid media by the microwave heating has been studied fundamentally.

2. Experimental

2.1. Materials

The ceramic UO_2 (depleted uranium) particles (450–550 μm) were made as the simulation kernel of the TRISO

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Table 1
The character of the UO_2 particles

Molecular formula	Diameter (μm)	Density (g/cm^{-3})	O/U ratio
UO_2 Method	450–550 Photo-electronic length measuring	⩾10.4 Pycnometric density	1.99–2.01 Thermogravimetry (TG)

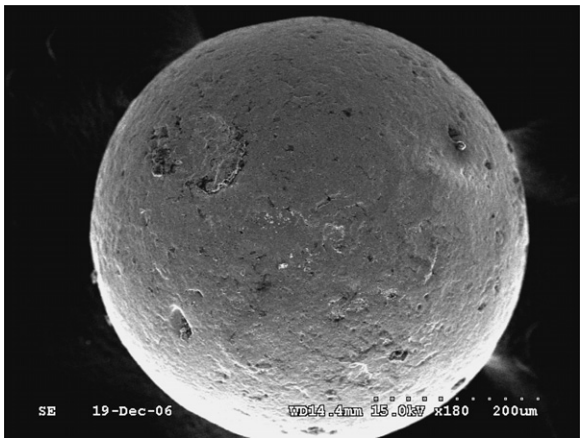

Fig. 1. Photos of the UO_2 particles.

coated fuel particles for fuel elements of the 10 MW high temperature gas-cooled reactor (HTR-10) in China. The characteristics of the particles are shown in Table 1. The diameter was determined by photo-electronic length measuring method [4]. Fig. 1 shows the photos of the UO_2 particles scanning by SEM. These UO_2 particles were made from the UO_2 $(NO_3)_2$ solutions by the method called total-gelation process (TGU) [5], which includes the following steps: preparation, gelation, drying, deoxidizing, and sintered with hydrogen at 1500 °C. The products are called 'ceramic' UO_2 particles compared with the conventional UO_2 particles.

2.2. Apparatus

A MARS 5 (microwave assisted reactor system) with the Teflon vessels was used to study the dissolution of UO_2 particles under a 600 W, 2.45 GHz microwave field [6]. The temperature of solution in the vessel was automatically controlled by regulating the microwave power output according to a temperature feedback signal.

The concentrations of UO_2^{2+} in the dissolution solution [7] were determined by the absorbance at 652 nm using spectrophotometer, with arsenazo III as the color-producing reagent [8].

2.3. Dissolution experiments

Firstly, 20 ml HNO_3 solution with an appropriate concentration was put in the Teflon vessel. UO_2 particles (~0.0500 g) were weighed out accurately and charged into the Teflon vessel. Teflon vessel is transparent to microwaves so that the HNO_3 solutions can absorb the maximum amount of microwave energy.

The solution could be rapidly heated to a designated temperature in MARS 5 system. The temperature of the solution is detected by the fiber thermometer which does not absorb the microwave energy and with the accuracy of ±1 °C. The UO_2 was dissolved in the solution under the microwave field for a certain time, and then the solution was filtrated by the filter paper to separate the raffinate particles. The filtrated solution was analyzed by the spectrophotometer to determine the concentration of the uranium (VI).

3. Shrinking core model

The dissolution of UO_2 particles in the acidic media is a heterogeneous reaction, so the dissolution reaction kinetic model of UO_2 particles in HNO_3 can be associated with the well-known shrinking core models, which can be classified into the diffusion control through liquid film, the surface reaction control and the diffusion control through product layers [6,9]. In the case of spherical particles, these models can be expressed as follows:

$$x = k_F t \quad \text{for film diffusion control,} \tag{1}$$

$$1-(1-x)^{1/3} = k_S t \quad \text{for surface reaction control,} \tag{2}$$

$$1+2(1-x)-3(1-x)^{2/3} = k_D t \quad \text{for product layer diffusion,} \tag{3}$$

where x is the reacted fraction at time t and k_F, k_S, k_D are apparent rate constants given in the following equations:

$$k_F = \frac{3bkC_{HNO_3}}{\rho}, \tag{4}$$

$$k_S = \frac{bkM(C_{HNO_3})^n}{\rho \cdot r_0}, \tag{5}$$

$$k_D = \frac{2bD_eMC_{HNO_3}}{\rho \cdot r_0^2}, \tag{6}$$

where b, stoichiometric coefficient; M, the molecular weight of reacted substance; ρ, the density of reacted particle; r_0, the initial particle radius; k, the intrinsic rate constant; D_e, effective diffusivity; C_{HNO_3}, the bulk concentration of HNO_3; n, the reaction order in the term of HNO_3 concentration. Although these models are derived from the assumption that the particles are spherical, they are applicable for various-shaped particles [9].

4. Results and discussion

The experimental program was setup to study the dissolution kinetics of UO_2 particles in nitric acid at different temperatures. The results were analyzed with different kinetic models to explore the reaction mechanism.

4.1. Dissolution ratios at various temperatures in 4–8 M HNO_3

The experiments were carried out in 4–8 M HNO_3 solution under a 600 W microwave field. The reaction temperatures were selected from 90 °C to 110 °C. The effect of temperature on the dissolution ratio of UO_2 particles are illustrated in Figs. 2–5. The experimental results show that the dissolution ratios increased quickly with the increase in temperatures. It was only 50% of the UO_2 particles dissolved in 4 M HNO_3 at 90 °C. However, when the temperature was increased to 110 °C, the dissolution ratio increased to 79%.

4.2. Effect of the HNO_3 concentration

The plots of the dissolution ratio *vs* time at different concentrations of HNO_3 are given in Figs. 6–9. It was found that the dissolution ratio increased with the reaction time and HNO_3 concentrations. At 100 °C within 40 min, only 59% of the UO_2 particles dissolved when the concentration of HNO_3 was 4 M; the value increased remarkably to 92% when the concentration of HNO_3 rose to 8 M.

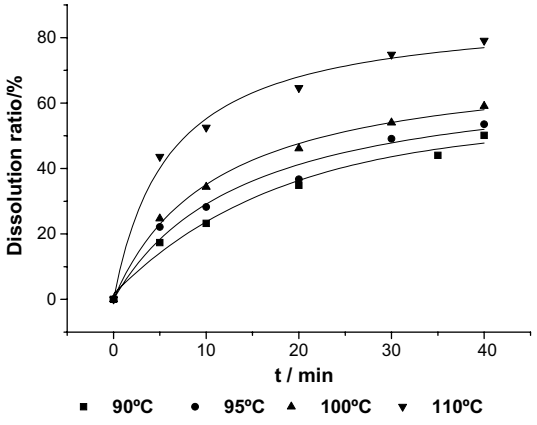

Fig. 2. Effect of temperatures on dissolution ratios in 4 M HNO_3.

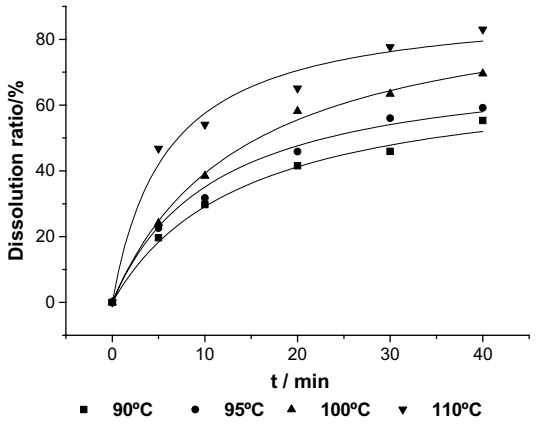

Fig. 3. Effect of temperatures on dissolution ratios in 5 M HNO_3.

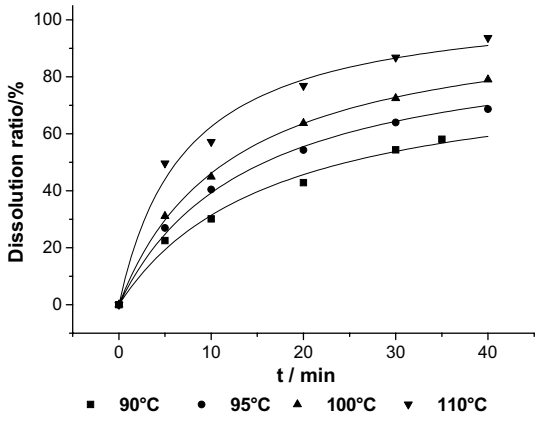

Fig. 4. Effect of temperature on dissolution ratios in 6 M HNO_3.

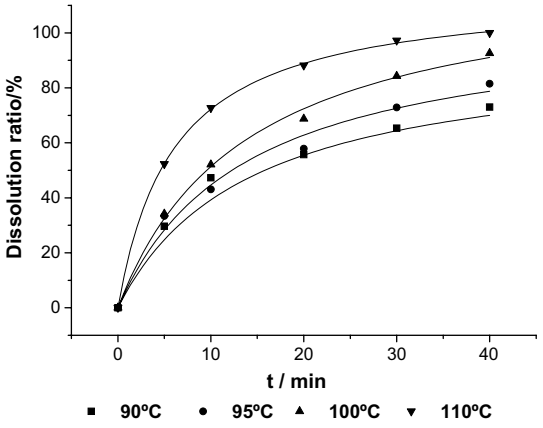

Fig. 5. Effect of temperature on dissolution ratios in 8 M HNO_3.

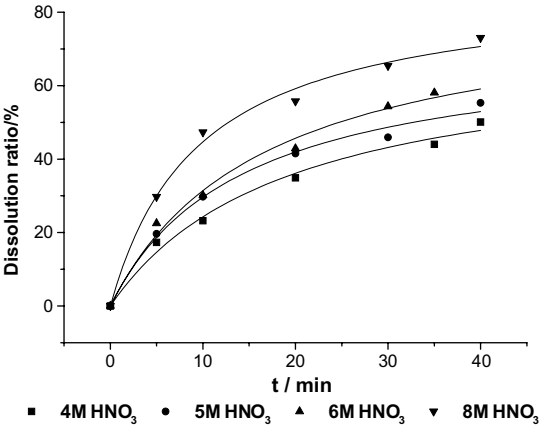

Fig. 6. Effect of HNO_3 concentrations on the dissolution at 90 °C.

4.3. Modeling of the dissolution kinetics

In the experiments, the dissolution process was under strong stirring, so the film diffusion was eliminated. The data in Figs. 2–5 were analyzed by the above shrinking core models (surface reaction control and product layer diffusion control); the results are given in Figs. 10–13 and

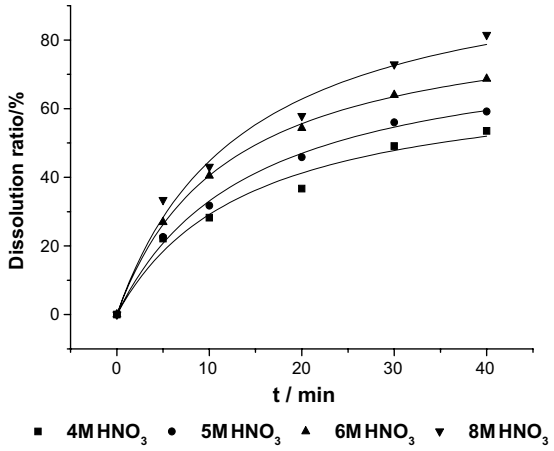

Fig. 7. Effect of HNO_3 concentrations on the dissolution at 95 °C.

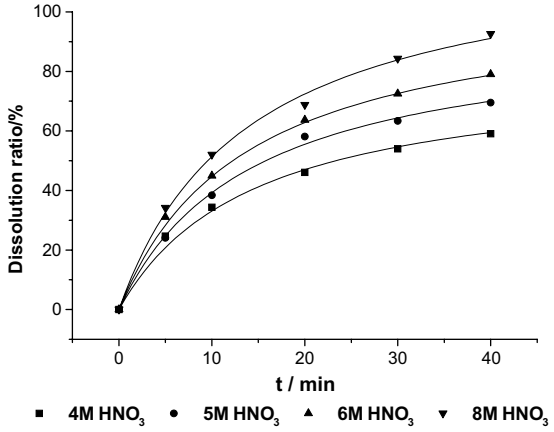

Fig. 8. Effect of HNO_3 concentrations on the dissolution at 100 °C.

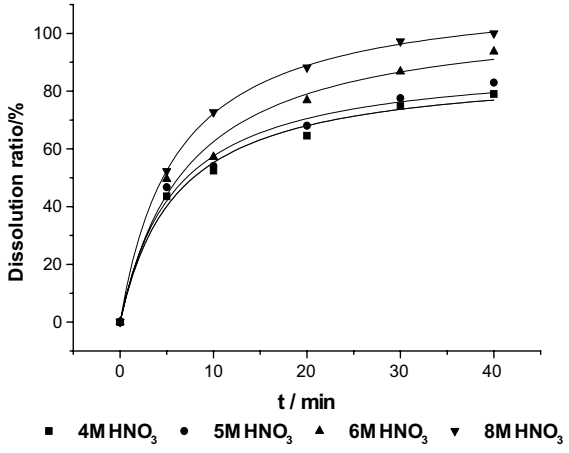

Fig. 9. Effect of HNO_3 concentrations on the dissolution at 110 °C.

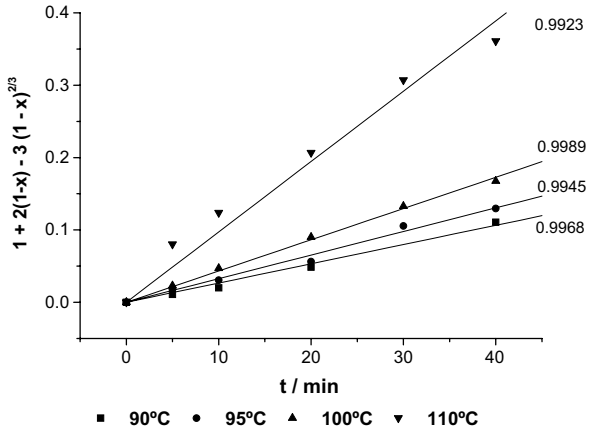

Fig. 10. Plot of $1 + 2(1 - x) - 3(1 - x)^{2/3}$ *vs* reaction temperatures in 4 M HNO_3.

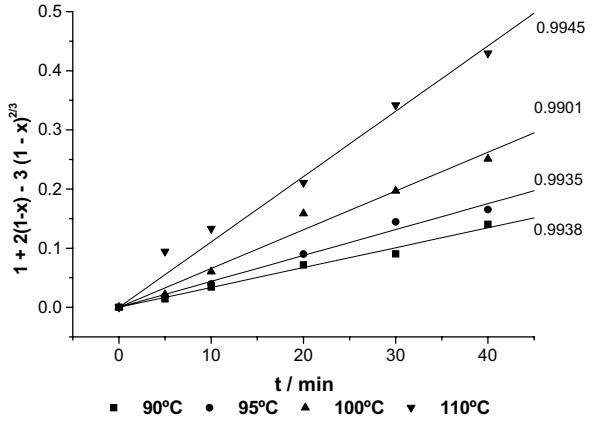

Fig. 11. Plot of $1 + 2(1 - x) - 3(1 - x)^{2/3}$ *vs* reaction temperatures in 5 M HNO_3.

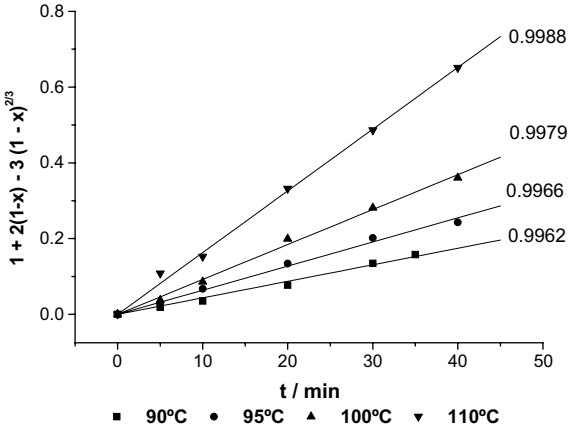

Fig. 12. Plot of $1 + 2(1 - x) - 3(1 - x)^{2/3}$ *vs* reaction temperatures in 6 M HNO_3.

Fig. 14 is an example of surface reaction control model for 8 M HNO_3. From Figs. 13 and 14, it can be seen that the results fit very well with the product layer diffusion control model other than surface reaction control model because the correlation coefficients are above 0.99. The comparisons of the others are the same as Figs. 13 and 14, not illustrated here. The good linear relationships shown in Figs. 10–13 demonstrate that the application of Eq. (3) in the dissolution process is reliable. Within the reaction temper-

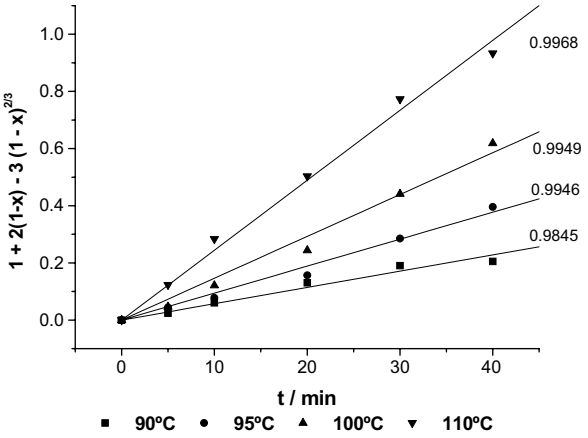

Fig. 13. Plot of $1 + 2(1 - x) - 3(1 - x)^{2/3}$ *vs* reaction temperatures in 8 M HNO_3.

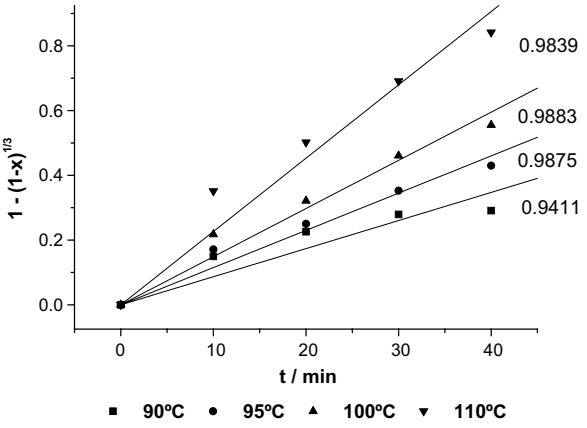

Fig. 14. Plot of $1 - (1 - x)^{1/3}$ *vs* reaction temperatures in 8 M HNO_3.

atures, the dissolution of UO_2 particles are controlled by the product layer diffusion under the 600 W microwave field in 4–8 M HNO_3 solutions.

According to Eq. (6), assuming that $k_D = f(T, r_0, C_{HNO_3})$, whereas r_0 is initial particle radius in the experiment (450–550 μm), k_D can be expressed as follows:

$$k_D = k_0 \, e^{-\frac{E_a}{R \cdot T}} \cdot C^{\alpha}_{HNO_3}, \tag{7}$$

$$\mathrm{Ln}(k_D) = \mathrm{Ln}(k_0) - \frac{E_a}{RT} + \alpha \mathrm{Ln}(C_{HNO_3}), \tag{8}$$

where k_0 and α are the constants to be determined.

The activation energy was calculated by the Arrhenius equation. The Arrhenius plots can be obtained from the values of reaction rate constant k_D, which can be obtained from the slopes of the plots at different temperatures and are shown in Fig. 15. The average activation energy for the dissolution of UO_2 particles is 73.2 ± 1.8 kJ/mol.

The plots of $\mathrm{Ln}(k_D)$ *vs* $\mathrm{Ln}(C_{HNO_3})$ are shown in Fig. 16. The slopes of these curves give the average α value of 1.58 ± 0.05.

By using the stepwise linear regression method, the values of E_a, k_0 and α can be obtained, respectively. The multiple correlation coefficient is 0.998. Hence, the reaction rate constant can be expressed as

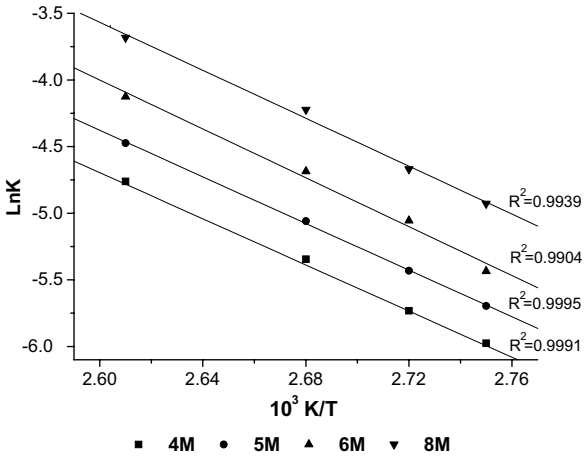

Fig. 15. Kinetic constants as a function of $1/T$ in various HNO_3 concentrations.

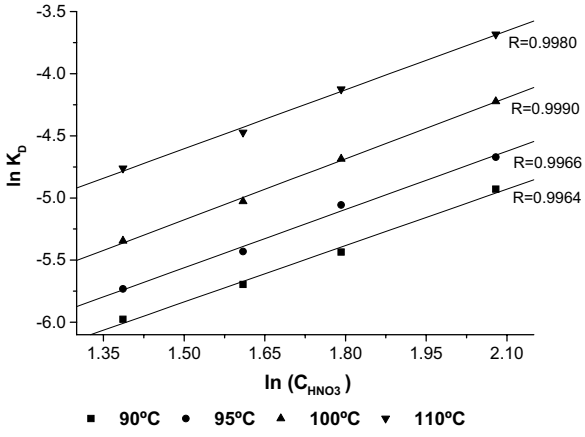

Fig. 16. The plots of $\mathrm{Ln}(K_D)$ *vs* $\mathrm{Ln}(C_{HNO_3})$.

$$k_D = 9.10 \times 10^6 e^{-\frac{73200}{R \cdot T}} \cdot C^{1.58}_{HNO_3}. \tag{9}$$

Thus, according to Eq. (3), the dissolution of the ceramic UO_2 particles under the present experimental conditions can be expressed as

$$1 + 2(1 - x) - 3(1 - x)^{2/3} = 9.10 \times 10^6 e^{-\frac{73200}{R \cdot T}} \cdot C^{1.58}_{HNO_3} \cdot t. \tag{10}$$

4.4. Discussion

It can be seen from Eq. (10) that the dissolution ratios of the UO_2 particles are dependent on the temperature and the HNO_3 concentrations ($\alpha = 1.58$). This fit very well with the fact that the dissolution ratios increased quickly with the increase in the reaction temperature and HNO_3 concentration.

In comparison with the dissolution kinetics reported by Taylor et al. [1], the diffusion control covers wider

conditions by microwave heating. Taylor reported that the dissolution rate was controlled by the diffusion of reacting species when the temperature was lower than the boiling point (above 95 °C) and the concentration of the HNO_3 was more than 6 M. However, under the microwave field, the dissolution rate was controlled by the diffusion model at 90–110 °C with HNO_3 concentrations of 4–8 M. The activation energy by the microwave heating is about 73 kJ/mol, which is higher than what have been reported by Taylor. The reason may be that the different model used for analyzing the dissolution data, and the dissolution process was under strong stir in this paper, however, the solution was not stirred in the experiment reported by Taylor.

The difference of the dissolution rate between conventional heating and microwave heating probably results from the different experimental conditions. For conventional heating, the energy must be conducted through the walls of the vessel containing the solution. However, the microwave heating is different with the conventional heating. It can directly heat the uranium dioxide and the nitric acid solution [3], allowing the temperature to rise much faster. The nitric acid and the uranium dioxide are both polar molecules with high value of the dielectric loss factor and can absorb microwaves significantly [10,11]. The mixture of the reaction species are heated rapidly and the reaction rate is improved remarkably.

5. Conclusions

The dissolution rate of UO_2 particles is highly dependent on the temperature and the HNO_3 concentrations. The dissolution rate increased with the reaction temperature and the HNO_3 concentrations. The studies on the dissolution kinetics show that the diffusion-controlled process can occur at lower temperature and HNO_3 concentration by microwave heating compared to conventional heating.

The dissolution of UO_2 in the HNO_3 solution under the microwave field of the experimental condition is controlled by the product layer diffusion control. The model constants can be determined by the linear regression of the reaction rate constant, and the dissolution kinetics of UO_2 particles at 90–110 °C can be expressed as Eq. (10).

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