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Low-temperature sintering mechanism on uranium dioxide

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Abstract Based on a point defect model, the mechanism of low-temperature sintering of uranium dioxide was studied in this paper. The diffusion coefficient of uranium in UO_{2+x}, sintering temperature and densification equation in low-temperature sintering were analyzed by both the point defect model and low-temperature sintering experiments. The results showed that the diffusion activation energy of uranium in over-stoichiometric UO_{2+x} was lowered by 3.0 ev than that in stoichiometric UO_2. And the diffusion coefficient of uranium in UO_{2+x} was proportional to x^2. In addition, the theoretical low temperature sintering temperature was calculated to be in the range of 1089–1151 °C, which indicated that it was necessary to maintain proper over-stoichiometric oxygen for low-temperature sintering process. Moreover, the calculation results by the point defect model matched perfectly with the experiment results, PDM might be a good model to describe the relationships between defects concentration and atmosphere composition.

Introduction

Recently, high-temperature sintering kinetics of UO_{2+x} [1, 2], diffusion coefficient of oxygen and uranium and diffusion equation [3, 4] have been widely studied. Belle [5] considered that the model of sintering UO_2 consisted of three parts: shrinkage of volume, spheroidization of void, growth of crystal. Since then many researchers have investigated low-temperature sintering of UO_2 pellets [6–8], however the low-temperature sintering mechanism was rarely reported. In this study, we investigated the low-temperature mechanism, feasibility and influencing factors of UO_2 pellets. We established a relationship between diffusion coefficient, pyknosis speed and partial pressure of oxygen (Po_2 or x). Based on this relationship, we could optimize some technological parameters for lower-temperature sintering of UO_2 pellets.

Volume diffusion coefficients of uranium ions in PDM

When sintering, uranium ions diffused by vacancy in UO_2. The diffusion behavior was described by the following equation:

$$D_U = D_V[V_U''''] \qquad (2.1)$$

where D_V was the diffusion coefficient of uranium vacancy, and D_U was the diffusion coefficient of uranium.

To simplify the discussion, we made the following assumptions: ① uranium vacancies diffused accurately by a three-dimensional random walk process in UO_2 crystals, and the transition direction was random, ② only volume diffusion was considered; surface diffusion and interface diffusion were neglected, ③ the uranium vacancies transmitted in UO_2 by exchanging positions with the nearest uranium ion only, ④ the lattice parameters of UO_2 crystals were considered to be constant when interstitial oxygen anions were dissolved in the crystals.

We assumed a component gradient existed along the *z*-axis in one-dimensional random walk process, and

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vacancies moved a distance of λ at each jump. The adjacent lattice surfaces were apart in a distance of λ, and the numbers of solute vacancies passing through two adjacent surfaces in unit area were n_1 and n_2, respectively. We also assumed the transition frequency, v, was the average value of each vacancy jumping out from the plane surfaces per second. Therefore, the vacancy flux of moving from plane 1 to plane 2 in unit time was:

$$J = \frac{n_1 - n_2}{2} v \tag{2.2}$$

And the component gradient in unit distance was:

$$\frac{n_1 - n_2}{\lambda^2} = -\frac{\partial c}{\partial z} \tag{2.3}$$

From (2.2) and (2.3), we obtained

$$J = -\frac{1}{2}\lambda^2 v \frac{\partial c}{\partial z} \tag{2.4}$$

From the first diffusion law, $J = -D\frac{\partial c}{\partial z}$ (2.5), we got the diffusion coefficient of one-dimensional random walk process

$$D = \frac{1}{2}\lambda^2 v \tag{2.5}$$

So the diffusion coefficient of three-dimensional random walk process was 1/3 of the D in (2.5) as we have assumed above. Note that the sub lattice structure of uranium ion is face-centered cubic, and we also know that the geometry parameter, f, was 0.781 [9]. Based on the above analyses, the following equation was derived to describe the diffusion coefficients of three-dimensional random walk process:

$$D_V = \frac{1}{6} f \lambda^2 v = 0.1302\lambda^2 v \tag{2.6}$$

We assumed that the jump frequency of uranium vacancy was v_0 and the energy barrier of transition was ΔG_m, then the diffusion coefficient of uranium ion was

$$D_U = 1.5624\lambda^2 v_0 \exp\left(-\frac{\Delta G_m}{kT}\right)[V_U'''''] \tag{2.7}$$

In combination with the results in literature [10], we got the equations underneath.

When the value of Po_2 or x was very small,

$$D_{Ux} \approx D_{U0} = 1.5624\lambda^2 v_0 \exp\left(-\frac{\Delta G_m + \Delta G_S - \Delta G_{Fo}}{kT}\right) \tag{2.8}$$

However, when the value of Po_2 or x was quite large or very large

$$D_{Ux} = 1.5624\lambda^2 v_0 \exp\left(-\frac{\Delta G_m + \Delta G_S - 2\Delta G_{Fo}}{kT}\right) x^2 \tag{2.9}$$

where D_{U0} was the diffusion coefficient of uranium ion in stoichiometry UO_2, D_{Ux} was the diffusion coefficient of uranium ion in over-stoichiometry UO_{2+x}. From (2.8) to (2.9), we know that the volume diffusion coefficient of uranium ion was related to temperature only when Po_2 or x was very small indicating the diffusion process of uranium ion was an intrinsic diffusion. At a certain temperature, the volume diffusion coefficient of uranium ion increased with the increment of Po_2 or x, then the diffusion process of uranium ion became an extrinsic diffusion. These findings were consistent with previous experimental results.

Note that D_0 and Q (activation energy of diffusion) can be expressed with the following equations.

When Po_2 or x was very small,

$$D_{00} = 1.5624\lambda^2 v_0 \tag{2.10}$$

$$Q_0 = \Delta G_m + \Delta G_S - \Delta G_{Fo} \tag{2.11}$$

When Po_2 or x was quite large,

$$D_{0x} = 1.5624\lambda^2 v_0 x^2 \tag{2.12}$$

$$Q_x = \Delta G_m + \Delta G_S - 2\Delta G_{Fo} \tag{2.13}$$

In the equations, Q_0 was the activation energy of diffusion in stoichiometry UO_2, and Q_X was the activation energy of diffusion in over-stoichiometry UO_{2+x}.

From (2.10) to (2.13) we found it was feasible to sinter uranium dioxide in low-temperature if the UO_{2+x} pellets were used. And there was a relationship between the diffusion activation energies of uranium ion:

$$Q_x - Q_0 = -\Delta G_{Fo} \tag{2.15}$$

From (2.14) we found that the diffusion activation energy of one uranium ion in UO_{2+x}, Q_x was lower than that in UO_2, Q_0. The difference in Gibbs free energy G_{Fo} was 3.0 ev. These findings were in good agreement with those reported by Matzke [11] if the diffusion activation entropy was ignored. When temperature was constant, the diffusion activation energy, Q, can be expressed as

$$Q = \Delta H - T\Delta S \approx \Delta H \tag{2.15}$$

The diffusion activation entropy of uranium ion in UO_{2+x}, ΔH_{Ux} was about 1.8–3.0 ev according to the

Table 1 Values of at 1500 °C

x	0.0045	0.033	0.08	0.1
D_{Ux} (other reports)	4.45×10^{-14} (Lindner)	8.15×10^{-14} (Hawkins)	5.33×10^{-13} (Matzke)	7.04×10^{-13} (Matzke)
D_{Ux} (this paper)	3.77×10^{-18}	2.03×10^{-16}	1.19×10^{-15}	1.86×10^{-15}
D^{b}_{Ux} (this paper)	1.15×10^{-15}	6.19×10^{-14}	3.64×10^{-13}	5.68×10^{-13}
D^{s}_{Ux} (this paper)	3.03×10^{-14}	1.63×10^{-12}	9.56×10^{-12}	1.49×10^{-11}

experimental results in literature [3–7]. Therefore, the diffusion activation energies of uranium ion were obtained as follows: $Q_x \approx 2.5$ ev and $Q_0 \approx 5.5$ ev. So, when Po_2 or x was quite large, the diffusion coefficient of uranium ion was

$$D_{Ux} = 1.5624\lambda^2 v_0 x^2 \exp\left(-\frac{2.5}{kT}\right) \quad (2.16)$$

Because the lattice constant of UO_2 was 5.474×10^{-10} m [12], and unidirectional transition frequency (v_0) was about 10^{-13}/s in solid. We obtained

$$D_{Ux} = 2.341 \times 10^{-6} x^2 \exp\left(-\frac{2.5}{kT}\right) \quad (2.17)$$

When the temperature was 1500 °C,

$$\lg D_{Ux} = -12.73 + 2\lg x \quad (2.18)$$

The above equation was almost the same with the experimental finding by Matzke [11] and Marin and Contamin [13]. Table 1 shows a comparison of D_{Ux} between the calculation and literatures. The results indicated that we could reduce the sintering temperature of uranium dioxide pellets by adding U_3O_8 powder that changed UO_2 to UO_{2+x}.

The temperature of low-temperature sintering uranium dioxide

Let T′ and T″ represent the sintering temperature of high-temperature sintering process and low-temperature sintering process, respectively. When $D_{U0} = D_{Ux}$, we had the following relationships between T″ and x or Po_2

$$\frac{Q_0 - \Delta G_{Fo}}{T''} = 2k\ln x + \frac{Q_0}{T'} \quad (3.1)$$

$$\frac{Q_0 - \Delta G_{Fo}}{T''} = 0.03633k + \frac{1}{3}k\ln Po_2 + \frac{Q_0}{T'} \quad (3.2)$$

From (3.1) to (3.2), the theoretical sintering temperature of low-temperature sintering process was calculated to be in the range of 1089–1151 °C when x = 0.25. This was in good agreement with the experimental value.

The sintering kinetics of low-temperature sintering uranium dioxide

The uranium vacancy transferred from neck surface to adjacent spherical face in a volume diffusion process. The following equations were used to describe this process.

$$\frac{dV}{dt} = J\,Sa^3 \quad (4.1)$$

$$S = 2\pi b\rho = \frac{\pi b^3}{r} \quad (4.2)$$

$$V = \pi b^2 \rho = \frac{\pi b^4}{2r} \quad (4.3)$$

$$J = D_{Ux}\frac{\Delta C_V}{\rho} \quad (4.4)$$

where *d*t was the time parameter, *d*V was the volume parameter, J was the number of uranium vacancies that leave the neck in an unit area and unit time, S was the area of neck, and a was the radius of uranium atoms.

Considered the interfacial force of powder was σ that was constant to certain pellets. The concentration of uranium vacancies was $[V_U^{''''}]$ based on the PDM calculations. According to the literature [14], we know that the difference of concentrations between uranium vacancies that form in neck surface and grain surface was given by the equation:

Table 2 Main properties of original powder

O/U	U (%)	Specific surface (m^2/g)	Loose density(g/cm^3)	Tap density (g/cm^3)	Impurity content(μg/g)	Granularity (μm)	Wet (%)
2.09–2.17	87.45	4.7	1.68	2.64	95.13	6.8	0.14

$$\Delta C_V = \frac{\sigma a^3 [V_U''''] }{kT} \quad (4.5)$$

Substituting (4.5) to Sintering Neck Model then followed by transpositions, we obtained the equation of neck diffusion kinetics:

$$\left(\frac{b}{r}\right)^5 = \frac{40\sigma a^3 D_{Ux}}{r^3 kT} t \quad (4.6)$$

This equation matched well with the result reported by Kingery, Huang [15] and Johnson. From (4.6), we know the growth speed of neck increased when the value of x increased. So over-stoichiometry of oxygens in uranium dioxide was necessary to achieve low temperature sintering of UO_2 pellets.

Assumed there were powder grains with K in mass that accumulated to form a pore after sintering. Thus the sintering density was:

Fig. 1 The appearances of sintering pellets in weak-oxidizing-atmosphere-sintering

$$\rho_t = \frac{K\rho_{th}}{K + 8\left(1 - \frac{b}{r}\right)^3} \quad (4.7)$$

where ρ_{th} and t were the theoretical density and sintering time, respectively.

Table 3 Results of oxidizing-atmosphere-sintering

Time	Temperature			
	800 °C	1000 °C	1200 °C	1400 °C
1 h	O/U = 2.155 ρ_1 = 6.851 (62.50%)	O/U = 2.118 ρ_1 = 9.171 (83.68%) d_1 = 8.679 e = 11.93%	O/U = 2.054 ρ_1 = 9.727 (88.75%) d_1 = 8.497 e = 5.63%	O/U = 2.033 ρ_1 = 10.221 (93.26%) d_1 = 8.380 e = 0.30%
2 h	O/U = 2.135 ρ_2 = 7.253 (66.18%)	O/U = 2.022 ρ_2 = 9.292 (87.78%) d_2 = 8.660 e = 10.33%	O/U = 2.022 ρ_2 = 9.807 (89.48%) d_2 = 8.460 e = 3.45%	O/U = 2.048 ρ_2 = 10.251 (93.53%) d_2 = 8.369 e = 0.50%
3 h	O/U = 2.096 ρ_3 = 7.716 (70.40%) d_3 = 9.237 e = 26.25%	O/U = 2.023 ρ_3 = 9.377 (85.56%) d_3 = 8.628 e = 10.02%	O/U = 2.014 ρ_3 = 9.900 (90.33%) d_3 = 8.427 e = 2.424%	O/U = 2.047 ρ_3 = 10.299 (93.97%) d_3 = 8.359 e = 0.40%

Fig. 2 The micro-structures of sintering pellets in weak-oxidizing-atmosphere-sintering

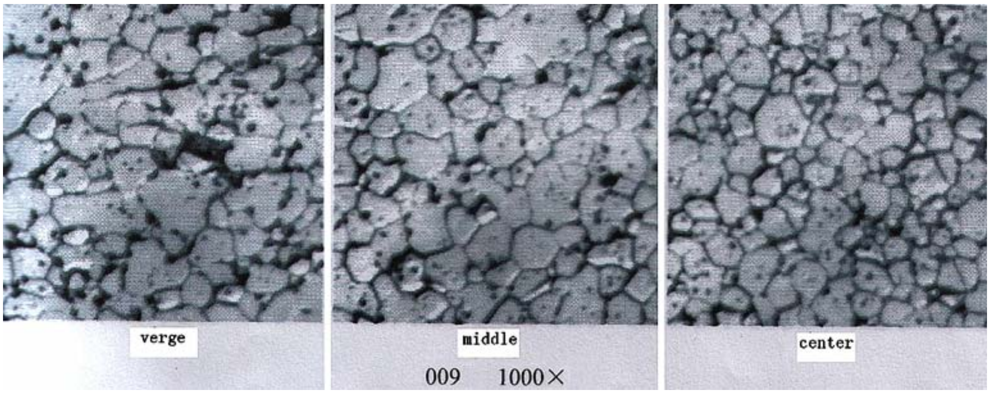

Table 4 Comparisons of theoretical linear shrinkage and testing datas

Sintering techniques		Theoretical value	Experimental value	Error value (%)
1200 °C	2–3 h	0.850	0.899	5.5
1400 °C	2–3 h	0.850	0.933	9.3

Experimental and model checking out

Materials and methods

The main properties of original powder are listed in the Table 2. The additive pellets were produced by industrial technologies. The additives include U_3O_8 (15.11 wt.%), ammonium oxalate (0.20 wt.%), and zinc stearate (0.10 wt.%). The original diameter, d_0 and original average density, ρ_0 of pellets were 14.00 mm and 5.825 g/cm [3], respectively.

The sintering experiments were carried out in a vertical molybdenum wire furnace which provided the highest temperature of 1600 ± 1 °C. High-purity N_2 (99.99%), high-purity H_2 (99.99%) and pure CO_2 (99.9%) were used. The oxidizing atmosphere was composed of N_2 + 1.5% CO_2. The samples were heated at a heating rate of less than 400 °C/h, then were held in the temperature range of 600–650 °C for 0.5 h. Subsequently they were cooled at a cooling rate of less than 400 °C/h.

The density and porosity of sintered pellets were examined by GB11927-89. O/U was measured by GB11842-89. And the grain size and diameter of pellets were measured by GB/T6394-2002 and micrometer, respectively.

Results and verification

The results of low-temperature sintering process experiments are summarized in Table 3. The appearance and microstructure of the as-produced pellets are shown in Fig. 1 and 2, respectively. From Table 3, we know that the equation [16], $x = 1.018\exp(0.017/T)Po_2^{\frac{1}{6}}$, was correct.

The calculation results of linear contraction are listed in Table 4. We can see that the difference between theoretical and experimental values was less than 10%.

Conclusions

Low-temperature sintering mechanism of uranium dioxide was for the first time studied by PDM. The essence of low-temperature sintering of uranium dioxide was activated sintering. The results showed that the diffusion activation energy for uranium in over-stoichiometric UO_{2+x} was lowered by 3.0 ev than that in stoichiometric UO_2, and $D_{Ux} \propto x^2$. Thus it was necessary to maintain proper over- stoichiometric oxygen for low-temperature sintering process.

The diffusion coefficient of uranium ion in UO_{2+x} can be expressed by the equation $D_{Ux} = 1.5624\lambda^2 v_0 x^2 \exp(-(2.5/kT))$, based on volume diffusion mechanism, the equations of growth sintering neck and densification kinetics were $(b^5/r^2) = (60\sigma a^3 D_{Ux}/kT)t$ and $\rho_t = Kd_{th}/(K + 8(1 - (b/r^3)))$, respectively.

The theoretical sintering temperature calculated by PDM was in the range of 1089–1151 °C, which perfectly matched with the experimental results.

The PDM ignored the effect of association of defects, but it could describe the relationships of defects concentration and atmosphere quite well. The findings in this study indicate that PDM could be an effective tool for investigating low-temperature sintering mechanism of uranium dioxide. We also predict that the PDM might be an effective tool for investigating low-temperature sintering mechanisms of other non-stoichiometric compounds. It might be helpful to decrease the sintering temperature when people manufacture industrial products.

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