Relation of Currents between Discrete Lattice Hopping Model and Continuum Diffusion Model on Oxidation of Alloys

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In the high temperature oxidation forming the thick oxide scale, the phenomenological continuum linear diffusion flux for low electric field under the electrical potential[1] has been used like well known Wagner's theory on pure metal[2] and binary alloys[3]. On the other hand, the current of the discrete lattice hopping model[4,5,6] for large electric field has been applied to very thin oxide film on pure metals. Here, we discussed the relation between the ion current in the oxide film on binary alloy according to the discrete lattice multi-element hopping model under the large electric field and the ion flux in the oxide scale by the continuum diffusion model for low electric field under the electrochemical potential. Finally, the expression of activity coefficient in electrical potential by various kinds of physical constants has been derived by the low electric field limit approximation and the continuum approximation on the ion current in the oxide film on binary alloys of the discrete lattice multi-element hopping model.

We propose the discrete lattice multi-element hopping model on the initial oxidation of alloys which is based on Fromhold's theory[6], then, the ion currents in the thin film on alloys of the initial oxidation can be generally expressed as follows.

$$J_k^{(s)} = \nu^{(s)} \cdot n_{k-1}^{(s)} \cdot \left[\frac{n_k^{(s)}}{\sum_{l=1}^{r} n_k^{(l)}} exp\left(-\frac{W^{(ss)} - Z^{(s)} e a^{(ss)} E_k}{k_B T} \right) + \sum_{t \neq s}^{r} \frac{n_k^{(t)}}{\sum_{l=1}^{r} n_k^{(l)}} exp\left(-\frac{W^{(st)} - Z^{(s)} e a^{(st)} E_k}{k_B T} \right) \right]$$
$$- \nu^{(s)} \cdot n_k^{(s)} \left[\frac{n_{k-1}^{(s)}}{\sum_{l=1}^{r} n_{k-1}^{(l)}} exp\left(-\frac{W^{(ss)} + Z^{(s)} e a^{(ss)} E_k}{k_B T} \right) + \sum_{t \neq s}^{r} \frac{n_{k-1}^{(t)}}{\sum_{l=1}^{r} n_{k-1}^{(l)}} exp\left(-\frac{W^{(ts)} - Z^{(s)} e a^{(ts)} E_k}{k_B T} \right) \right] \quad (1)$$

In the above expression of the current of s-th species, symbols are common ones[6], except for $W^{(st)}$ of potential barrier height and $a^{(st)}$ of the distance between s-th and t-th cations and so on. We assume here that s,t = A, B (binary alloy) and $a = a^{(AA)} = a^{(AB)} = a^{(BB)} = a^{(BA)}$. Then, the current of A-th cation can be shown from Eq.(1) as follows.

$$J_k^{(A)} = \nu^{(A)} exp\left(-\frac{W^{(AA)}}{k_B T} \right) \left[n_{k-1}^{(A)} \frac{n_k^{(A)} + n_k^{(B)} \alpha_A^{AB}}{n} exp\left(\beta^{(A)} E_k\right) - n_k^{(A)} \frac{n_{k-1}^{(A)} + n_{k-1}^{(B)} \alpha_A^{BA}}{n} exp\left(-\beta^{(A)} E_k\right) \right], \quad (2)$$

where

$\alpha_A^{AB} = exp\left(\left(W^{(AA)} - W^{(AB)}\right)/k_B T\right)$, $\beta^{(A)} = Z^{(A)} ea/k_B T$,
$\alpha_A^{BA} = exp\left(\left(W^{(AA)} - W^{(BA)}\right)/k_B T\right)$ and $n = n_k^{(A)} + n_k^{(B)}$.

The above ion current Eq. (2) can be followed if potential barriers are symmetric, i.e., $\alpha_A^{AB} = \alpha_A^{BA}$

$$J_k^{(A)} = \nu^{(A)} exp\left(-\frac{W^{(AA)}}{k_B T} \right) \left[\alpha_A^{AB} \left\{ n_{k-1}^{(A)} exp\left(\beta^{(A)} E_k\right) - n_k^{(A)} \cdot exp\left(-\beta^{(A)} E_k\right) \right\} + \left(1 - \alpha_A^{AB}\right) \frac{n_{k-1}^{(A)} n_k^{(A)}}{n} \left\{ exp\left(\beta^{(A)} E_k\right) - exp\left(\beta^{(A)} E_k\right) \right\} \right] \quad (3)$$

We expand the exponential terms of electric field in the above equation and if the square term of the electric field is very small, i.e., $\left(\beta^{(A)} E_k\right)^2 << 1$, then, Eq. (3) can be shown as follows.

$$J_k^{(A)} = \nu^{(A)} exp\left(-\frac{W^{(AA)}}{k_B T} \right) \left[\alpha_A^{AB} \left\{ \left(n_{k-1}^{(A)} - n_k^{(A)}\right) + \left(n_{k-1}^{(A)} + n_k^{(A)}\right) \cdot \left(\beta^{(A)} E_k\right) \right\} + \left(1 - \alpha_A^{AB}\right) \frac{n_{k-1}^{(A)} n_k^{(A)}}{n} 2\left(\beta^{(A)} E_k\right) \right] \quad (4)$$

Here, we use the next continuum approximate equations[5].

$n_{k-1}^{(A)} - n_k^{(A)} \cong -4a^2 \left[\partial C(x)/\partial x\right]_{x=x_k}$,

$n_{k-1}^{(A)} + n_k^{(A)} \cong 4aC(x_k)$ and $E_k \cong -\left[\partial V(x)/\partial x\right]_{x=x_k}$

Eq. (4) can be finally derived using the definition that

$$D^{(A)} = 4a^2 \nu^{(A)} exp\left(-\frac{W^{(AA)}}{k_B T} \right).$$

$$J_k^{(A)} = -D^{(A)} C^{(A)}(x) \left[\frac{\partial \ln C^{(A)}(x)}{\partial x} + \frac{Z^{(A)} e}{k_B T} \frac{\partial V}{\partial x} + \left(\alpha_A^{AB} - 1\right) \cdot \left\{ \frac{\partial \ln C^{(A)}(x)}{\partial x} + \frac{Z^{(A)} e}{k_B T} \left\{ 1 - \frac{C^{(A)}(x)}{C} \right\} \left\{ 1 - a^2 \left(\frac{\partial \ln C^{(A)}(x)}{\partial x} \right)^2 \right\} \cdot \frac{\partial V}{\partial x} \right\} \right] \quad (5)$$

On the other hand, the flux by the continuum diffusion model for low field with the electrical potential can be definitely expressed as follows[1].

$$J^{(A)} = -D^{(A)} C^{(A)}(x) \left[\frac{\partial \ln \gamma^{(A)} C^{(A)}(x)}{\partial x} + \frac{Z^{(A)} e}{k_B T} \frac{\partial V}{\partial x} \right] \quad (6)$$

So, we can derive the expression of activity coefficient from comparing Eq. (5) and Eq. (6).

$$\frac{\partial \ln \gamma^{(A)}}{\partial x} = \left(\alpha_A^{AB} - 1\right) \left[\frac{\partial \ln C^{(A)}(x)}{\partial x} + \frac{Z^{(A)} e}{k_B T} \left\{ 1 - \frac{C^{(A)}(x)}{C} \left\{ 1 - a^2 \left(\frac{\partial \ln C^{(A)}(x)}{\partial x} \right)^2 \right\} \right\} \frac{\partial V}{\partial x} \right] \quad (7)$$

We will be able to express the activity coefficients under various kinds of conditions used in the electrical potential for showing the ion flux of high temperature oxidation by the above Eq. (7).

References

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