13.10 Migration Mechanisms and Growth of Mobile Bubbles

- ***Now we let bubbles move too.***
  - ***Distinguish between as fabricated (some He) and equilibrium (Xe filled)*** **bubbles**

13.10.1. Atomic Mechanism of Bubble Mobility Due to Surface Diffusion

Remember, surface atoms are in constant motion, the slightest imbalance can cause bubbles to move.

13.10.2 Random Bubble Motion

There are two diffusivities of major importance

- ***Surface Diffusivity (D_s)***
- ***Bubble Diffusivity (D_b)***

In chapter 7;

$$D_s = \frac{\lambda_s^2 \Gamma_s}{4} \qquad \text{(2 dimensional)}$$

total jump frequency of molecules on surface

$$D_b = \frac{\lambda_b^2 \Gamma_b}{6} \qquad \text{(3 dimensional)}$$

jump frequency of bubble

To relate λ_s to λ_b, note that from the cube model of figure 13.18

$$\lambda_b = \frac{\text{distance that bubble moves}}{\text{\# of jumps to move bubble } \Delta x}$$

$$= \frac{\Delta x}{\left(\frac{l^3 \Delta x}{\Omega \lambda_s}\right)} = \frac{\Omega \lambda_s}{l^3}$$

For a spherical bubble;

$$\lambda_b = \left(\frac{a_o^3}{\frac{4\pi R^3}{3}}\right)\lambda_s$$

Since # of surface atoms = $\left(\frac{4\pi R^2}{a_o^2}\right)$

Frequency of bubble jumps;

$$\Gamma_b = \left(\frac{4\pi R^2}{a_o^2}\right)\Gamma_s$$

This gives;

$$D_b = \frac{3 a_o^4 D_s}{2\pi R^4}$$

or;

$$D_b = \left[\frac{3 a_o^4 D_{so}}{2\pi} \exp\left\{-\left(\frac{E_s}{kT}\right)\right\}\right] \bullet \left(\frac{1}{R^4}\right)$$

Small bubbles move faster than large ones

13.10.3 Directed Bubble Migration in a Temperature Gradient

Introduction of bubble disturbs temperature profile (see figure 13.19)

One finds that ;

$$\left(\frac{dT}{dx}\right)_b > \left(\frac{dT}{dx}\right)_{normal}$$

or;

$$\left(\frac{dT}{dx}\right)_b = \frac{3}{2}\left(\frac{dT}{dx}\right)$$

Note that the flux of atoms along surfaces (chapter 7) is;

$$J_s = \left(-\frac{D_s Q_s^* C_s}{kT^2}\right) \bullet \left(\frac{dT}{dx}\right)_b$$

and;

$$v_b = \left(-\frac{3 D_s Q_s^* a_o}{kT^2 R}\right) \bullet \left(\frac{dT}{dx}\right)$$

Note Q_s^* (heat of transport) must be positive because bubbles move up a temperature

gradient
Olander calculates for

$R = 100$ Å $a_o = 3$ Å $T = 1000°K$

$$Q_s^* = 415 \frac{kJ}{mole} \quad \frac{dT}{dx} = 4000 \frac{°K}{cm}$$

$$D_s = 5 \times 10^{-7} \frac{cm^2}{sec}$$

gives;

$$v_b = 3 \times 10^{-6} \frac{cm}{sec}, \quad 0.2592 \frac{cm}{day}$$

$$1.814 \frac{cm}{week}$$

But T changes with time, so we cannot extrapolate too long

13.10.4 General Treatment of Bubble Mobility

Fred Nicols (now at ANL) has been a major contributor in this area

$$v_b = \text{mobility x force} = M_b F_b = \frac{D_b F_b}{kT}$$

Nicols relates macroscopic and microscopic forces to find;

$$F_b = \left(\frac{2\pi R^3}{a_0^3}\right)\left(\frac{Q_s^*}{T}\right)\left(\frac{dT}{dx}\right)$$

13.10.5 Bubble Migration by Volume Diffusion

Consider the effect of vacancy motion outside the bubble
Need to get new expressions for bubble jump frequency and jump distance.

{ See Figure 13.20}

Assuming that a bubble is a perfectly absorbing sphere;

$$\Gamma_b = \frac{4\pi R^2 D_{vol}}{a_o^4}$$

Jump distance

$$\lambda_b = \left(\frac{3a_o^3}{4\pi R^3}\right) \bullet \sqrt{\overline{\lambda_v^2}}$$

Problem of determining this distance has been treated by Olander

$$\overline{\lambda_v^2} = 2Ra_o$$

Remember that

$$D_b = \frac{\lambda_b^2 \Gamma_b}{6}$$

Which produces (for Brownian motion);

$$D_b = \left(\frac{3a_o^3}{4\pi}\right)\left(\frac{1}{R^3}\right) D_{vol}$$

For surface diffusion $D_b \quad \frac{1}{R^4}$ **Have to get for moving species**

Next, consider the effect of a temperature gradient;

$$v_b = \frac{D_b F_b}{kT}$$

$$\text{where } F_v = -\left[\frac{Q_v^*}{T}\right] \bullet \left(\frac{dT}{dx}\right)_b$$

and Q_v^* **= heat of vacancy transport**
≈ energy of self diffusion

Nicols finds;

$$v_b = \left\{\frac{D_{vol} Q_v^*}{kT^2}\right\} \bullet \left(\frac{dT}{dx}\right)$$

Problem 13.2

Problem 13.2

a.) What is the root mean squared distance traveled in 40 days by a 20 Å diameter bubble undergoing Brownian motion in UO_2 at 1400 °C

b.) Recalculate a.) in a temperature gradient of 2000 °C/cm

Assume that the bubble diffusivity is governed by surface diffusion and $Q_s^* = 415$ kJ/mole

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a.) From Ch. 7

$$r^2 = 6D_b t = \frac{9a_o^4 D_s t}{\pi R^4}$$

eq. 13.214

use $a_o = 3$ Å

$t = 40 \cdot 24 \cdot 3600 = 3.46 \times 10^6$ s

$R = 10$ Å

$T = 1400°C = 1673$ °K

eq. 13.216

$$D_s = 4 \times 10^5 \cdot \exp(-108/RT)\ \text{cm}^2/\text{s}$$

$$= 2.77 \times 10^{-9}\ cm^2/s$$

$$\sqrt{r^2} = \left(\frac{9 \bullet 3^4 \bullet 2.77x10^{-9} \bullet 3.46x10^6}{\pi 10^4}\right)^{\frac{1}{2}}$$

$$= 0.015\ cm$$

b.) Thermal Gradient Migration

eq 13.219

$$r = \left(\frac{3D_s Q_s^* a_o}{RkT^2}\right) \bullet \left(\frac{dT}{dx}\right) t$$

$$r = \left(\frac{3 \bullet 2.77x10^{-9} \bullet 100x10^3 \bullet 4.18 \bullet 3 \bullet 2000 \bullet 3.46 \bullet 10^6}{10 \bullet 1.38x10^{-23}\left(\frac{J}{^\circ K}\right)[1673]^2 \bullet 6.02x10^{23}}\right)$$

$$= 0.310\ cm$$

In other words, the bubble moves almost 21 times farther in a temperature gradient

13.10.6 Bubble Migration in a Stress Gradient

Trick is to calculate the force on a bubble as it moves from x to x + dx and the stress changes from σ to $\sigma + d\sigma$.

$$F_b = -\frac{dG_b}{dx} \qquad \text{(at constant temp.)}$$

Gibbs free energy of bubble

Three contributions to G_b;

1.) Change in free energy of contained gas, dG_g

2.) Change in free energy of system due to change in surface area, dG_s

3.) Change in strain energy of solid, dE_{solid}

For an Ideal Gas;

$$dG_b = - p\ dV = - p(4\pi R^2 dR)$$

For surface energy;

$$dG_s = \gamma\ (8\pi R dR)$$

or, $$dG_g + dG_s = -4\pi R^2 \left\{ p - \left(\frac{2\gamma}{R}\right) \right\} dR$$

since $p - \left(\frac{2\gamma}{R}\right) = \sigma$

Need to get this in terms of x

Use;

$$\left(\sigma + \left[\frac{2\gamma}{R}\right]\right) \bullet \left(\frac{4\pi R^2}{3}\right) = mkT$$

differentiating;

$$\frac{dR}{d\sigma} = -\left(\frac{R^2}{3\sigma R + 4\gamma}\right)$$

but,

$$dR = \left(\frac{dR}{d\sigma}\right) \bullet \left(\frac{d\sigma}{dx}\right) dx$$

So;

$$dR = -\left(\frac{R^2}{3\sigma R + 4\gamma}\right) \bullet \left(\frac{d\sigma}{dx}\right) dx$$

This gives;

$$\left(\frac{dG_g}{dx}\right) + \left(\frac{dG_s}{dx}\right) = \left\{\frac{4\pi R^4 \sigma}{3\sigma R + 4\gamma}\right\}\left(\frac{d\sigma}{dx}\right)$$

For elastic energy, start with

$$E_{el} = \frac{\sigma^2}{2K}$$ **Bulk Modulus**

and end up with;

$$\frac{dE_{solid}}{dx} = -\left[\frac{2\pi\sigma R^3}{3K}\right] \bullet \left\{\frac{3\sigma R + 8\gamma}{3\sigma R + 4\gamma}\right\} \bullet \left(\frac{d\sigma}{dx}\right)$$

Put it all together;

$$F_b = -\left\{\frac{4\pi R^2\sigma}{3\sigma R + 4\gamma}\right\} \bullet \left[1 - \left(\frac{3\sigma R + 8\gamma}{6RK}\right)\right] \bullet \left(\frac{d\sigma}{dx}\right)$$

For small bubbles and low σ

$3\sigma R << 4\gamma$

$$F_b = -\left(\frac{\pi R^4\sigma}{\gamma}\right) \bullet \left(\frac{d\sigma}{dx}\right)$$

For large bubbles and high stresses;

$$F_b = -\left(\frac{4\pi R^3}{3}\right) \bullet \left(\frac{d\sigma}{dx}\right)$$

Bubbles always move down a stress gradient !

$$\frac{\left(F_b\right)_{stress}}{\left(F_b\right)_{temp}} = \frac{\left(R\sigma^2 a_o^3\right)}{\left(2\gamma kT\left[\frac{Q^*\sigma}{kT}\right]\right)} \bullet \frac{\left(\frac{1}{\sigma}\right)\left(\frac{d\sigma}{dx}\right)}{\left(\frac{1}{T}\right)\left(\frac{dT}{dx}\right)} \approx 0.01$$

13.10.7 Bubble Growth by Coalescence

Two main contributors;

- *Greenwood and Speight (1963)*
- *Gruber (1967)*

Both assumed ;
- *perfect gas*
- *mechanical equilibrium*
- *Surface diffusion*
- *Random or gradient migration*
- *No resolutioning*
- *No pinning*

Greenwood and Speight Model

- *Did not consider directed motion;*

1.) Post Irradiation Annealing
- **Perfect Gas**
- **No Size Distribution**

$$R = 1.48\left(\frac{a_o^4 D_s MkT}{\gamma}\right)^{\frac{1}{5}} t^{\frac{1}{5}}$$

number of gas atoms/cc

2.) In -Pile

$$Y_{Xe}Ft = mN$$

$$\frac{dN}{dt} = \frac{Y_{Xe}\dot{F}}{m} - 16\pi RD_b N^2$$

assumes that all bubbles are born at R

----

after several steps;

$$R = 1.28\left[\frac{a_o^4 D_s Y_{Xe} \dot{F} kT}{\gamma}\right]^{\frac{1}{5}} t^{\frac{2}{5}}$$

and swelling

$$\frac{\Delta V}{V} = 1.48\left(a_o^4 D_s\right)^{\frac{1}{5}}\left[Y_{Xe} \dot{F}\left(\frac{kT}{2\gamma}\right)\right]^{\frac{6}{5}} t^{\frac{7}{5}}$$

This over predicts the swelling because it does not account for gas atoms escaping

Gruber's Method

He considered the

a.) production, and

b.) destruction of m sized bubbles

After a great deal of more exact formulations;

$$R = 1.32\left(\frac{a_o^4 D_s m kT}{\gamma}\right)^{\frac{1}{5}} t^{\frac{1}{5}}$$

remember that S&G used 1.48

Figure 13.22

Note how much more effective coalescence is than single atom absorption

However both predictions are too optimistic because of neglecting of pinning to dislocations and G.B.'s

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Improvements

$$\frac{dC_m}{dt} = k_{1,m-1}CC_{m-1} - k_{1,m}CC_m - b'C_m$$
$$+\frac{1}{2}\sum\left(1+\delta_{j,m/2}\right)k_{m-j,j}C_{m-j}C_j$$
$$-\sum\left(1+\delta_{j,m}\right)k_{m,j}C_mC_j$$

But still have not included

- **spatial variations of defect concentration**
- **No pinning**

13.11 Pinning of Bubbles by Dislocations and Grain Boundaries

- **Vacancy Clusters**
- **Interstitial Clusters**
- **Precipitates of FP**
- **Dislocation Lines**
- **Grain Boundaries**

Model see figure 13.23 for dislocations

$$F_b = 2t_d \cos F$$

line tension

If dislocation and temperature gradient is perpendicular, then,

$$R_d = \left\{ \frac{a_o^3 b^2 G T}{\pi Q_s^* \left(\frac{dT}{dx} \right)} \right\}^{\frac{1}{3}}$$

critical pulloff radius

<u>Grain</u> <u>Boundaries</u>

See Figure 13.24

let γ_{gb} = grain boundary tension

$$F_b = 2\pi R \gamma_{gb} \sin \Phi \cos \Phi$$

when γ = 300 dynes/cm
critical radius = 4000 Å

Study Figure 13.25 for critical bubble radii

- **Note that surface diffusion is more important in UO_2**

- **Because of better thermal conductivity, there is a lower dT/dx**

13.12 Bubl Code

(Transport) • Grass Code - C.Y. Li - coalescence

(Monte Carlo) • Bubl Code - Nicols - includes pinning

In Bubl code

1.) Bulk coalescence neglected
2.) Resolution neglected
3.) Nucleation ignored

Cell approach - Fig. 13.26 - size of grains

- **all gas starts out as small uniform sized bubbles**

- **Coalescence can occur on dislocation by adjacent bubbles growing or by flux of incident bubbles**

- **Bubbles move until they hit GB**

- **Released at cracks**

Swelling due to

1.) Bubbles at dislocations

2.) Bubbles in transit from disloc. to GB

3.) Bubbles trapped at GB

4.) Bubbles in transit from GB to cracks