Study of irradiation defect kinetics in metal systems

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1. Introduction

Not only nuclear society but also various academic societies are interested with reaction of bimolecular kinetics. The first quantification approach published at 1917 by Smoluchowski [1]. And then Waite expanded his accomplishment with elegant expression [2]. These theoretical approach had been exclusive properties of chemistry or bioengineering. However after observation of severe radiation degradation of dimensional instability [3], this bimolecular reaction kinetics became most powerful research tool for prediction or analysis of radiation defect behaviour.

Gosele and Woo are most representative researchers in reaction kinetics of irradiation defect [4, 5]. Gosele found the generalized reaction formula of radiation defect. Also He development methodology to reflect diffusion anisotropy of non-cubic structure by changing the normal coordinate system [4]. After several years Woo successfully predict irradiation growth and creep phenomena base on Gosele's works [5]. Diffusion anisotropy effect on defect reaction with each type of sinks was systemically organised. Hence behaviour of dislocation loop which is representative radiation sink in zirconium materials had been analysed with change of dimensional instability.

Recently there is the significant increasing of simulation performance, hence basic parameter of reaction kinetic is calculated by first principle method. However there is certain limitation of computation simulation because there is no way to derive the reason of discrepancy between experimental and simulation results. Therefore in this study reaction kinetics of radiation defect with sink in structural metric, specifically zirconium and it alloy, was studied and dimensional instability was calculated by rate theory.

2. Collision theory

Collision theory is about quantitative analysis of reaction rate. This research part, as one of the heart of chemistry, can be used for the discussion of reactions between simple species in the various phase. However many research or study had been only focused on gas phase because it is hard to image the reaction kinemics in the solid of liquid phase. However, thanks to efforts of many researcher, reactions kinetics is quantitatively expressed by reaction probability

2-1 probability density

In 1957 Waite formulate the general equation for reaction kinetics in condensed materials system. Reaction probability was expressed by define probability distribution as follow

$$\bar{\rho}_{Ai}(r_A, t)dV_A/V \tag{1}$$

Where $\bar{\rho}_{Ai}$ is probability that A_i is in the volume element dV_A at r_A

$$\rho_{Ai(Bj)}(r_A, t; r_B)dV_A/V \tag{2}$$

Where $\rho_{Ai(Bj)}$ is Probability that A_i is in the volume element dV_A at r_A, t given that B_j is at r_B

$$C_A(r_A, t) = 1/V \sum_i^{NA^0} \bar{\rho}_{Ai}(r_A, t) \tag{3}$$

Where $C_A(r_A, t)$ microscopic density of A particle

$$\rho_{ij} = \rho_{Ai(Bj)}\bar{\rho}_{Bj} = \bar{\rho}_{Ai}\rho_{Bj(Ai)} \tag{4}$$

Where ρ_{ij} pair probability distribution. By assuming that the A and B particle is randomly distributed, $\bar{\rho}_{Ai}$ is independent of position and are functions of time only. Hence $\rho_{Ai(Bj)}$ is the only the functions of r_A, t and at the given position of the B atom. Therefore the macroscopic pair probability is

$$C_{AB}(r_A, r_B, t)dV_A dV_B = 1/V \sum_i^{NA^0} \sum_i^{NB^0} \rho_{ij}(r_A, r_B, t)\, dV_A dV_B \tag{5}$$

Where $C_{AB}(r_A, r_B, t)$ is average number of A or B atom which is paired with counter parts in dV_A and dV_B at r_A, r_B, t.

2-2 Joint probability density change by diffusion

Joint probability is changed by flux to outward of $dV_A dV_B$. In order to consider the flux of particle, probable vector velocity concept was developed and expressed as below

$$-\left[\nabla_A\left(V_A\rho_{Ai(Bj)}\bar{\rho}_{Bj}\right)+\nabla_B\left(V_B\rho_{Bj(Ai)}\bar{\rho}_{Ai}\right)\right] \quad (6)$$

Where V_A is probable vector velocity which term is described without potential field as below.

$$V_A=-D_A\nabla_A ln\rho_{AiB(j)} \quad (7)$$

Therefore total joint probability could be expressed as below

$$\frac{\partial\rho_{ij}}{\partial t}=\left(\frac{\partial\rho}{\partial t}\right)_{chem}+D_A\nabla_A^2\rho_{ij}+D_B\nabla_B^2\rho_{ij} \quad (8)$$

Where $\frac{\partial\rho_{ij}}{\partial t}$ is total change of pair probability distribution due to chemical reaction and diffusion.

2-3 Joint probability density change by reaction

Not only diffusion but also chemical reaction cause the change of joint probability density. By considering triplet probability, chemical reaction is

$$\left(\frac{\partial\rho}{\partial t}\right)_{chem}=f_{ij}(t)\rho_{ij} \quad (9)$$

$$f_{ij}(t)=\frac{1}{\bar{\rho}_{Ai}}\sum_{k\neq i}^{NB^0}\left[\frac{\bar{\rho}_{Ai}}{dt}\right]_{Bk}+\frac{1}{\bar{\rho}_{Bi}}\sum_{m\neq i}^{NA}\left[\frac{\bar{\rho}_{Bj}}{dt}\right]_{Am} \quad (10)$$

Where $f_{ij}(t)$ is summation of probability of the reaction A_i with $B_k\ (k\neq j)$ and the B_j with $A_m\ (m\neq i)$

Therefore final expression of chemical joint probability is

$$\frac{\partial\rho_{ij}}{\partial t}=f_{ij}(t)\rho_{ij}+D_A\nabla_A^2\rho_{ij}+D_B\nabla_B^2\rho_{ij} \quad (11)$$

From this equation general solution is derived with complicate mathematics. Cartesian coordinate was changed in twice and new variable was suggested. Finally the general solution is

$$\frac{\partial C_A}{\partial t}=\frac{\partial C_B}{\partial t}=4\pi r_0^2 DC_A^0C_B^0\,\rho_{ij}(r,t) \quad (12)$$

3. Diffusion anisotropy difference

In case of isotropic materials, reaction kinetics was easily formulated and calculated with general theory of collision. However in case of anisotropy materials, traditional approach do not allow to predict irradiation degradation behaviour. In order to overcome this problem, Gosele distort the Cartesian coordination and recalculate chemical reaction within such coordination

$$g_{ii}=\left(\frac{\partial x}{\partial\xi^i}\right)^2+\left(\frac{\partial y}{\partial\xi^i}\right)^2+\left(\frac{\partial z}{\partial\xi^i}\right)^2 \text{ (i = 1,2,3)} \quad (13)$$

From this coordination, reaction probability is expressed as

$$\phi_\infty=\frac{4\pi\bar{D}\beta B}{\left[a-\exp\left(-\frac{\beta B}{r_0}\right)\right]} \quad (14)$$

Therefore irradiation defect and sink reaction is determined by potential field, temperature, and sink radius.

4. Discussion

The aim of this study is understanding of reaction kinetics of irradiation defect in metal system. Until now various researcher try to unveil the fundamental principle of reaction behavior, it is not easy work because limitation of experimental technic do not allow to imagine the specific behavior of irradiation defect in condensed metal. Hence simplified analytical method developed and predict the irradiation degradation behavior based on reaction kinetics. However recently computer simulation could suggest the specific reaction kinetics with development of advanced theory and technology. Unfortunately computation results and analytical solution are not seems to have a similar behavior. This discrepancy should be revised and reformulate the analytical method to collect approach.

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