Initial Oxidation Rate Law of Binary Alloy s with Equal Ion Valence

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   The studies on initial oxidation of materials are important in elucidating the oxidation mechanism in the thin film stage and on the basis of passive film growth. Historical model on initial oxidation phenomena of pure metals in thin film stage was firstly proposed by Mott[1], which was expanded and elaborated upon by Cabrera and Mott[2]. This model was referred to as the inverse logarithmic law of the Mott-Cabrera theory. The Mott theory was expanded to taking in the contribution of ionic concentration gradient to the nonlinear diffusion current by Fromhold[3]. He also proposed the hopping model based on the discrete lattice and presented the results of numerical analysis[3]. However, theories on the initial oxidation of materials have been confined to pure metals. Here, we derived analytically the initial oxidation rate law of binary alloys, which produced the single layer solid solution oxide film with the equal valence of ions.

   We propose the discrete lattice multi-element hopping model, then, the ion currents in the thin film on alloys of the initial oxidation can be generally expressed as follows.

$$J_k^{(s)} = \nu^{(s)} \cdot n_{k-1}^{(s)} \cdot \left[\frac{n_k^{(s)}}{\sum\limits_{l=1}^{r} n_k^{(l)}} exp\left(-\frac{W^{(ss)} - Z^{(s)} ea^{(ss)} E_k}{k_B T} \right) \right.$$

$$\left. + \sum\limits_{t \neq s}^{r} \frac{n_k^{(t)}}{\sum\limits_{l=1}^{r} n_k^{(l)}} exp\left(-\frac{W^{(st)} - Z^{(s)} ea^{(st)} E_k}{k_B T} \right) \right]$$

$$- \nu^{(s)} \cdot n_k^{(s)} \left[\frac{n_{k-1}^{(s)}}{\sum\limits_{l=1}^{r} n_{k-1}^{(l)}} exp\left(-\frac{W^{(ss)} + Z^{(s)} ea^{(ss)} E_k}{k_B T} \right) \right.$$

$$\left. + \sum\limits_{t \neq s}^{r} \frac{n_{k-1}^{(t)}}{\sum\limits_{l=1}^{r} n_{k-1}^{(l)}} exp\left(-\frac{W^{(ts)} - Z^{(s)} ea^{(ts)} E_k}{k_B T} \right) \right] \quad (1)$$

In the above expression of the current of s-th species, symbols are common ones[3], 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 = A, B (binary alloy), $Z = Z^{(A)} = Z^{(B)}$ (i.e., equal ionic valence),

$a = a^{(AA)} = a^{(AB)} = a^{(BB)} = a^{(BA)}$ and $E_k = E_0 = V / X$

(i.e., homogeneous electric field). Then, the current of A-th cation can be shown from Eq.(1) as follows, if a strong electric field can be set up (i.e., $ZeaE_0 \gg k_B T$).

$$J_k^{(A)} = \nu^{(A)} \cdot n_{k-1}^{(A)} \cdot \left[\frac{n_k^{(A)}}{n} exp\left(-\frac{W^{(AA)} - ZeaE_0}{k_B T} \right) \right.$$

$$\left. + \frac{n^{(B)}}{n} \cdot exp\left(-\frac{W^{(AB)} - ZeaE_0}{k_B T} \right) \right] \quad (2)$$

The current of B-th cation can be expressed as well. The initial oxidation rate of oxide film growth on binary alloy can be defined as follows[3]. $\dfrac{dX}{dt} = \Omega \cdot \left\{ J_k^{(A)} + J_k^{(B)} \right\}$ (3)

By substituting Eq. (2) and others into Eq. (3), the initial oxidation rate of binary alloy (A-B) becomes

$$\frac{dX}{dt} = u\left(n_{k-1}^{(A)}, u_k^{(A)} \right) \cdot exp\left(X_1 / X \right)$$

$$= \Omega \cdot \nu^{(B)} \cdot exp\left(-\frac{W^{(BB)}}{k_B T} \right) \cdot u_0 \left(n_{k-1}^{(A)}, n_k^{(A)} \right) \cdot exp\left(X_1 / X \right)$$

(4)

In the Eq. (4) $X_1 = ZeaV / k_B T$, Ω volume per a cation, and $\nu^{(B)}$ jump frequency and also u_0 is shown as follows.

$$u_0\left(n_{k-1}^{(A)}, n_k^{(A)} \right) = n_{k-1}^{(A)} \cdot \left[\nu_B^A \cdot \frac{n_k^{(A)} \cdot \alpha_B^A + \left(n - n_k^{(A)} \right) \cdot \alpha_B^{AB}}{n} \right.$$

$$\left. + \frac{n - n_{k-1}^{(A)}}{n_{k-1}^{(A)}} \cdot \frac{\left(n - n_k^{(A)} \right) + n_k^{(A)} \cdot \alpha_B^{BA}}{n} \right] \quad (5)$$

where $\nu_B^A = \dfrac{\nu^{(A)}}{\nu^{(B)}}$, $\alpha_B^A = exp\left(\dfrac{W^{(BB)} - W^{(AA)}}{k_B T} \right)$ and so on.

Integrating Eq. (4) yields $t + t_0 = \dfrac{1}{u} \int\limits_0^X exp\left(-X_1 / x \right) dx$ (6)

If we replace x=X/y, Eq. (6) can be translated as follows.

$$\frac{u}{X} \cdot \left(t + t_0 \right) = \int\limits_1^\infty exp\left(-\frac{X_1}{X} \cdot y \right) \cdot y^{-2} dy \quad (7)$$

This integral of the right side is the exponential integral[4] as same as R. Ghes used to check numerically the inverse logarithmic law of Mott-Cabrera theory in detail[5]. The exponential integral can be approximated by the next expansion equation [5].

$$E_n(z) \cong z^{-1} \cdot exp(-z) \left[1 - n \cdot z^{-1} + O\left(z^{-2} \right) \right] \quad (8)$$

Since $z = X_1 / X \gg 1$, the above approximate expansion equation becomes as follows in the case of n=2.

$$E_2(z) \cong z^{-1} \cdot exp(-z) \quad (9)$$

Therefore, the initial oxidation rate law of binary alloys with equal ionic valence can be obtained as follows.

$$\frac{1}{X} = -\frac{1}{X_1} \cdot ln\left(\frac{t}{X^2} \right) - \frac{1}{X_1} \cdot ln\left[X_1 \cdot u\left(n_{k-1}^{(A)}, u_k^{(A)} \right) \right] \quad (10)$$

   The above initial oxidation rate law depends on areal density distribution in the oxide film. If metal ion A is dilute, the areal density $n_k^{(A)}$ can be obtained as the extended theory of the single hopping model[3] under the steady state condition and homogeneous-field limit.

$$n_k^{(A)} = n_0^{(A)} + \left(n_N^{(A)} - n_0^{(A)} \right) \cdot \frac{\gamma_N - C_{eff}}{\gamma_k - C_{eff}} \cdot \frac{\gamma_k - 1}{\gamma_N - 1} \quad (11)$$

where $n_0^{(A)}$ and $n_N^{(A)}$ are areal densities at alloy/oxide-film and oxide-film/gas interfaces respectively,

$\gamma_k = exp\left(2ZeaE_0 k / k_B T \right)$, $C_{eff} = \left(\nu_B^A \alpha_B - 1 \right) / \left(\alpha_B - 1 \right)$.

   Consequently, equations (10) and (11) mean that the inverse logarithmic type initial oxidation rate law of dilute binary alloys can be expressed by the areal densities at the both interfaces and physical constants.

References
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