Russian Research Center" Kurchatov Institute"



Charge State Effects of Radiation Damage on Microstructure Evolution in Dielectric Materials

under Neutron and Charged Particle Irradiations

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Non-adiabatic dynamics and radiation damage in nuclear materials

14-18 November 2011, ICTP, Trieste, Italy

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Materials for Fission and Fusion Reactors

Graphite Materials : Graphite, C-C composits

Metallic Materials: Austenitic Steels, Ferritic – martensitic Steels, ODS materials, V-alloys

Ceramic Materials: SiC – composits, Al2O3, MgO, ZrO2

Difference between metals and dielectrics

Metals:

- Point defects are neutral
- Electric field does not exist in the matrix

Dielectrics (Ceramic Materials):

- Point defects can have effective charge
- Electric field exists in the matrix under the influence of an applied electric field
- Driving force due to an electric field can have a strong effect on diffusivity of charged point defects



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BACKGROUND

Oxide Ceramic Materials $(e.g.\alpha - Al_2O_3)$ **in Fusion Reactors**:

- ***** Insulating Materials
- ***** *RF* **Window Materials**

International Thermonuclear Experimental Reactor (**ITER**) **Environment:**

Electric Field: 0.1 –100 (*kV/m*)
 Temperature: 50 –700 (*K*)
 Damage Rate: 10⁻¹⁰- 10⁻⁷ (*dpa/s*)

Physical Model of denuded zone formation in irradiated materials

Denuded zone $(\mathbf{E}_0 = \mathbf{0})$





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Main Equations:

Diffusion equations for point defects

$$G - \alpha C_{I}C_{V} - \frac{dj_{I}}{dz} = 0, \quad G - \alpha C_{I}C_{V} - \frac{dj_{V}}{dz} = 0,$$
 (1)

G is the generation rate of point defects under irradiation, α is the recombination coefficient, $\alpha = \mu (D_I + D_V)$ D_I, D_V are diffusion coefficients of intestinal atoms and vacancies

Diffusion currents of point defects

 $j_{I} = -D_{I} \frac{dC_{I}}{dz} + \frac{qD_{I}C_{I}}{kT} \frac{d\varphi}{dz}, \quad j_{V} = -D_{V} \frac{dC_{V}}{dz} - \frac{qD_{V}C_{V}}{kT} \frac{d\varphi}{dz} \quad (2)$ $\varphi \text{ is the potential of internal electric field }, \quad E = -\nabla \varphi$ kT is the temperature

DETERMINATION OF EFFECTIVE CHARGE STATES FOR POINT RADIATION DEFECTS IN FUSION CERAMIC MATERIALS

A.I. Ryazanov, A.V. Klaptsov, C. Kinoshita, K. Yasuda, 2004

Main Aim:

To suggest experimental method for measurements of an effective charge for point radiation defects in fusion ceramic materials

Content:

Introduction
Physical Model
Main Equations
Results
Observations
Conclusion

Poisson equation

$$\Delta \varphi = -\frac{4\pi}{\varepsilon \omega} \left(qC_V - qC_I + eC_h - eC_e \right) \tag{3}$$

Total electric current

$$J = -q(j_{I} - j_{V}) = q\left(D_{I}\frac{dC_{I}}{dz} - D_{V}\frac{dC_{V}}{dz}\right) + \frac{q^{2}}{kT}\left(D_{I}C_{I} + D_{V}C_{V}\right)E = J_{0} \quad (4)$$

Boundary conditions:

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$$C_{I}(z=0)=0, \quad C_{I}(z\to\infty)=C_{I}^{0}, \quad C_{V}(z=0)=0, \quad C_{V}(z\to\infty)=C_{V}^{0} \quad (5)$$

$$J_{0}=\left(q\left(D_{I}\frac{dC_{I}}{dz}-D_{V}\frac{dC_{V}}{dz}\right)+\frac{q^{2}}{kT}(D_{I}C_{I}+D_{V}C_{V})E\right)_{z=0}=\sigma\omega E_{0}$$

Assumption:

$$C_{I} \approx C_{I}^{0} + C_{I}^{1} \left(|C_{I}^{1}| < < C_{I}^{0} \right), \quad C_{V} \approx C_{V}^{0} + C_{V}^{1} \left(|C_{V}^{1}| < < C_{V}^{0} \right)$$
(6)

Equations (1)-(3) have the following form

$$\frac{d^{2}C_{I}^{1}}{dz^{2}} + \frac{qE_{0}}{\epsilon kT}\frac{dC_{I}^{1}}{dz} - \left[\frac{\alpha C_{V}^{0}}{D_{I}} + \frac{4\pi q^{2}C_{I}^{0}}{\epsilon \alpha kT}\right]C_{I}^{1} - \left[\frac{\alpha C_{I}^{0}}{D_{I}} - \frac{4\pi q^{2}C_{V}^{0}}{\epsilon \alpha kT}\right]C_{V}^{1} = 0,$$

$$\frac{d^{2}C_{V}^{1}}{dz^{2}} - \frac{qE_{0}}{\epsilon kT}\frac{dC_{V}^{1}}{dz} - \left[\frac{\alpha C_{I}^{0}}{D_{V}} + \frac{4\pi q^{2}C_{V}^{0}}{\epsilon \alpha kT}\right]C_{V}^{1} - \left[\frac{\alpha C_{V}^{0}}{D_{V}} - \frac{4\pi q^{2}C_{I}^{0}}{\epsilon \alpha kT}\right]C_{I}^{1} = 0$$
(7)

Solutions of equations (7) have the following form

$$C_I^1, C_V^1 \sim \exp(-\lambda_{\min} z)$$
⁽⁸⁾

 λ_{\min} is the minimum positive roots of the equation:

$$\left(\lambda^{2} - \frac{qE_{0}}{\varepsilon kT}\lambda - \frac{\alpha C_{V}^{0}}{D_{I}} - \frac{4\pi q^{2}C_{I}^{0}}{\varepsilon \omega kT}\right) \left(\lambda^{2} + \frac{qE_{0}}{\varepsilon kT}\lambda - \frac{\alpha C_{I}^{0}}{D_{V}} - \frac{4\pi q^{2}C_{V}^{0}}{\varepsilon \omega kT}\right) = \left(\frac{\alpha C_{I}^{0}}{D_{I}} - \frac{4\pi q^{2}C_{V}^{0}}{\varepsilon \omega kT}\right) \left(\frac{\alpha C_{V}^{0}}{D_{V}} - \frac{4\pi q^{2}C_{I}^{0}}{\varepsilon \omega kT}\right).$$

Size (L) of denuded zone is equal

$$L = 1/\lambda_{\min}$$
⁽¹⁰⁾

1.Absence of an external electric field ($E_0 = 0$ **)**



Denuded zone size in ceramics:

$$L_{E} \approx \sqrt{\frac{\varepsilon \omega kT}{8\pi q^{2}}} \left(\frac{\mu D_{I}}{G}\right)^{1/4}, L_{T} \approx \left(\frac{D_{V}^{2}}{\mu D_{I}G}\right)^{1/4}$$

$$L_T \approx \left(\frac{D_V}{\mu G}\right)^{1/4}$$

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Temperature dependence of denuded zone size



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TEM micrograph of SiCf/SiC composites after implantation with 3 MeV helium and annealing at T = 1673 K for 1 h (A.Hasegawa et. al. 1999)



TEM image of neutron (HFR) irradiated Al₂O₃ (4.6x10²⁵ m⁻²) (R.J.M.Konings et. al. 1998)



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TEM image of neutron (HFR) irradiated CeO₂ (4.6x10²⁵ m⁻²) (R.J.M.Konings et. al. 1998)



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Depth-dependent microstructure of MgAl₂O₄ (spinel) irradiated by 2 MeV Al⁺ at 650 C to a peak damage 14 dpa (S.J.Zinkle 1992)



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Depth-dependent microstructure of MgAl₂O₄ irradiated by 2 MeV Al⁺ at 650 C to a peak damage 100 dpa (S.J.Zinkle 1992)



Defect free zones near surface and grain boundaries in MgAl₂O₄ (spinel) irradiated by 2 MeV Al⁺ at 650 C to a peak damage 14 dpa (S.J.Zinkle 1992)



Microstructure of Al₂O₃ in the vicinity of surface and grain boundary irradiated by 2 MeV Al⁺ at 650 C to a peak damage 1 dpa (S.J.Zinkle 1992)



Temperature dependence of denuded zone size



Temperature dependence of denuded zone size



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Dependence of denuded zone size on an applied electric field



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Dependence of $\Delta L_E(E)$ **on an applied electric field**



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Dependence of $\Delta L_E(E)$ **on an applied electric field**



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Dependence of $\Delta L_E / L_E^2$ on applied electrical field



Objective and outline

➤To understand the difference in the nucleation-andgrowth process of defect clusters in α -Al₂O₃ with and without an electric field.

(1) Ion irradiation : kinetics of dislocation loops formation
 (2) Ion irradiation : other characteristic defect clusters
 (3) Neutron irradiation

K. Yasuda et al., ICFRM-11, 2003

Specimens and irradiation conditions





Evaluation of electric field by FEM code ANSYS



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Neutron irradiation at JMTR



Experimental observation of dislocation loop density in Al₂O₃ irradiated at 760 K with 100keV He⁺ ions to a fluence of 1x10²⁰ m⁻² with and without electric field of 100 kVm⁻¹ (K.Yasuda, K.Tanaka, C.Kinoshita 2002)



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TEM data in α-Al₂O₃ irradiated with 100 keV He⁺ ions at 870 K (K.Yasuda, K.Tanaka, C.Kinoshita 2002)



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Number of interstitials included in DLs



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Radiation Swelling in SiC under neutron and charged fast particle irradiations

Radiation Swelling in SiC

Ion beam irradiation and Surface profile characterization



Experimental Measurement of Radiation Swelling



$\Delta V/V (\Phi_{av}) \cong \Delta Z/d$

 Φ_{av} – Averaged dpa profile,

- $\Delta Z\,$ Height of step between irradiated and no irradiated area,
- **d** Penetration depth of irradiated sample.

Dose dependence of radiation swelling in SiC



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Temperature dependence of swelling of SiC



Dislocation Loop in Dielectrics



System of Equations

$$D_m \Delta C_m + \frac{q v_m}{kT} D_m \nabla (C_m \nabla \varphi) = 0$$
$$\Delta \varphi = -\frac{4\pi}{\varepsilon \omega} \left(\sum_m q v_m C_m + \rho \right)$$

Boundary Conditions



Theoretical model of radiation swelling in SiC

Radiation swelling (S_{tot}) is determined in ceramic materials by the following relation

$$S_{tot} = \sum_{K=1}^{2} C_{IK} e_{IK} + \sum_{K=1}^{2} C_{VK} e_{VK} + \omega \sum_{S,K} (n_{IK}^{S} e_{IK} + n_{VK}^{S} e_{VK})$$

 e_{α} is the dilatation of point defect type α ($\alpha = I$ for integratical atoms, $\alpha = V$ for vacancies and $\alpha = He$ for helium atoms), ω is the atomic volume, is the total number of point defects of the type α absorbed by sinks of the type *s* (loops, voids) in an unit volume,

 $C_{\alpha k}$ is the concentration of point defects for the two components: k=1=Si , k=2=C in SiC

$$\frac{dC_{VK}}{dt} = G_{VK} - j_{VK}(\rho_D + \rho_L) - \alpha D_{IK}C_{IK}C_{VK}$$
$$\frac{dC_{IK}}{dt} = G_{IK} - j_{IK}(\rho_D + \rho_L) - \alpha D_{IK}C_{IK}C_{VK} - \mu (D_{I1} + D_{I2})C_{I1}C_{I2}$$

 G_{VK}, G_{IK} are the generation rates of vacancies and interstitial atoms *k*-th components, D_{IK}, D_{VK} are the diffusion coefficients of interstitial atoms and vacancies *k*-th component, ρ_d is the dislocation density, ρ_L is the dislocation loop density ($\rho_L = 2\pi R_L N_L$).

The dislocation loop density is determined from the following relation

$$\omega \frac{dN_{L}}{dt} = \mu (D_{I1} + D_{I2}) C_{I1} C_{I2}$$

The growth rate of dislocation loop with loop radius R in ceramic materials taking into account the absorption of two types of interstitial atoms and vacancies and remaining of stoichiometric of two components in dislocation loop is given by the following relation

$$\frac{dR_L}{dt} = \frac{\pi r_0}{b} \sum_{K} \left(j_{IK}^n - j_{VK}^n \right) = \frac{4\pi}{b \ln\left(\frac{8R}{r_0}\right)} \frac{D_{I1}C_{I1}D_{I2}C_{I2} - D_{V1}C_{V1}D_{V2}C_{V2}}{D_{I1}C_{I1} + D_{I2}C_{I2} + D_{V1}C_{V1} + D_{V2}C_{V2}}$$

The initial conditions (at t = 0):

$$C_{IK}(t=0) = 0$$
 $C_{VK}(t=0) = 0$ $R_L(t=0) = a$

Main parameter values used for numerical calculations of radiation swelling in SiC

$G_1 = G_{Si}$	Point defect generation rate of Si atoms	3.10 ⁻³ dpa/s
$G_2 = G_c$	Point defect generation rate of C atoms	1.10 ⁻³ dpa/s
E_{mV}^{Si}	Silicon vacancy migration energy	2.3 eV
E_{mV}^{C}	Carbon vacancy migration energy	2.0 eV
E_{ml}^{Si}	Silicon interstitial migration energy	0.4 eV
E_{ml}^{C}	Carbon interstitial migration energy	0.3 eV
E_{FV}^{Si}	Silicon vacancy formation energy	2.5 eV
E_{FV}^{c}	Carbon vacancy formation energy	2.4 eV
$ ho_{\scriptscriptstyle D}$	Network dislocation density	$10^{10} \mathrm{cm}^{-2}$
$e_{_{V1}} = e_{_{V2}}$	Vacancy dilatation	-0.1
a	Lattice parameter	5.14×10^{-8} cm

$$D_{VK} = D_{VK}^{\circ} \exp(-E_{mV}^{\kappa} / T), \text{ (where } D_{V1}^{\circ} = D_{V2}^{\circ} = 10^{-2} \, cm^{-2}),$$

$$N_{L} = N_{L}^{\circ} \left[\exp(E_{m1}^{1} / T) + \exp(E_{m1}^{2} / T)\right]^{1/2}, \text{ (where } N_{L}^{\circ} = 3.10^{12} \, cm^{-3}).$$

The time dependence of dislocation loop growth at different irradiation temperatures



Dose dependence of radiation swelling in SiC at different irradiation temperatures



The comparison of experimental and theoretical temperature dependencies of radiation swelling in SiC.



INSTABILITY OF INTERSTITIAL CLUSTERS UNDER ION AND ELECTRON IRRADIATIONS IN CERAMIC MATERIAL

A.I. Ryazanov, A.V. Klaptsov, C. Kinoshita, K. Yasuda, 2004

Experimental

- Specimens: 13mol% Y2O3-ZrO2 single crystal (Earth Jewelry Co.)
 surface orientation: (111)
- Irradiation:
 - ions: 100 keV He+ at 870 K, up to 1x1020 ions/m2
 - 4 keV Ar+ at 300 K
 - 300 keV O+ at 470-1070 K, up to 5x1019 ions/m2
 - electrons: 1000 keV at 470-1070 K, up to 1.4x1027 e/m2
 - electron irradiation subsequent to ion irradiation:
 - 100-1000 keV electrons at 370-520 K
- Observations:
 - in situ and ex-situ TEM
 - HVEM (JEM-1000, HVEM lab., Kyushu University)
 - TEM (JEM-2000EX, HVEM lab., Kyushu University)
 - TEM-accelerator facility (JEM-4000FX, TIARA, JAERI-Takasaki)

Defect clusters in yttrium-stabilized zirconia

-300 keV O+ions: 5.1x1017 ions/m2 at 470 K -200 keV electrons at 370 K



Instability of Interstitial Clusters



Characteristic features of the extended defects in yttrium stabilized zirconia

- irradiation condition: under 100-1000 keV electron irradiation subsequent to ion irradiation (100 keV He⁺, 300 keV O⁺, 4keV Ar⁺)
- strong strain and stress fields
- very high growth rate \approx 1-3nm/sec
- preferential formation around a focused electron beam
- preferential formation at thick regions
- critical radius: 1.2 μm
 - sudden conversion to the dislocation network
 - repeat nucleation, growth and conversion to dislocation structure on dislocation lines

Cross section for displacement in ZrO2

under electron irradiation



Growth rate of radiation defects in ZrO2



Theoretical model

Growth rate of electrostatic charge (*Q*) on the dislocation loop with *R* radius is equal

$$\frac{dQ}{dt} = N \langle \sigma \rangle_I \Phi \approx \frac{\pi R^2}{a^2} \langle \sigma \rangle_I \Phi$$

A.Ryazanov, V.Klapzov, JETP Letters, 2005

 $\langle \sigma \rangle_{I}$ is the cross-section of electron-electron elastic Reserford scattering ϕ is the electron flux, *a* is the lattice spacing

$$\langle \sigma \rangle_I = \int_I^{E_0} \frac{d\sigma}{dE} \, dE = 4\pi a_0^2 \frac{E_R^2}{IE_0} \left(1 - \frac{I}{E_0} \right),$$

 $E_R = 13.6 \ \exists B$ - is the Ridberg energy, $\partial_0 = 0.53$ A is the Bohr radius E_0 is the electron energy

Electrical field (E) near the charged dislocation loop is equal

$$E \approx \frac{Q}{\varepsilon R} \sqrt{\frac{1}{2\rho R}},$$

Elastic stress field due to polyarization of a matrix with the disribution of electrical field (*E*) is equal

$$\sigma_{ik} = \frac{\varepsilon}{4\pi} \left(E_i E_k - \frac{E^2}{2} \delta_{ik} \right), \quad \sigma \le \sigma_{th} = \frac{\mu}{2\pi}$$

Time dependence of elastic stress field near charged dislocation loop

$$\sigma\approx \frac{Q^2}{16\pi\varepsilon\rho R^3}\approx \left(\frac{3}{20}\right)^2\frac{\pi R}{\varepsilon\rho a^4}\langle\sigma\rangle_I^2(\Phi t)^2.$$

 $\sigma_{th}~=~\mu/2\pi~pprox~6~ imes~10^{10}~{
m dyn}$ / ${
m 'cm^2}~~\Phi=10^{11}~{
m e/m^2cek}$

$$R = 600 \text{ nm}, E_0 = 200 \text{ KeV}, t = 280 \text{ sec}$$

Shear stress component induced by charged dislocation loop



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Strain-field induced by charged dislocation loop



Normal stress component induced by charged dislocation loop



Total normal stress component induced by charged dislocation loop



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Summary

- Electron-irradiation subsequent to ion-irradiation induces anomalous large defect clusters with strong stress and strain filed in yttria-stabilized cubic zirconia (YSZ).
- Such defect clusters are considered to be oxygen clusters (platelets), which are formed due to the production of displacement damage in oxygen sublattice in multicomponent ceramic:Y₂O₃-ZrO₂.
- Under irradiation, the growth of charged defect clusters can result in multiplication of dislocation network in fusion ceramics due to ionization processes and charge accumulation on dislocation loops.