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Towards the mathematical model of rim structure formation

M. Kinoshita *

Central Research Institute of Electric Power Industry, 2-11-1 Iwadokita Komaeshi, Tokyo 201, Japan

Abstract

The high burnup LWR UO_2 fuels show a notable micro-structural change around the pellet outer zone which is called the rim structure. It is observed at temperatures as low as 400°C so that fission track and cascade mixing could be the key mechanism. SEM observation revealed that the structure primarily appears on free surfaces of UO_2, indicating that strong sink for point defects may play a big role. And as generic observations, increase of lattice parameter indicates extensive amounts of vacancies are stored in high burnup fuel, which may induce the restructuring interacting with dislocations of high density at high burnup. Considering these observations a model of reaction-diffusion process of defects with irradiation induced transport is proposed. The equations are investigated numerically. The model indicates that an instability starts when the dislocation network starts intensive interaction with vacancy flux which is modified by interstitial diffusion between spatial segments. It appeared to be similar to the Turing type instability which indicates that the rim structure formation is one kind of the self-organizing processes of open reaction-diffusion systems. © 1997 Elsevier Science B.V.

1. Introduction

High burnup LWR UO_2 fuels show a notable micro-structural change around the pellet outer rim. This structure has a morphology like cauliflower. Observations by high resolution electron microscopes revealed that the sizes of newly formed grains are from 100 to 300 nm which is incomparably smaller than the original grain sizes of around 10 μm. Large gas bubbles of around 1 μm diameter are found in the neighbor of the new grains and resultantly fuel porosity is increased. The present observations indicate the final structure is formed by several stages of high burnup induced restructuring processes. The final rim structure is formed at around 7% FIMA [1–3]. In order to tailor experimental investigations systematically, development of a mathematical model, which describes the global process, is highly appreciated.

A formulation of restructuring dynamics was proposed by Rest [4]. It describes immobilization of dislocations by pairs of vacancies and fission product solute and resultant increase of local energy at nucleation sites. Also Kataoka proposed a model of defect clustering and accumulation which may result in the restructuring [5]. These analyses assume association and dissociation of tri-vacancies and fission products, which form V–FP pairs or slightly larger defect complexes. Here the vacancy is considered as the primary defect that contributes to the restructuring. The growth of pores after the restructuring indicates that extensive amounts of vacancies were transported during the process. However at low temperatures of 1000 K, the defects, such as dislocations, could not be moved by thermal activation. As those defects certainly move by reactions with vacancies, defect reactions should have a primary role in the restructuring process.

This paper proposes a mathematical description of reaction-diffusion processes of defects produced by irradiation and UO_2/fission product mixture. The system is considered as open reaction–diffusion system and the process at non-equilibrium semi-steady state is concerned. A set of equations is established and investigated numerically. The conditions to start a mathematical instability, which breaks the spatial homogeneity by a kind of the Turing mechanism [6,7], is investigated.

2. Experimental observation

There are several experimental observations that assist the model development [8–14]. Especially, present infor-

* Tel.: +81-3 3480 2111; fax: +81-3 3480 7956; e-mail: moto@criepi.denken.or.jp.

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mation related to the role of point defects and rare gas atoms in the formation process could be summarized as follows.

(1) The rim structure is observed at the pellet periphery where the temperature is as low as 400°C so that the irradiation induced activation is the key mechanism [2].

(2) SEM observation revealed that the new structure primarily appears on free surfaces of UO_2 [8]. This indicates strong sinks for point defects and the production bias, which enhances vacancy concentration, take a role for the structure formation.

(3) Fuel of smaller grain size, having a larger grain boundary area, shows more intensive development [11,14]. This also indicates strong sinks for point defects take a role for the formation.

A significant feature of the rim structure is the presence of large pores, which may contain Xe/Kr gases. There are a large number of them with diameters of around 1 μm. The restructured new grains of 100–200 nm are visible at inner surfaces of the pores [13]. The pores do not seem to be originated from the fabrication. Therefore large amounts of irradiation produced vacancies were consumed to make this structure.

In the un-restructured area at the same burnup, a large number of small bubbles with a diameter of 2–3 nm (10^{24} bubbles/m^3) and 10–12 nm (10^{23} bubbles/m^3) are observed [10,13]. The smaller bubbles contain solid precipitates and Xe/Kr gas, which occupies most of the corresponding lattice sites in the bubbles. On the other hand the larger 10 nm bubbles have more volume than the atoms of gas and precipitates, and they have the capability to reserve excess vacancies.

Annealing experiments, at the highest temperature of 1800 °C, shows lattice parameter shrinkage of around 0.18% at 60 MWd/kgu, which corresponds to 0.5% volumetric shrinkage [14]. If it is caused by elimination of accumulated vacancies, this shrinking volume may correspond to the amount of vacancies in the matrix and the estimated density is a large amount of $1.2 \times 10^{26}/m^3$. This indicates vacancies may take a role in the restructuring process.

SEM observation of the rim structure identified a new subgrain system with mottled surfaces at big pores [8]. It is a dome like structure with circular bases of 1–2 μm diameter separated by a high degree of porosity. Each dome is further divided into smaller grains of 0.1–0.2 μm diameter. This double structure of domes and grains could be a result of the principal mechanism of the restructuring process. Similar fractal type structure is produced by a mathematical bifurcation in reaction–diffusion equations so that the mathematics of such equations, especially study of complex systems, could be applicable to this problem.

3. Proposal of a model

One fission event generates the following two kinds of primary products: (1) approximately 5×10^3 free interstitials (I) and vacancies (V) of uranium atoms, (2) two atoms of fission product elements (FP), including approximately 0.3 atoms of rare gases. The developing process of the defect structures is controlled by how these are consumed. The flow of these defects is the key to understand the rim structure formation. If these 5×10^3 vacancies are fully utilized for the swelling, 2 days of irradiation provide 100% swelling at the LWR irradiation condition (3×10^{19} fission/m^3).

Another contribution of the fission event is the atomic mixing by fission track cascades. This induces resolution of fission gas and vacancies from bubbles or FP-vacancy complexes. Any place in the fuel experiences the mixing at every half of an hour in the LWR fuel condition.

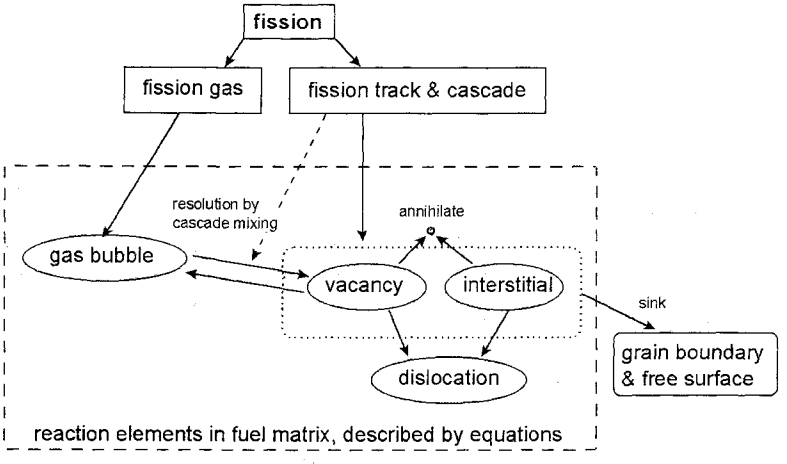

Fig. 1. Production, reaction, flow and annihilation of fission produced defects and atoms.

The processes of these defect reaction and flow are summarized in Fig. 1. Here a uranium vacancy may organize a tri-vacancy, V, which consists of one uranium site and two oxygen sites. At the operating fuel temperature, oxygen is mobile and balances of charge form the vacancy complex. The vacancies are not mobile by thermal activation at the temperature and it only diffuses by the fission cascade mixing. On the other hand, uranium interstitial, I, has much lower migration energy than the uranium vacancies and they migrate even at room temperature. If grain boundaries or free surfaces of pores are neighboring, I annihilates at these sinks. As the produced number of V and I are the same, V with slower diffusion stays in the matrix and eventually the population of V increases.

Additionally the population of vacancies in the fuel is extensively increased by trapping reactions with fission products, which form vacancy complexes. The most contributed traps are the Xe/Kr bubbles. The fission cascade mixing releases the vacancies into the matrix from bubbles and the other vacancy complexes. Therefore V in matrix and V in bubbles are in quasi-equilibrium with reactions of trapping and release.

The loops of interstitial dislocations are developed by absorbing I as irradiation proceeds. As the length of the I-loops is proportional to the square of the number of I in the loop, the growth rate is proportional to the square root of the absorbed number of I. Therefore this initial stage of I-loop growth is a comparatively modest process. However, as the accumulated dislocations start to compose networks, the dislocation becomes edge type with straight lines. Then the growth mechanism may change and absorption of one I may increase one lattice length of the network dislocation.

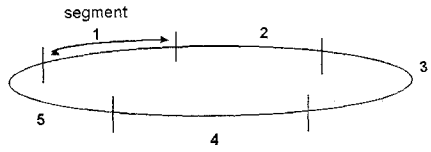

Fig. 2. Segmentation for the numerical analysis with cyclic boundary condition.

Considering the processes of Fig. 2, a set of reaction–diffusion equations is proposed as follows:

$$\frac{\partial C_v}{\partial t} = Q_v - K_{iv}C_iC_v - K_{gb}D_vC_v + K_{br}(C_{vS} - C_{vSx}) - K_{vb}C_{vS}C_v - K_{id}(\rho_d)D_vC_v - D_v\nabla^2 C_v, \quad (1)$$

$$\frac{\partial C_i}{\partial t} = Q_i - K_{iv}C_iC_v - K_{gb}D_iC_i - K_{id}(\rho_d)D_iC_i - D_i\nabla^2 C_i, \quad (2)$$

$$\frac{\partial C_{vS}}{\partial t} = Q_x + K_{vb}C_{vS}C_v - K_{br}(C_{vS} - C_{vSx}), \quad (3)$$

$$\frac{\partial \rho_d}{\partial t} = a_0K_{id}(\rho_d)D_iC_i - a_0K_{id}(\rho_d)D_vC_v. \quad (4)$$

Here, the symbols and their assumed values are listed in Table 1. Some of the reaction coefficients and source terms are described below. $K_{id}(\rho_d)$ indicates it is a function of ρ_d. The target functions of C_v, C_i are the numbers of V and I in unit volume. C_{vS} is the number of V trapped in bubbles and clusters in unit volume. It includes tri-vacancies with single rare gas atom (Xe/Kr) and larger V clusters with some gas atoms. C_{vSx} is the number of gas atoms in bubbles and clusters. ρ_d is the dislocation density

Table 1
Values of constants and coefficients used in the model

Property	Symbol	Value	Ref.
Cell size of UO_2	a_0	5.47×10^{-10} m	[a]
Volume of UO_2 lattice cell	Ω	4.1×10^{-29} m^3	[a]
Generation coeff. of I/V by fission	ξ_i, ξ_v	5×10^3	[a]
Generation coeff. of rare gas by fission	ξ_x	0.3	[a]
Pre-exponential of U-interstitial migration	D_i^0	1×10^{-8} m^2/s	[16]
Activation energy of U interstitial	E_i^0	0.2 eV	[16]
Pre-exponential of U-Vacancy migration	D_v^0	1×10^{-7} m^2/s	[16,17]
Activation energy of U vacancy	E_v^0	2.4 eV	[16,17]
Coeff. of fission enhanced diffusion	η	2×10^{19} m^5	[4]
Number of interaction sites of I/V recombination	Z_{iv}	500	[a]
Number of interaction site at grain boundary	Z_{gb}	6	[a]
Original grain radius of UO_2	r_{g1}	10^{-6}	[a]
Sink distance in grain	r_{s1}	10^{-7} m	[a]
Number of recombination sites of V and bubble	Z_{vb}	10	[a]
Radius of bubbles	R_b	10^{-9} m	[a]
Interaction volume of fission track	V_t	6×10^{-23} m^3	[15]
Number of interaction site of I and dislocation	Z_L	100	[a]

[a] Assumed values in the present calculations.

Table 2
Starting conditions of the calculation

Property	Symbol	Value	Ref.
Vacancy population in matrix	C_v	5.35×10^{24} 1/m^3	[a]
Interstitial population in matrix	C_i	2.16×10^{14} 1/m^3	[a]
Vacancies in bubbles and gas atom clusters	C_{vS}	1.02×10^{25} 1/m^3	[a]
Dislocation density	ρ_d	1×10^{15} m/m^3	[12]

[a] Assumed values in the present calculations.

that is dislocation line length in unit volume. Q_i, Q_v, Q_x are generation rates of I, V and fission product rare gas atoms,

$$Q_i = \xi_i \dot{f}, \tag{5}$$

$$Q_v = \xi_v \dot{f}, \tag{6}$$

$$Q_x = \xi_x \dot{f}. \tag{7}$$

Here, a_0 is the lattice constant of UO_2 and $\dot{f}$ is the fission rate. For the diffusion coefficients, fission induced acceleration is considered only for V diffusion of uranium:

$$D_i = D_i^0 e^{-E_i/kT}, \tag{8}$$

$$D_v = D_v^0 e^{-E_{vi}/kT} + \eta \dot{f}. \tag{9}$$

The recombination rate of V and I, i.e., K_{iv}, is

$$K_{iv} = Z_{iv} D_i \Omega / a_0^2, \tag{10}$$

where Ω is UO_2 lattice cell volume. The sink intensity of grain boundary, K_{gb}, is

$$K_{gb} = Z_{gb}/(r_{g1} r_{s1}), \tag{11}$$

which is set at the same value for both I and V. The reaction coefficients of V and bubble, K_{vb}, is

$$K_{vb} = Z_{vb} \Omega D_v / R_b^2, \tag{12}$$

$$N_{v0} = (4\pi/3) R_b^3 / \Omega, \tag{13}$$

where R_b is the bubble radius and N_{v0} is the number of vacancies in one bubble. The rate coefficient of vacancy resolution from bubbles, K_{br}, is

$$K_{br} = 2 V_t \dot{f}, \tag{14}$$

where V_t is the interaction volume of the fission track [14]. Interaction radius of fission track is evaluated as 6 nm where local temperature exceeds the melting temperature for a short time. For the resolution of vacancy from bubbles in Eq. (3), C_{vSx}, the number of fission gas atoms in bubbles, is calculated from gas inventory in fuel. An initial value is set at the starting burnup of the calculation as 0.985×10^{25} m^{-3}. It increases by generation of gas atoms during irradiation by an increment of $Q_x \Delta t$ for each time interval.

The interstitial flux to bubbles is not included in Eq. (3) as the considered nm sized bubbles have excess pressure of fission gas that may prevent absorption of interstitials. However, these bubbles are coexisting with dislocation lines, interstitials are eventually absorbed by dislocations and contribute to their growth. This effect could be described by Eq. (4). The growth of dislocation network, that is the increase of dislocation density of ρ_d, is calculated with a rate coefficient, K_{id}, which describes absorption of I into dislocations. As dislocations and networks have one-dimensional or two-dimensional reaction cross-sections with point defects, K_{id} may have complex functional dependence on ρ_d. In this model it is assumed to be linear as a first approximation:

$$K_{id} = Z_L \rho_d. \tag{15}$$

On the other hand vacancy flux into the dislocation reduces the line length and annihilates the network. Here, the same coefficient of Eq. (15) is used for this reaction in the present model.

4. Calculation results

The numerical analysis was made for a one-dimensional spatial geometry with cyclic boundary condition as shown in Fig. 2. The width of spatial segments was set as 20 nm. The number of connected segments is only 5 in this calculation as the aim is to find the existence of instability. Table 2 summarizes the starting equilibrium conditions of the variables. The value of C_{vS} in Eq. (3) is obtained by multiplying the observed number density of nm sized gas bubbles by TEM [13] and N_{v0} of Eq. (13). The dislocation density is provided considering TEM observations around the critical burnup, 7% FIMA, of the rim structure formation [12,13]. We used a number which is one order higher than the observed values considering its increasing trend

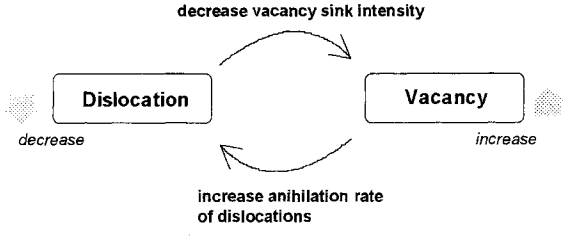

Fig. 3. Mechanism of instability occurred at vacancy-dislocation reaction.

with burnup. The starting values of vacancy and interstitial populations are determined by pre-calculations where a steady state of concerned high burnup conditions is achieved. The main calculation was made for a relatively short time interval, looking for possible transient instabilities.

The first case of calculation was made without any modification of coefficients and initial conditions, keeping spatial homogeneity. The results show no instability. The second case of calculations was made to find spatial instability such as that Turing investigated [6,7]. Modifications were made for the starting conditions as follows. (1) Starting dislocation density was set 0.01% less than others for one spatial segment No. 1. This provides spatial disturbance. (2) The diffusion coefficient of I between segments was increased by a factor 2. The result shows spatial instability at 3×10^4 s as shown in Fig. 4. The mechanism is schematically shown in Fig. 3. This scheme is a kind of self-catalytic reaction.

The variation of dislocation density (ρ_d) and V, I, V trapped in bubbles (C_{vs}) are shown in Figs. 4–7 for each

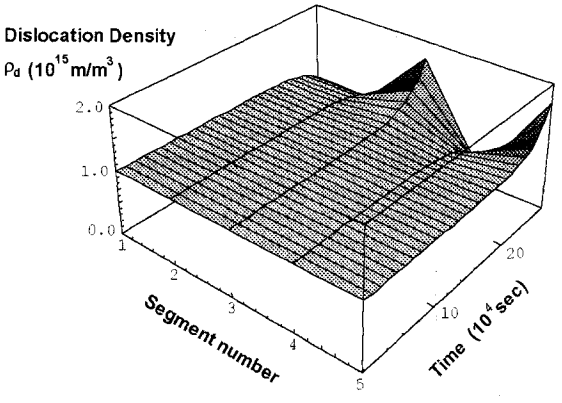

Fig. 4. Spatial instability observed at evolution of dislocation density.

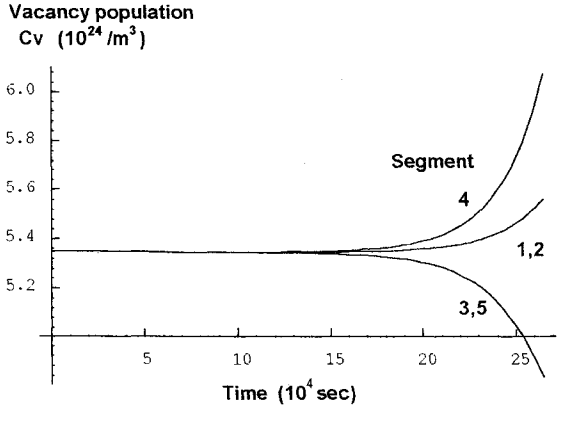

Fig. 5. Variation of vacancy population occurred at the spatial instability.

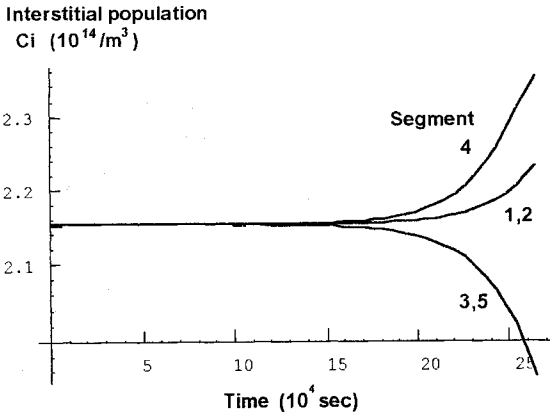

Fig. 6. Variation of interstitial population occurred at the spatial instability.

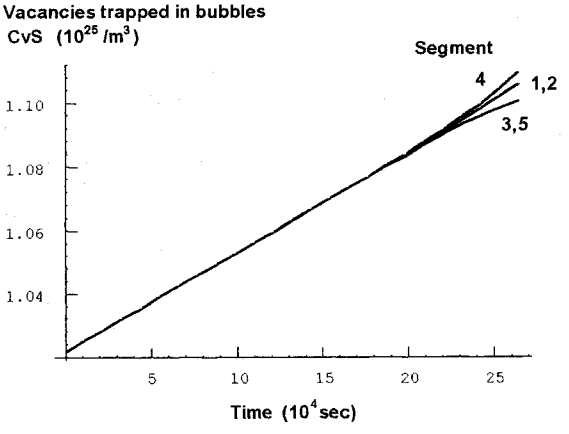

Fig. 7. Variation of vacancy population trapped in bubbles at the spatial instability, excluding vacancies associated to Xe/Kr atoms.

segment. For segment 1, the initial dislocation density was set 0.01% lower than the density of others. Then three variables of V, I and V_b increase rapidly, and ρ decreases in segment 1. On the other hand segments 3 and 5 show opposite behavior where the three variables decreases and the dislocation density increases. This instability was caused by interstitial flows between segments. The observed instability has a spatial variation and also an oscillating behavior in time axis. The vacancy diffusion between segments has an effect to suppress the instability.

5. Discussion

The proposed set of model equations is a first trial of the mathematical description of the rim structure formation. The calculation results are categorized as one of the Turing instabilities, which were caused by spatial diffusions that connect neighboring cells and non-linear chemi-

cal reactions in each cell [6]. This instability is popularly studied in chemical reactions and also in radiation damages in metals. However, it was not considered for defect reactions in nuclear fuel materials so far. While the presented model in this paper is not complete for the whole process, calculations confirmed presence of instabilities in the system of the defect complex. This instability may trigger other non-linear processes, which finally completes the structural change.

Model predictions and comparison with experimental observations are not sufficient at present. The incubation period of the structure formation was not modeled in this work. It was an intentional strategy as the non-linearity of the reaction process changes at several stages of the intermediate burnup. The integral of these processes requires extensive efforts. Therefore we have concentrated our work to look for instabilities at the restructuring. The model calculation shows that the instability develops the new structure in days. SEM investigations show heterogeneous development of the structure [8]. If the development rate is as fast as the model prediction, heterogeneity could be caused by statistical variance of the initiation process. As the restructuring seems to start at grain boundaries or pore surfaces at earlier burnup [8,11,14], the variation of sink strength for point defects may contribute to the early initiation of the structure formation. For further studies, the effects of temperature, fission rate and burnup on the threshold of the instability could be investigated by analytical investigations of the proposed model.

Some equations of the proposed model should be improved further. While the vacancy trap model of Eq. (3) is primitive, it may trace a principal behavior of the vacancy storage in the high burnup fuel. The fission gas release from bubbles to grain boundaries is not included and it could be implemented in the model without much difficulty. The growth rate of the network dislocations is the key non-linearity of this model and the reliance and accuracy of the model should be investigated further. In the reaction–diffusion framework, however, an essential weakness exists in the concept of dislocations. The vacancies and interstitials are well defined as far as the lattice sites are intact. Therefore their dynamics could be described by mean field theories and activity potential is also usable to construct equations. On the other hand, the dislocation is a three-dimensional object which disturb lattice sites and the mean field theory is not effective. Consequently further investigation is necessary to have a reasonable reaction rate description for the dislocations.

6. Conclusion

Fission damage produces a large amount of point defects. Based on reactions of point defects and atomic mixing generated by fission track and cascades, a model of the rim structure formation is proposed. A set of reaction–diffusion equations is composed for vacancies and interstitials of uranium, vacancies trapped in rare gas bubbles, and dislocation network. The experimental observations were fully utilized to define the initial condition of the analysis. The spatial diffusion processes were explicitly and numerically solved assuming one-dimensional geometry with cyclic boundary condition. The calculation shows that instabilities start as a result of reactions of vacancies, interstitials and dislocation networks and it produces a heterogeneous sink structure. This indicates that the rim structure could be started by this instability of non-linear interactions.

As the instability was observed with least assumptions, proposed reaction–diffusion equations is a good start to construct a framework to describe the rim structure formation mathematically.

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