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Mechanisms of the defect formation and diffusion of cations on the surface of uranium dioxide nanocrystals: Molecular dynamics study

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ABSTRACT

Mass transfer and cation diffusion mechanisms on the surface of UO_2 nanocrystal were investigated by the high-speed MD method using GPU. Stoichiometric uranium dioxide nanocrystals of 12,000 ions were simulated with two interaction potentials sets.

Three regions on the nanocrystal surface with significantly different activation energies were separated. It is shown that the overall mass transfer on the surface is limited by the diffusion of cations on edges connecting (100) facets. The calculated diffusion activation energy of 5.2 eV is close to the experimental one of 4.7 eV. Estimations of the thickness of the diffusion surface layer were carried out.

It is shown that the diffusion of cations in the bulk is fully associated with the migration of Schottky cation vacancies, which are formed on (100) surfaces. The calculated formation energy of a Schottky trio of 6.6 eV is close to the experimental estimation of 6.5 eV, but significantly differs from the value of 9.8 eV, derived by the standard lattice statics method.

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1. Introduction

In ionic crystals with the fluorite structure, which include uranium dioxide, the mobility of cations is extremely low up to the melting point, and the cationic sublattice shows a major influence on mass transfer processes on the surface and in the bulk of material. The detailed clarification of mechanisms of the defect formation and diffusion on the surface of uranium dioxide nanocrystals is important due to its key influence on different technological characteristics of ceramic oxide nuclear fuel (sintering, high temperature creep, melting) during fabrication and maintenance.

Because of obvious experimental difficulties there are quite a few data in the literature relating to the diffusion of cations in the uranium dioxide, both on the surface and in the bulk. Matzke in his works [1,2] gives recommendations on the diffusion of cations from the analysis of existing experimental data; at that estimations of diffusion activation energies have significant error, due to the dispersion of experimental data. Moreover, results of experimental studies of the cation diffusion on the surface are some integral values, since it is impossible to distinguish contributions of surfaces of different types. The thickness of the diffusion surface layer cannot be experimentally estimated too.

It is interesting to investigate mechanisms of the defect formation and cation diffusion on the surface of uranium dioxide nanocrystals by high-performance molecular dynamics method using the graphics processing unit. Fully controlled simulation conditions allow us to derive cation diffusion coefficients on different surfaces of the nanocrystal in its equilibrium shape of an octahedron with truncated corners (the so-called Wulff shape) and to estimate the thickness of the surface diffusion layer.

The equilibrium shape of nanocrystals is identical to the equilibrium shape of pores in uranium dioxide and its structure analogues (compare [3,4]). Therefore, all results obtained for the nanocrystal surface are valid for the surface of pores. Mechanisms of the mass transfer on the surface of pores, as well as the migration of pores in the bulk, have its own fundamental and practical interest.

2. Simulation method

2.1. MD details

In this study we used self-made program for simulations using classical molecular dynamics (MD) method, with the calculation of forces using graphics processing unit (graphics cards Ati Radeon 5870, 6970) and with pair interaction potentials in the approximation of rigid ions. MD method was described in detail in our previous work [5].

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The mobility of cations in fluorite-type systems is extremely low, even at temperatures close to the melting point. Therefore, in this work we investigated the diffusion of cations with only two sets of interaction potentials – MOX-07 and Arima-05. According to comparison results based on reproducibility of macroparameters in UO_2 by MD [6,7], the first potential is one of the best, and the second have medium quality. Moreover, for MOX-07 potential superionic transition in nanocrystals occurs (and cation diffusion we explore in the superionic state), and with Arima-05 potential, nanocrystals are melted before superionic transition. Thus, we can try to estimate the influence of the superionic state on the diffusion of cations.

For both potentials we used the MD time step equals to $3.5 \cdot 10^{-15}$ s. Simulations were carried out under isolated boundary conditions – a crystal of finite size in a vacuum. UO_2 nanocrystal was consisted of 12,000 ions, was relaxed and had an equilibrium shape of a truncated octahedron – the so-called Wulff shape. Octahedron facets have the surface type of (1 1 1) and truncated corners have the type of (1 0 0). At the equilibrium the ratio of surface areas of different types was S(1 0 0)/S(1 1 1) ≈ 0.15 for both potentials.

Diffusion coefficients (DC), according to the random walk theory, can be derived from the mean square displacement (MSD):

$$\begin{aligned} &\lim_{t\to\infty}\left[\frac{1}{N}\sum_{I}(\mathbf{r}_I(t)-\mathbf{r}_I(0))^2\right] = C\cdot D\cdot t \\ &D = \mathrm{const}\cdot[V_U^{4-}]\cdot\exp(-E_m/\mathrm{kT}) \\ &[V_U^{4-}] = C_0\cdot\exp\{-(E_{\mathrm{Sh}}-E_{\mathrm{AF}})/\mathrm{kT}\} \end{aligned} \tag{1}$$

where t is the simulation time, N the number of particles for MSD calculation, $\mathbf{r}_I$ the vector of particle "I", D is the self-diffusion coefficient, k the Boltzmann constant, T the temperature. In fluorite-type crystals the diffusion of cations occurs via vacancy mechanism with the formation of Schottky defects. The DC for the vacancy mechanism is defined as the product of the vacancy concentration $[V_U]$ on the probability of ion migration to the adjacent vacancy. E_m is the ion migration energy to the adjacent vacancy, C is the constant which is selected depending on the dimension of the diffusion (three-, two- or one-dimensional). For stoichiometric uranium dioxide, according to the Lidiard and Matzke model (see for example [8]), the formation energy of cation vacancies is equal to the formation energy E_{Sh} of Schottky defects (in the form of separated to infinity vacancies) minus the formation energy E_{AF} of anti-Frenkel (oxygen) vacancies.

2.2. Rotation of the nanocrystal

Due to the low mobility of uranium cations (rare diffusion hopes) a non-zero rotation of the nanocrystal strongly influences on the resulting DC. Correction of the nanocrystal rotation was performed at each MD step by calculating the angular velocity $\boldsymbol{\omega}$ of the nanocrystal as a whole, which is associated with the system angular momentum $\mathbf{L}$:

$$\begin{aligned} &\mathbf{v}_\mathrm{I} = \boldsymbol{\omega}\times\mathbf{r}_\mathrm{I} \\ &\mathbf{L} = \sum_{\mathrm{I=1}}^{\mathrm{N}}[\mathbf{r}_\mathrm{I}\times(\mathrm{m_I}\mathbf{v}_\mathrm{I})] \\ &\mathbf{v}_\mathrm{I}^\mathrm{c} = \mathbf{v}_\mathrm{I} - \boldsymbol{\omega}\times\mathbf{r}_\mathrm{I} \end{aligned} \tag{2}$$

where $\mathbf{v}_\mathrm{I}$, $\mathbf{r}_\mathrm{I}$ are the velocity and coordinate of the "I" particle, $\mathbf{v}_\mathrm{I}^\mathrm{c}$ the velocity of the "I" particle after the procedure of rotation correction. However, even with such correction, the nanocrystal slowly rotates in a random manner, and this slow chaotic rotation cannot be neglected in long-term simulations (about hundreds of nanoseconds). The reason of this rotation is probably the unbalanced mass transfer on the surface of the nanocrystal. This rotation is especially noticeable during relaxation of the cubic nanocrystal to its equilibrium shape of the octahedron with truncated corners, and during simulations at high temperatures.

Rotation of the crystal was estimated by the rotation of its lattice planes. As a numerical criterion an angle from dot product between the unit vector of the world coordinate system and the normal of the crystal lattice plane, derived based on averaged by 500 MD steps coordinates of cations in the inner region of the nanocrystal, was taken.

To eliminate the effect of rotation of the nanocrystal as a whole we used "local" cation coordinates, in the coordinate system with normal vectors of lattice planes as unit vectors, to calculate the MSD in (1). Lattice planes were calculated every 500 MD steps during simulation. Dependences of spatial angles of rotation from the simulation time, as well as results of MSD calculations using ordinary and "local" coordinates of cations in the inner region of the nanocrystal, are shown in Fig. 1.

Estimation of the DC from the MSD curve without rotation correction (Fig. 1 – 1) would give a reasonable value of $1.7 \cdot 10^{-9}$ cm^2/s, although the slope of the MSD curve is solely associated with the rotation of the nanocrystal.

All of the above is even more significant for the nanocrystal surface, since surface cations are far away from the center of rotation. Therefore, all further MSD and DC were derived from "local" coordinates of cations. In general, we can state that the slow chaotic rotation of the nanocrystal decreases with increasing number of particles and with decreasing the simulation temperature.

2.3. Surface cation selection

The definition of the surface as a set of surface cations, selected by the number of nearest cations, as well as the approximation of the surface by the Wulff shape, were describe in details in our previous paper [9]. In this study the surface was defined and approximated by the Wulff shape every 500 MD steps. With that not only surface (outermost) cation layer was selected, but also next-to-surface cation layers, which can also be approximated by the Wulff shape. In each cation layer we defined three groups of cations – actually all cations in the layer, cations in the center of (1 1 1) facets, and cations on (1 0 0) surface type, including adjacent edges. The latter group was selected so because of the relatively small number of cations on (1 0 0) facets, due to their relative small area. Below these groups of cations in a given layer will be denoted as "_all", "_111" and "_100"; for the third and subsequent next to surface layers groups "_100" were not defined due to the small number of cations in them. The total number of cations in the simulated nanocrystal was 4000, in the outmost surface layer there were

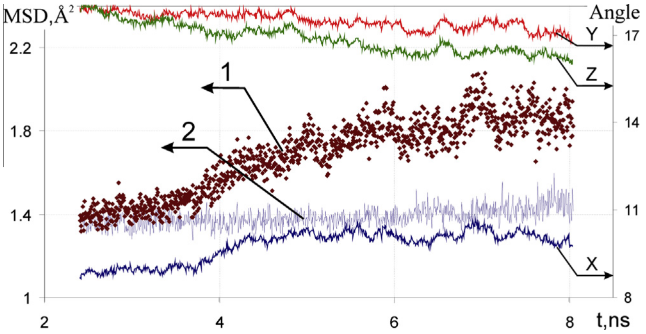

Fig. 1. (1) ordinary calculated mean square displacement of cations through initial and final coordinates, (2) MSD with rotation correction, derived with cation coordinates in the "local" coordinate system of the crystal lattice. On the right axis spatial rotation angles of the crystal lattice are shown. Simulation temperature was 3140 K.

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