ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

Application of a Mechanistic Model for Radiation-Induced Amorphization and Crystallization of Uranium Silicide to Recrystallization of UO_2*

ANL/ET/CP--90386
CONF-960815--1

J. Rest

July 1996

* Work supported by U.S. Department of Energy, Office of Arms Control and Nonproliferation, under Contract W-31-109-Eng-38.

Invited paper to be presented at the International Workshop on Interfacial Effects in Quantum Engineering to be held August 21-23, 1996 in Mito, Japan.

Application of a Mechanistic Model for Radiation-Induced Amorphization and Crystallization of Uranium Silicide to Recrystallization of UO_2*

by

J. Rest

Energy Technology Division
Argonne National Laboratory
Argonne, Illinois U.S.A.

Abstract

An alternative mechanism for the evolution of recrystallization nuclei is described for a model of irradiation-induced recrystallization of UO_2 wherein the stored energy in the material is concentrated in a network of sinklike nuclei that diminish with dose due to interaction with radiation-produced defects. The sinklike nuclei are identified as cellular dislocation structures that evolve relatively early in the irradiation period. A generalized theory of radiation-induced amorphization and crystallization, developed for intermetallic nuclear materials, is applied to UO_2. The complicated kinetics involved in the formation of a cellular dislocation network are approximated by the formation and growth of subgrains due to the interaction of shock waves produced by fission-induced damage to the material.

* Work supported by U.S. Department of Energy, Office of Arms Control and Nonproliferation, under Contract W-31-109-Eng-38.

1. Introduction

The peripheral region of UO_2 fuel pellets reveals an increasingly porous microstructure with burnup [1-4]. Observations of this "rim effect" show that an extremely fine-grained structure formed by recrystallization of the original grains is associated with this porous microstructure. TEM observations [5] of the formation mechanism of the recrystallized region show that dislocation density increases with burnup. Low-angle boundaries begin to form above 7.5 to 8 x 10^{20} fissions/cm^3. Subdivided grains 20-30 nm in size and with high-angle boundaries due to the accumulation of an extremely high density of subboundaries, together with recrystallized grains 50-200 nm in size and adjacent to the subdivided grain region, are observed in fuel irradiated to $\approx$ 2.1 x 10^{21} fissions/cm^3.

This is essentially the physical picture that was proposed as the basis of a model for irradiation-induced recrystallization wherein the stored energy in the material is concentrated in a network of sinklike nuclei that diminish with dose due to interaction with radiation-produced defects [6]. The sinklike nuclei are identified as cellular dislocation structures that evolve relatively early in the irradiation period. Impurities formed during fissioning of the material diffuse as vacancy-impurity complexes to cell walls where they effectively pin the wall, i.e., dislocation movement to and from the wall is hindered. The walls containing no impurities continue to undergo subgrain coalescence that results in viable nuclei for recrystallization. Recrystallization is induced when the energy per nucleus is high enough that the creation of grain-boundary surfaces is offset by the creation of strain-free volumes, with a resultant net decrease in the free energy of the material. This formulation was shown to provide a plausible interpretation of the fission density at which grain subdivision begins.

Nevertheless, the idea that vacancy-solute pairs formed during irradiation of UO_2 migrate to cell walls and pin the wall is based on indirect [6] and not on any direct experimental evidence. The primary purpose of this paper is to show that an alternative mechanistic description of the evolution of recrystallization nuclei, consistent with observation, can be achieved by a utilization of a generalized theory of radiation-induced amorphization and crystallization developed for intermetallic nuclear materials.

2. Model

The model for radiation-induced recrystallization described in Ref. 6 is based, in part, on the following assumptions:

- A cellular dislocation structure evolves relatively early in the irradiation period.
- Impurities formed during fissioning of the material diffuse to cell walls as vacancy/impurity complexes. The impurities effectively pin the wall, i.e., dislocation movement to and from the wall is retarded.

- Not all cell walls are uniformly affected by impurities; the walls that contain no impurities continued to undergo subgrain coalescence, which results in viable recrystallization nuclei.

Based on the above discussion, a number C_S of recrystallization nuclei are assumed per unit volume of material. It appears that these nuclei form relatively early in the irradiation period at low values of stored energy and that they are associated with microstructural features such as subgrain-boundary triple points or walls of cellular dislocation structures. Recrystallization nuclei act as sinks for irradiation-produced defects. As the irradiation proceeds, the nuclei are eliminated by interaction with vacancy-solute pairs. In other words, the concentration of impurities reduces the mobility of the interface. Many potential solute atoms are produced during fission, e.g., gas atoms and rare earths. Thus, the available stored energy is concentrated on fewer and fewer nuclei (one can consider that the nuclei are holes in the material and that they act as stress concentrators), with a resultant increase in average energy per nucleus. Recrystallization is induced when the energy per nucleus is high enough to offset the creation of a grain boundary surface by creating a strain-free volume, with a resultant net decrease in the free energy of the material.

The concentration of recrystallization nuclei, c_s, is given by

$$\frac{1}{c_s}\frac{dc_s}{dt} = -\frac{28\pi\, r_{sm} c_I D_{vI} \omega_4^v c_v}{\Omega\left(c_i + 7\omega_3^v/12\omega_0^i\right)\omega_0^i}, \qquad (1)$$

where c_v, c_i and c_I are the vacancy, interstitial, and impurity concentrations, respectively, r_{sm} is the annihilation radius of a recrystallization nucleus/vacancy-solute pair, D_{vI} is the diffusivity of the vacancy-solute pair, and Ω is the atomic volume. ω_0^v and ω_0^i are the jump frequencies of vacancies and interstitials, respectively, unperturbed by the presence of a solute atom; ω_3^v and ω_4^v are the jump rates of vacancies away from and toward nearest neighbor nuclei of solute atoms.

The concentration of viable recrystallization nuclei, which results from the integration of Eq. 1, is quite different from that given by classical nucleation theory in that the concentration decreases with fluence instead of increasing with irradiation, until the nucleation barrier is surmounted and the higher energy state of the crystal forms. In the present case, the nuclei are formed early in the irradiation by the damage process at relatively low values of strain energy. As the irradiation proceeds and the nuclei are eliminated by interaction with the vacancy-solute pairs, the available stored energy is concentrated in fewer and fewer nuclei, thus increasing the energy per nucleus.

Recrystallization is induced when the energy per nucleus is high enough that the creation of grain-boundary surfaces is offset by the creation of strain-free volumes, with a resultant net decrease in the free energy of the material. The stored energy, E_s, is taken to be concentrated in the network,

c_s, and is assumed to have a rate of change with respect to a change in c_s given by Boltzmann's law, i.e.,

$$\frac{dE_s}{dc_s} = -\frac{kT}{c_s} \quad . \tag{2}$$

By equating c_s obtained from Eq. 1 to the value of c_s obtained from Eq. 2 where a relatively small energy fluctuation can allow the system to jump over the energy barrier and cause the creation of a relatively defect-free crystal of material, a relation for the value of the fission density (m-3) at which recrystallization will occur is obtained.

As discussed in the introduction, the idea that vacancy-solute pairs formed during irradiation of UO_2 migrate to cell walls and pin the wall is based on indirect [7] and not on any direct experimental evidence. Thus, it is of interest to ascertain other potential mechanisms for the evolution of the recrystallization nuclei (i.e., as compared to that expressed by Eq. 1). A rate-theory model [8] for ion-induced crystallization and amorphization of U_3Si has been generalized to include U_3Si_2 [9]. The model is based on the fact that the bombardment of solids by energetic particles produces displacements of the host atoms and thus damage to the structure of the solids. If the damage energy is sufficiently high, displacement cascades containing hundreds of atoms each are produced. Molecular-dynamics simulations of ion collisions with a crystalline substrate show that the early stages of cascade development are characterized by the formation of shock waves [10], and that, in some materials (e.g., Si, U_3Si, U_3Si_2) amorphous material is left after the cascades cool to ambient temperature [11]. In other materials (such as UO_2), the "molten" material within the damage cascade crystallizes upon "cooling." Within the context of the model, the bombarding ions produce clusters of amorphous material that are considered centers of expansion (CE), or excess free volume zones. Simultaneously, centers of compression (CC) are created in the material. The CCs are local regions of increased density that travel through the material as an elastic (e.g., acoustic) shock wave. The CEs can be annihilated upon contact with a sufficient number of CCs, forming either a crystallized region that is indistinguishable from the host material, or a region with a slight disorientation (crystallized grain). The CCs can also annihilate each other upon contact, forming either oriented or slightly disoriented crystal structures. Crystallized grains grow by accumulating additional CCs. Full amorphization (or full crystallization) is calculated on the basis of achieving a volume fraction consistent with the close packing of spherical entities.

The generalized model has been applied to ion-irradiation and in-reactor experiments on U_3Si and U_3Si_2 and provides an interpretation for the amorphization curve (dose required to amorphize the material as a function of temperature), for the ion-radiation-induced nanoscale polycrystallization of these materials at temperatures above the critical temperature for amorphization, as well as for the role of the small crystallites in retarding amorphization.

To apply this model to UO_2, the same methodology was used as that used to determine U_3Si_2 properties from those used for U_3Si: the activation energies for crystallization of an amorphous cluster by a CC and for irradiation-enhanced crystallization were decreased by the ratio of the

melting temperature of U_3Si_2 and UO_2, the activation energies for thermal crystallization and for grain growth due to interaction between a CC and a crystallized grain were increased by the ratio of the melting temperature, and the number of CE's created per dpa was reduced by the ratio of the UO_2 and U_3Si_2 densities. In addition, it is assumed that for UO_2, the amorphus clusters formed in the damage cascades are very unstable and quickly crystallize. This is consistent with ion irradiation data that shows that UO_2 remains crystalline at 20K [12].

Figure 1 shows the calculated grain density and grain diameter using Eqs. 1-10 as a function of fission density for an irradiation at 623 K and an average fission rate of 1 x 10^{13} fissions/cm^3/s. The calculated grain density peaks relatively early in the irradiation period. Unlike U_3Si and U_3Si_2, where crystallized grain nuclei are formed primarily by the annihilation of amorphous clusters by shock waves, recrystallization nuclei in UO_2 are formed by the interaction between shock waves. CC annihilation upon contact, forming either oriented or slightly disoriented crystal structures, may depend on the close proximity of vacancies or vacancy clusters. This process is also present in the intermetallics, but at a much reduced level as compared to that provided by CC-CE annihilation. Also shown in Fig. 1 is the concentration of viable recrystallization nuclei, $C_{s,}$ which results from the integration of Eq. 1. Comparing C_s with the calculated grain density confirms the interpretation that these nuclei form relatively early in the irradiation period at low values of stored energy and that they are associated with microstructural features such as subgrain-boundary triple points or walls of cellular dislocation structures. It is clear from Fig. 1 that subsequent to the initial buildup of crystallized grains, C_s follows the trend of the calculated density of crystallized grains obtained from the theory of ratiation-induced amorphization and crystallizaiton. In addition, the behavior of the calculated crystallized grain diameter as a function of burnup is consistent with the observations reported by Nogita and Une [5,13]: that low-angle boundaries begin to form above $\approx$ 7.5 x 10^{20} fissions/cm^3 (indicated by a circled 1 in Fig. 1), and that subdivided grains 20-30 nm in size and recrystallized grains 50-200 nm in size adjacent to the subdivided grains exist in fuel irradiated to about 2 x 10^{27} fissions/m3 (indicated by a circled 3 in Fig. 1). The theory of radiation-induced recrystallization (i.e., the intersection of Eqs. 1 and 2) predicts that recrystallization is initiated at $\approx$ 1.5 x 10^{21} fissions/cm^3 (indicated by a circled 2 in Fig. 1).

Fig. 2 Shows calculated intergranular fission-gas-bubble size distributions made using GRASS-SST [14] with and without the effects of subgrain growth/grain-boundary sweeping. The irradiation conditions and grain growth kinetics shown in Fig. 1 were utilized in the calculation. For the case of no grain growth, a fixed grain size of 120 nm was used. The results shown in Fig. 1 demonstrate that subgrain growth and boundary sweeping result in a coarsened intergranular bubble distribution. In addition, the GRASS-SST calculations show that the intergranular bubbles have interconnected forming grain-boundary tunnels, in agreement with observation [13]. The formation of a recrystallized region within the fuel can lead to a substantial increase in fission-product release [15].

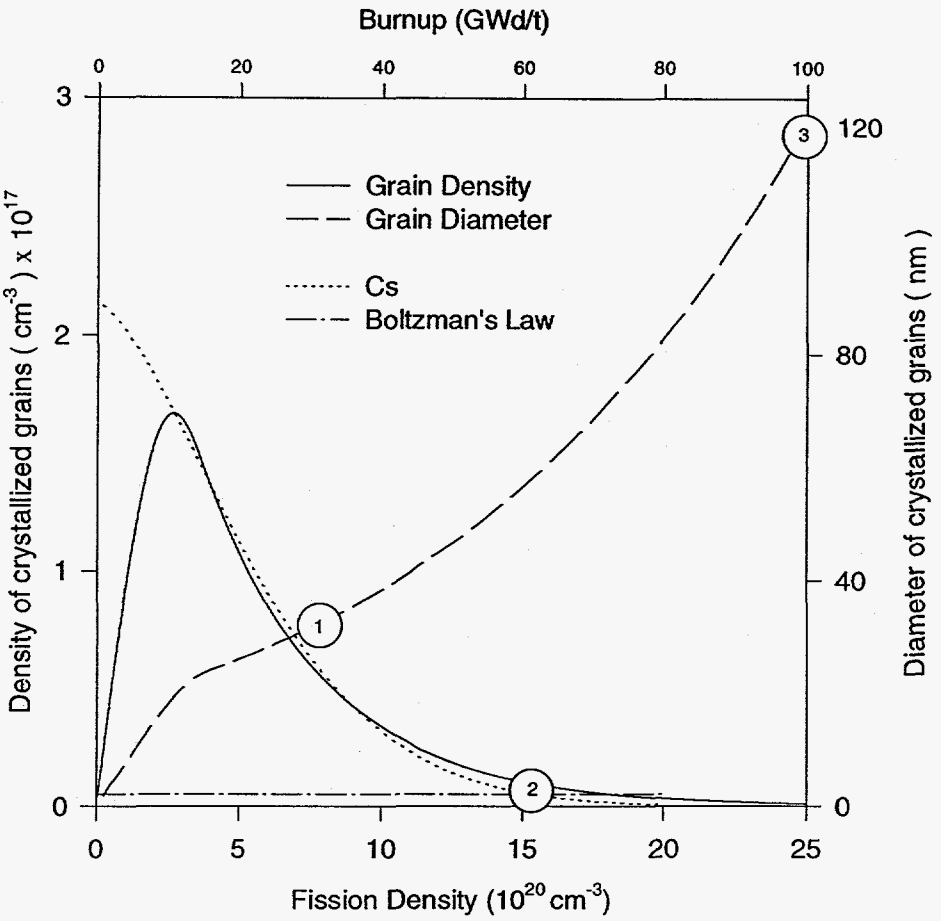

Fig. 1. Calculated grain density and grain diameter using the theory of radiation-induced amorphiztion and crystallization as a function of fission density for irradiation at 623 K and average fission rate of 1 x 10^{13} fissions/cm^3/s. Also shown is concentration of viable recrystallization nuclei, $C_{s,}$ which results from integration of Eq. 1. Observations reported by Nogita and Une [5,12]: low-angle boundaries begin to form above $\approx$ 7.5 x 10^{20} fissions/cm^3 (indicated by a circled 1), and subdivided grains 20-30 nm in size and recrystallized grains 50-200 nm in size exist in fuel irradiated to $\approx$ 2 x 10^{21} fissions/cm^3 (indicated by a circled 3). Prediction of the theory of radiation-induced recrystallization (given by the intersection of Eqs. 1 and 2), that recrystallization is initiated at $\approx$ 1.5 x 10^{21} fissions/cm^3 , is indicated by a circled 2.

7. Discussion

An estimate of the cell size of a cellular dislocation structure evolved from shock-wave interaction can be obtained from a consideration of the limited range of energies at which a damage event may be able to create a great enough density of fast recoils to form a shock wave [16]. For U in U, the maximum energy transfer is about 0.5 Kev and occurs at an energy of about 4 Kev. If one

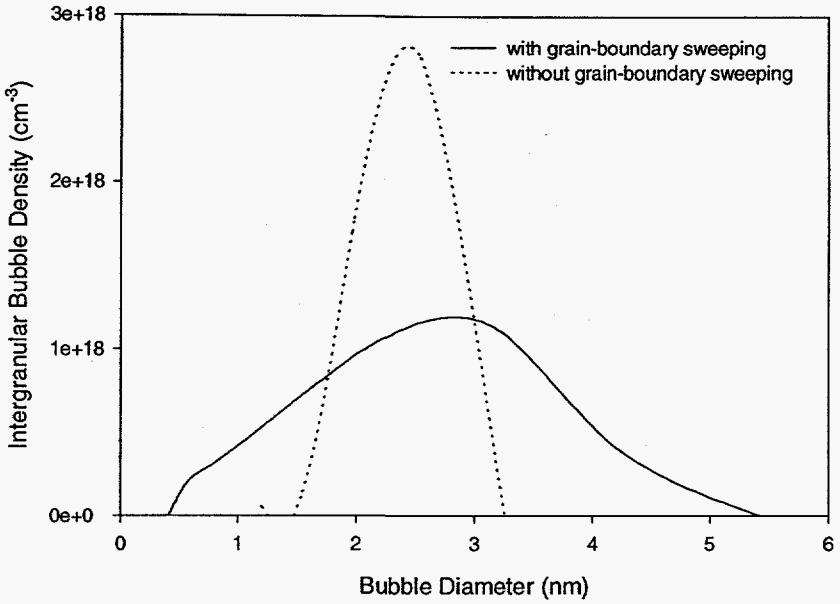

Fig. 2 Calculated intergranular fission-gas-bubble size distributions made using GRASS-SST [15] with and without the effects of subgrain growth/grain-boundary sweeping. The irradiation conditions and grain growth kinetics shown in Fig. 1 were utilized in the calculation.

assumes that this energy transfer goes into creating dislocation loops having a radius equal to the Burgers vector, then in UO_2 a CC interaction will produce about 15 loops. Coalescence of these loops into a cubic cellular configuration results in a cell size of about 2 nm.

In the more "stable" UO_2, amorphous clusters do not survive cascade "cooling." It is possible that a crystallized region is formed in the wake of cascade solidification, but this would lead to very high crystallization rates (in U_3Si, nanocrystals are formed above the critical temperature for amorphization at a rate of about one per ion), leading to saturation of the material with nanocrystals within several tenths of a dpa. In this case, in order to explain the evolution of the dislocation and subgrain structure reported in Ref. 13, a mechanism of nanocrystal destruction would have to be postulated which would be strong enough to delay the filling of space with crystallized material from several dpa to thousands of dpa. Observations of UO_2 irradiated at room temperature with 500 Kev Xe ions to 10^{16} ions/cm^2 are not consistent with this mechanism [12]. Instead, the observations show an increased dislocation density and the presence of small subgrains separated with the edges of the dislocations. Thus, within the context of the model presented in this paper, it seems plausible to postulate that the primary mechanism available to form recrystallized grain nuclei is CC-CC annihilation.

References

[1] N.E. Cunningham, M.D. Freshley, and D.D. Lanning, J. Nucl. Mater. 188 (1992) 19.

[2] T. Kameyama, T. Matsumura, and M. Kinoshita, Proc. ANS Topical Meeting on LWR Fuel Performance, Avignon, France, 1991, p. 620.

[3] K. Une, K. Nogita, S. Kashibe and M. Imamura, J. Nucl. Mater. 188 (1992) 65.

[4] L.E. Thomas, C.E. Beyer, and L.A. Charlot, J. Nucl. Mater. 188 (1992) 80.

[5] K. Nogita and K. Une, Nucl. Instr. and Meth. B 91 (1994) 301.

[6] J. Rest and G.L. Hofman, J. Nucl. Mater. 210 (1994) 187.

[7] S.J. Zinkle, R.A. Dodd and G.L. Kulcinski, Proc. on Effects of Radiation on Materials, 12th Int. Symp., ASTM-STP 870, eds. F.A. Garner and J.S. Perkin (American Society for Testing and Materials, Philadelphia, 1985) p. 363.

[8] J. Rest, J. Nucl. Mater. 225 (1995) 308.

[9] J. Rest, Submitted to J. Nucl. Mater.(1996).

[10] D. Stock, M. Nitscke, K. Gartner, and T. Kandler, Radiation Effects and Defects in Solids 129(1993) 14.

[11] T. Diaz de la Rubia and G.H. Gilmer, UCRL-116382 (1994).

[12] L.M. Wang and Hj. Matzke, to be published in the J. Nucl. Mater. (1996).

[13] K. Nogita and K. Une, J. Nucl. Mater. 226 (1995) 302.

[14] J. Rest, NUREG/CR-0202, ANL-78-53. Argonne National Laboratory (1978).

[15] J. Rest and G.L. Hofman, J. Nucl. Mater. 223 (1995) 192-195.

[16] K.B. Winterbon, Radiation. Effects. Letters., 57 (1980) 89-92.