Void Formation Induced by the Divergence of the Diffusive Ionic Fluxes in Metal Oxides Under Chemical Potential Gradients

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ABSTRACT

When metal oxides are exposed to chemical potential gradients, ions are driven to diffusive mass transport. During this transport process, the divergence of ionic fluxes offers the formation/annihilation of oxides. Therefore, the divergence of ionic flux may play an important role in the void formation in oxides. Kinetic equations were derived for describing chemical potential distribution, ionic fluxes and their divergence in oxides. The divergence was found to be the measure of void formation. Defect chemistry in scales is directly related to the sign of divergence and gives an indication of the void formation behavior. The quantitative estimation on the void formation was successfully applied to a growing magnetite scale in high temperature oxidation of iron at 823 K.

Key words: Chemical potential distribution, Divergence of ionic fluxes, Void formation, Magnetite, Volume fraction of voids in oxide scales

1. Introduction

In many processes operated at elevated temperatures, metal oxides, $M_{a}O_{b}$, are frequently exposed under chemical potential gradients. The typical processes are energy conversion with solid oxide fuel cell (SOFC) and gas separation with a membrane of metal oxide. The ions in the metal oxide are mobile at the operation temperature as shown in Fig. 1(a). At the left side where the oxygen chemical potential is low, metal oxide dissociates as

$$M_{a}O_{b} \rightarrow aM^{2+} + \frac{b}{2}O_{2} + 2ae^{-}$$  (1)

and the resulting metal cation migrates to the right side with high oxygen chemical potential where the reverse reaction of (1) takes place. This process forces the membrane into movement from the side with lower oxygen potential to that with higher oxygen potential. Simultaneously oxygen enters into the metal oxide at the right side as

$$O_{2} + 4e^{-} \rightarrow 2O^{2-}$$  (2)

and the resulting oxide ion moves to the left side where the reverse reaction of (2) takes place. This gives the oxygen permeation.

In the case of the complex oxide with more than two types of cations, all cations tend to move to the right hand side with higher chemical potential of oxygen. The diffusivities of cations differ each other. The more rapid diffusing cation will be enriched at the right hand side, which phenomenon is called as the kinetic demixing. If the chemical potential difference becomes larger, the oxides may kinetically decompose. Schmarzried and his coworkers have extensively dealt with these phenomena and reviewed in his book.

In high temperature oxidation of metals as shown in Fig. 1(b), the oxide scale is exposed to chemical potential gradients. The ionic constituents are driven by the potential gradients and diffuse through the oxide. The metal ion diffuses from the lower oxygen potential side at the metal/scale interface to the higher side at the scale/gas interface. The oxide ion diffuses to the opposite direction. This situation is basically the same as that in Fig. 1(a) except for the fact that metal

\[ \text{Fig. 1. Schematic illustration of a metal oxide under oxygen potential difference. (a) oxide membrane, (b) high temperature oxidation of metals.} \]
ion is injected at the left hand side with low chemical potential of oxygen. These kinetic processes have been analyzed under quasi-steady state condition where divergence of ionic flux is ignored. However, concentration of point defects in metal oxides depends basically on oxygen potential so that diffusion coefficients vary in oxides under a potential distribution. This situation gives non-zero divergence, resulting in microstructure development such as void formation.

Fig. 2 shows the cross section of a ferritic steel of Fe-9Cr in a heat exchanger in a power plant after service around 848 K for 70000 h. The steel was oxidized by steam. The outer scale is Fe$_3$O$_4$ and the inner one is (Fe,Cr)$_3$O$_4$. Many voids are observed in the outer scale and voids are accumulated at the interface between the inner and outer scales. The void formation may determine performance and life of the electrochemical devices at high temperatures. This paper is the modified review from the previous one$^2$ and presents equations describing mass transport and the validity of the equations confirmed by observation of high temperature oxidation of metals.

Wagner$^3$ presented the rigorous expression of the parabolic rate constant for high temperature oxidation of metals. This expression was implicitly assumed the steady state diffusion with the divergence to be zero. However, void formation and additional oxide growth within the scale may be caused by the non-zero divergence of fluxes of constituent ions. Maruyama et al.$^4$ proposed that void formation in a growing oxide scale formed in high temperature oxidation of metals is explained by the evaluation of the divergence of ionic fluxes. Ionic transport is driven by the electrochemical potential gradients and the electrochemical potential is reduced to the chemical potential in oxide scales of electronic conductor. The chemical potential distribution was estimated under the assumption that the major ionic flux is responsible to establish the distribution as a first approximation. They have also demonstrated its validity in magnetite scale formed in high temperature oxidation of iron at 823 K. They have improved this treatment in which all ionic fluxes were taking account into the calculation of the chemical potential distribution and quantitatively explained the position and the volume of voids formed in the magnetite scale.$^5$

This paper describes how well the divergence of ionic fluxes explains void formation, the relation between the defect chemistry and the void formation in the scale.

2. Mass transport in an ionic compound of $M_a^zX_b^{2z}$ under chemical potential gradients and void formation$^6$

2.1. General background

In the crystalline compound of $M_a^zX_b^{2z}$ being close to stoichiometry, there are charged species of the metal cation with the ionic charge of $z_M$ (positive integer), the non-metal anion with the ionic charge of $z_X$ (negative integer), excess hole with $z_h^e (= +1)$ and excess electron with $z_e^e (= -1)$. The following three relations are existed.

$$a z_M^e + b z_X^e = 0$$ (3)
$$c_M^e z_M^e + c_X^e z_X^e = 0$$ (4)
$$\frac{c_M^e}{a} = \frac{c_X^e}{b} = \frac{1}{V_{M_a^zX_b^{2z}}}$$ (5)

where $c$ is the concentration (mol m$^{-3}$) and $V_{M_a^zX_b^{2z}}$ is the molar volume of $M_a^zX_b^{2z}$.

If the compound is placed under the chemical potential gradients, the electrochemical potential gradients appear through the compound. The charged species in the electrochemical potential field are driven and forced to move. In the case of the compound to be a metal oxide (Fig. 3), the cation flows from the lower oxygen potential side toward the higher side and anion flows in the opposite way. During the mass transport process, the stoichiometric ratio of cation and anion, i.e., the ratio of sublattice sites shall be maintained and the change of the amount of the compound is related to the divergences of ionic fluxes in the following manner.

$$\frac{\partial n_{M_a^zX_b^{2z}}}{\partial t} = - \frac{1}{a} \frac{\partial J_M^e}{\partial x} = - \frac{1}{b} \frac{\partial J_X^e}{\partial x}$$ (6)
where the left-hand term is the change in number of mole of the compound, $M_{a}X_{b}$, and $J_{i}$ (mol/m²s) is the flux of a species, i. This relation gives the divergences of flux of ionic charge to be zero.

$$\frac{\partial (z_{M}J_{M} + z_{X}J_{X})}{\partial X} = -(az_{M} + bz_{X})(\frac{\partial n_{M,X}}{\partial t}) = 0$$  \hspace{1cm} (7)

Therefore, the ionic charge flux is independent of x.

$$z_{M}J_{M} + z_{X}J_{X} = H$$  \hspace{1cm} (8)

where $H$ is a constant, independent of position.

In the case of negligibly small interactions between constituents, the flux of a species, i expressed as follows

$$J_{i} = -c_{i}B_{i} \frac{\partial \eta_{i}}{\partial X}$$  \hspace{1cm} (9)

where $B$ is the absolute mobility (mol/J⁻¹m²s⁻¹), $\eta$ the electrochemical potential (Jmol⁻¹) and $x$ the coordination (m). The origin of the coordination is fixed at the initial surface of metals. The Nernst-Einstein relation gives

$$\frac{\partial \eta_{e}}{\partial X} + \frac{\partial \eta_{h}}{\partial X} = 0$$  \hspace{1cm} (10)

where $D$ is the self diffusion coefficient (m²s⁻¹), $R$ the gas constant (8.31 Jmol⁻¹K⁻¹) and $T$ the absolute temperature (K). The electrochemical potential is defined as

$$\eta_{i} = \mu_{i} - z_{i}\eta_{e}$$  \hspace{1cm} (11)

where $\mu$ is the chemical potential (Jmol⁻¹) and $\eta_{e}$ the electrochemical potential of electron.

Through the oxide, the following electro-neutrality condition shall be maintained.

$$z_{M}J_{M} + z_{X}J_{X} + z_{e}J_{e} + z_{h}J_{h} = 0$$  \hspace{1cm} (12)

where $e$ and $h$ are excess electron and hole, respectively. The Gibbs-Duhem relation gives

$$c_{M} \frac{\partial \eta_{M}}{\partial X} + c_{X} \frac{\partial \eta_{X}}{\partial X} = c_{M} \frac{\partial \mu_{M}}{\partial X} + c_{X} \frac{\partial \mu_{X}}{\partial X} = 0$$  \hspace{1cm} (13)

2.2. Chemical potential distribution in the compound, $M_{a}X_{b}$

$$H = z_{M}J_{M} + z_{X}J_{X}$$

$$= z_{M}(-c_{M}B_{M} \frac{\partial \mu_{M}}{\partial X}) + z_{X}(-c_{X}B_{X} \frac{\partial \mu_{X}}{\partial X})$$

$$+ z_{e}c_{e}B_{e} \frac{\partial \mu_{e}}{\partial X} + z_{h}c_{h}B_{h} \frac{\partial \mu_{h}}{\partial X}$$

$$= -\frac{1}{x}(z_{M}c_{M}B_{M} + z_{X}c_{X}B_{X}) \frac{\partial \mu_{M}}{\partial X} + (z_{e}c_{e}B_{e} + z_{h}c_{h}B_{h}) \frac{\partial \mu_{e}}{\partial X}$$

$$+ \frac{1}{x}(z_{M}c_{M}B_{M} + z_{X}c_{X}B_{X}) \frac{\partial \mu_{M}}{\partial X} + (z_{e}c_{e}B_{e} + z_{h}c_{h}B_{h}) \frac{\partial \mu_{e}}{\partial X}$$

$$= -\frac{1}{x}(z_{M}c_{M}B_{M} + z_{X}c_{X}B_{X}) \frac{\partial \mu_{M}}{\partial X} + (z_{e}c_{e}B_{e} + z_{h}c_{h}B_{h}) \frac{\partial \mu_{e}}{\partial X}$$

(14)

For the sake of brevity, the following simplification is made

$$\alpha = z_{a}c_{M}B_{M} + z_{X}c_{X}B_{X}$$  \hspace{1cm} (15)

and $\alpha$ is related to an ionic contribution to the charge transport.

The reaction between excess electron and hole is expressed as

$$null = e^{-} + h^{+}$$  \hspace{1cm} (16)

The sum of electrochemical potentials of hole and electron is equal to the sum of the chemical potentials as shown in the following equation.

$$\frac{\partial \eta_{e}}{\partial X} + \frac{\partial \eta_{h}}{\partial X} = 0$$  \hspace{1cm} (17)

The Eqs. (13), (8) and (17) provides

$$-H = z_{e}J_{e} + z_{h}J_{h}$$

$$= (-1)(-c_{e}B_{e} \frac{\partial \eta_{e}}{\partial X}) + (1)(-c_{h}B_{h} \frac{\partial \eta_{h}}{\partial X})$$

$$= (c_{e}B_{e} + c_{h}B_{h}) \frac{\partial \eta_{e}}{\partial X} = \beta \frac{\partial \eta_{e}}{\partial X}$$  \hspace{1cm} (18)

For the sake of brevity, the following simplification is made

$$\beta = c_{e}B_{e} + c_{h}B_{h}$$  \hspace{1cm} (19)

and $\beta$ is related to an electronic contribution to the charge transport.

The Eqs. (14) and (18) gives

$$-z_{X}H = \frac{\alpha \beta}{\alpha + \beta} \frac{\partial \mu_{X}}{\partial X}$$  \hspace{1cm} (20)

Integration of Eq. (20) from $\ell$ ($\mu_{X}^{i}$) to $L$ ($\mu_{X}^{ii}$) gives

$$(-z_{X}H) \int_{\ell}^{L} \frac{\partial \xi}{\partial X} = -z_{X}H(L - \ell) = \int_{\ell}^{L} \frac{\alpha \beta}{\alpha + \beta} \frac{\partial \mu_{X}}{\partial X}$$

(21)

On the other hand, integration of Eq. (20) from $\ell$ ($\mu_{X}^{i}$) to $x$ ($\mu_{X}^{ii}$) gives

$$(-z_{X}H) \int_{\ell}^{x} \frac{\partial \xi}{\partial X} = -z_{X}H(x - \ell) = \int_{\ell}^{x} \frac{\alpha \beta}{\alpha + \beta} \frac{\partial \mu_{X}}{\partial X}$$

(22)

By dividing Eq. (22) by Eq. (21), one obtains the chemical potential distribution

$$\frac{x - \ell}{L - \ell} = \frac{\int_{\ell}^{x} \frac{\alpha \beta}{\alpha + \beta} \frac{\partial \mu_{X}}{\partial X}}{\int_{\ell}^{L} \frac{\alpha \beta}{\alpha + \beta} \frac{\partial \mu_{X}}{\partial X}} = \frac{\int_{\ell}^{x} \frac{\alpha \beta}{\alpha + \beta} \frac{\partial \mu_{X}}{\partial X}}{k}$$

(23)

The differentiation of Eq. (23) gives the chemical potential gradient of X as

$$\frac{\partial \mu_{X}}{\partial X} = k(\alpha + \beta) \frac{\partial \mu_{X}}{\partial X}$$

(24)

and the Eqs. (18) and (20) gives the electrochemical potential gradient as

$$\frac{\partial \eta_{X}}{\partial X} = \frac{\beta}{\alpha + \beta} \frac{\partial \mu_{X}}{\partial X} = t_{e} \frac{\partial \mu_{X}}{\partial X} = \frac{k}{\alpha \ell}$$

(25)

where $t_{e}$ is the electronic transference number.
2.3. Formation of voids and the excess compound in scales

The change in number of mole of the compound in a unit time \( \frac{\partial n_{M,X}}{\partial t} \) is a measure of microstructure development.

The negative value gives voids and the positive one gives the excess compound.

From the Eqs. (10) and (25), the flux of non-metal is expressed as

\[
J_X = -c_X B_X \frac{\partial \eta_X}{\partial t} = -\frac{k c_X B_X}{\alpha (L - \ell)} \tag{26}
\]

The change in number of mole of the compound in a unit time can be evaluated using the divergence of the flux,

\[
\frac{\partial n_{M,X}}{\partial t} = \frac{1}{b} \frac{\partial J_X}{\partial t} = \frac{k c_X}{b (L - \ell)} \frac{\partial B_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t}
\]

\[
= k c_X (\alpha + \beta) \frac{\partial B_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= (\alpha + \beta b k (z_X)^2) c_X c_Y B_X B_X
\]

\[
= \frac{1}{b} \frac{\partial B_X}{\partial \mu_X} \left( 1 - \frac{1}{B_X} \frac{\partial B_M}{\partial \mu_X} \right) \tag{27}
\]

When the X in the crystal is equilibrated with X in the gaseous atmosphere,

\[
2X = X
\]

the following thermodynamic relations are valid,

\[
2 \mu_X = \mu_X + RT \ln P_{X}\]

\[
2 \mu_X = \hat{\mu}_X = RT \partial (\ln P_{X}) \tag{29}
\]

Using Eqs. (11) and (29), the last term of the right hand side in the Eq. (27) is written as

\[
\frac{1}{B_X} \frac{\partial B_X}{\partial \mu_X} = \frac{\partial \ln B_X}{\partial \mu_X} - \frac{\partial \ln B_M}{\partial \mu_X}
\]

\[
\frac{1}{RT} \frac{\partial \ln D_X}{\partial \ln P_X} \frac{\partial \ln P_X}{\partial \mu_X}
\]

\[
\frac{2}{RT} \frac{\partial \ln D_X}{\partial \ln P_X} \frac{\partial \ln D_X}{\partial \ln P_X}
\]

\[
1 \frac{\partial B_X}{\partial \mu_X} \frac{\partial B_M}{\partial \mu_X} \frac{\partial \mu_X}{\partial t}
\]

Finally, the Eq. (27) is written as

\[
\frac{\partial n_{M,X}}{\partial t} = 2 (\alpha + \beta b k (z_X)^2) c_X c_Y D_X D_X
\]

\[
= \frac{1}{z_X} \frac{\partial \ln D_X}{\partial \ln P_X} \frac{\partial \ln D_X}{\partial \ln P_X}
\]

\[
= \frac{1}{z_X} \frac{\partial \ln D_X}{\partial \ln P_X} \frac{\partial \ln D_X}{\partial \ln P_X}
\]

\[
1 \frac{\partial B_X}{\partial \mu_X} \frac{\partial B_M}{\partial \mu_X} \frac{\partial \mu_X}{\partial t}
\]

\[
= \frac{2}{RT} \frac{\partial \ln D_X}{\partial \ln P_X} \frac{\partial \ln D_X}{\partial \ln P_X}
\]

\[
= \frac{2}{RT} \frac{\partial \ln D_X}{\partial \ln P_X} \frac{\partial \ln D_X}{\partial \ln P_X}
\]

3. Kinetic and thermodynamic parameters in high temperature oxidation of metals

In the high temperature oxidation of metals, the growth of the outer scale is caused by the outward diffusion of cation and that of inner scale by the inward diffusion of anion.

3.1. Growth rate of the outer scale

The growth rate of the outer scale is equal to the velocity of movement of the interface II and is described as

\[
\frac{dL}{dt} = V_{Mox} \frac{1}{a} J_X^1 = -V_{Mox} c_X B_X \frac{\partial \eta_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= -V_{Mox} b k c_X B_X \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= -V_{Mox} b k c_X B_X \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

where \( V_{Mox} \) is the molar volume of \( M_{ox}^{x}X_{ox}^{x} \). Introduction of Eq. (3) into Eq. (32) gives

\[
\frac{dL}{dt} = V_{Mox} k z_X^2 c_X^2 B_X \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= -V_{Mox} k z_X^2 c_X^2 B_X \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= -V_{Mox} k z_X^2 c_X^2 B_X \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

3.2. Growth rate of the inner scale

The growth rate of the inner scale is equal to the velocity of movement of the interface I and is described as

\[
\frac{dL}{dt} = V_{Mox} \frac{1}{b} J_X^1 = -V_{Mox} c_X B_X \frac{\partial \eta_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t}
\]

\[
= -V_{Mox} k z_X^2 c_X^2 B_X \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= -V_{Mox} k z_X^2 c_X^2 B_X \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

3.3. Ratio of thickness of inner and outer scales

Eqs. (33) and (34) gives the ratio of growth rates of inner and outer scales

\[
\frac{dL}{dt} = \frac{z_X^2 c_X^2 B_X}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= \frac{z_X^2 c_X^2 B_X}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= \frac{z_X^2 c_X^2 B_X}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

The ratio of thickness of inner and outer scales is expressed as

\[
\frac{dL}{dt} = \frac{z_X^2 c_X^2 B_X}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

This fact indicates that the ratio is always constant and determined by the kinetic factors at both interfaces.

3.4. Growth rate of the total scale

\[
\frac{dL}{dt} = \frac{dL}{dt} \frac{dL}{dt} \frac{dL}{dt} \frac{dL}{dt}
\]

\[
= \frac{V_{Mox} k}{V_{Mox} k} \frac{1}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= \frac{V_{Mox} k}{V_{Mox} k} \frac{1}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= \frac{V_{Mox} k}{V_{Mox} k} \frac{1}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]

\[
= \frac{V_{Mox} k}{V_{Mox} k} \frac{1}{z_X^2 c_X^2 B_X} \frac{\partial \mu_X}{\partial \mu_X} \frac{\partial \mu_X}{\partial t} \frac{\partial \mu_X}{\partial t}
\]
where

\[ k_{p \rightarrow o} = \frac{V_{o \rightarrow x} k}{b \alpha^2} \left( \frac{z_m^2 c_m^x B_m^x}{\alpha^2} + \frac{z_n^2 c_n^x B_n^x}{\alpha^2} \right) \]  

(39)

The value in the parenthesis being larger than unity is the indication of the void formation in the scale. Eq. (38) provides the parabolic rate law

\[ (L - \frac{\ell}{2})^2 = 2k_{p \rightarrow o} t \]  

(40)

3.5. Void formation in the scale during oxidation

Amount of voids formed in the scale is related to the difference in fluxes at the interface II and the interface I.

\[ \frac{dV_{\text{void}}}{dt} = \frac{V_{o \rightarrow x}}{b} (J_{\alpha}^x - J_{\alpha}^x) \]

\[ = \frac{V_{o \rightarrow x} k}{b(L - \frac{\ell}{2})} \left( \frac{c_m^x B_m^x}{\alpha^2} - \frac{c_n^x B_n^x}{\alpha^2} \right) \]

\[ = \frac{V_{o \rightarrow x} k}{b(2k_{p \rightarrow o} t)^{\frac{1}{2}}} \left( \frac{c_m^x B_m^x}{\alpha^2} - \frac{c_n^x B_n^x}{\alpha^2} \right) = \left( \frac{V_{o \rightarrow x} k}{2b \alpha^2} \right)^{\frac{1}{2}} \]

\[ \times \left( \frac{z_m^2 (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}} - (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}})}{(\alpha^2 (\alpha^2)^{\frac{1}{2}}} \right) \]

\[ \times \left( \frac{z_m^2 (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}} + z_n^2 (c_n^x B_n^x)^{\frac{1}{2}} (c_m^x B_m^x)^{\frac{1}{2}}}{(\alpha^2 (\alpha^2)^{\frac{1}{2}}} \right) \]

(41)

The integration of Eq. (41) gives

\[ V_{\text{void}}^{\text{ox}} = \left( \frac{2V_{o \rightarrow x} k}{b \alpha^2} \right)^{\frac{1}{2}} \]

\[ \times \left( \frac{z_m^2 (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}} - (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}})}{(\alpha^2 (\alpha^2)^{\frac{1}{2}}} \right) \]

\[ \times \left( \frac{z_m^2 (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}} + z_n^2 (c_n^x B_n^x)^{\frac{1}{2}} (c_m^x B_m^x)^{\frac{1}{2}}}{(\alpha^2 (\alpha^2)^{\frac{1}{2}}} \right) \]

(42)

3.6. Volume fraction of void in scales

The volume fraction of voids in scales \( f_v \) is expressed as

\[ f_v = \frac{V_{\text{void}}^{\text{ox}}}{(L - \frac{\ell}{2}) \times 1 \times 1} \]

\[ = \frac{z_m^2 (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}} - (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}})}{(z_m^2 (c_m^x B_m^x)^{\frac{1}{2}} (c_n^x B_n^x)^{\frac{1}{2}} + z_n^2 (c_n^x B_n^x)^{\frac{1}{2}} (c_m^x B_m^x)^{\frac{1}{2}})} \]

\[ \times \frac{1}{(\alpha^2 (\alpha^2)^{\frac{1}{2}}} \times \frac{1}{(\alpha^2 (\alpha^2)^{\frac{1}{2}}} \]

(43)

This is independent of time because both the volumes of void and scale obey the parabolic law.

4. Relation between and the defect structure in metal oxides

The sign of \( \frac{\partial n}{\partial t} \) is identical to that of the last term in Eq. (31). The negative sign expects the formation of voids. Diffusivities are directly related to defect concentration, \([d]\), as

\[ c_i D_i = [d] D_i \]

(44)

where \( c_i \) and \( D_i \) are the concentration of ion and the defect diffusion coefficient, respectively. These two values are regarded to be constant. Therefore, the last term in Eq. (31) is written as

\[ N = \frac{\partial \ln D_o}{\partial \ln P_{o_2}} - \frac{\partial \ln D_m}{\partial \ln P_{o_2}} = \frac{\partial \ln [d_o]}{\partial \ln P_{o_2}} - \frac{\partial \ln [d_m]}{\partial \ln P_{o_2}} \]

(45)

The typical examples are demonstrated in binary metal oxides which form in high temperature oxidation of metals and alloys.

4.1. Metal oxides with major defects of the Schottky type

Intrinsic electronic defect reaction is

\[ \text{null} = e^+ + h^- \]

(46)

and its equilibrium constant is

\[ K_e = [e^+][h^-] \]

(47)

where \( e^+ \) and \( h^- \) are electron and hole, respectively.

The Schottky-type defect reaction is

\[ \text{null} = aV_{M}^{2+} + bV_{O}^{2+} \]

(48)

and its equilibrium constant is

\[ K_s = [V_{M}^{2+}] [V_{O}^{2+}] \]

(49)

The incorporation of oxygen into the metal deficient oxide is expressed as

\[ \frac{b}{2} O_2 = aV_{M}^{2+} + bO_0^+ + az_m h^- \]

(50)

and the equilibrium constant is

\[ K_{OX} = [V_{M}^{2+}] [h^-]^{az_m} P_{O_2}^b \]

(51)

The electrical neutrality condition is

\[ z_m [V_{M}^{2+}] = [h^-] \]

(52)

and

\[ K_{OX} = z_m [V_{M}^{2+}] ^{az_m} P_{O_2}^b \]

(53)

The vacancy concentration of metal ion is

\[ [V_{M}^{2+}] \propto P_{O_2} \]

(54)

and the vacancy concentration of oxygen ion is

\[ [V_{O}^{2+}] \propto P_{O_2}^{-2(1+2z_m)} \]

(55)

The sign of the Eq. (56) is always negative.

4.2. Metal oxides with major defects of the Frenkel type

The Frenkel type defect reaction in metal ion site is

\[ \frac{\partial \ln [V_{M}^{2+}]}{\partial \ln P_{O_2}} - \frac{\partial \ln [V_{M}^{2+}]}{\partial \ln P_{O_2}} = \frac{1}{2(a + b)} \]

(56)

The sign of the Eq. (56) is always negative.
The anihilation of oxygen from the metal excess oxide is expressed as
\[ \frac{\partial n}{\partial t} - \frac{\partial J}{\partial x} = \text{Negative} \]

and the equilibrium constant is
\[ K = \left[ M^{z_m^*}_b \right] \left[ V_{M}^{z_m^*} \right] \]  

The concentration of metal interstitial ion is
\[ K_{\text{OX}} = z_M \left[ M^{z_m^*}_b \right]^{\left(1+z_m^*\right)} \frac{P_{O_2}^b}{P_{O_2}^b} \]

The vacancy concentration of oxide ion is derived from eqns. (49), (58) and (63),
\[ \left[ V_{O}^{z_o^*} \right] \propto P_{O_2}^{-2(1+z_o^*)} \]

The sign of Eq. (65) depends on the sign of numerator of the last term.

Table 1 summarizes the relation of defect structure and the microstructure development. In the scale of metal deficient oxide, it is expected that voids always form. The typical oxides are NiO, CoO and FeO. Fe\(_3\)O\(_4\) and Cr\(_2\)O\(_3\) under the high oxygen pressures belong to this category because both oxides are metal deficient with metal ion vacancy as a major defect. There are three possibilities in the scale of metal excess oxide. In oxides with \(a > b\) such as Li\(_2\)O, the sign is negative and the void formation is expected. In the case of \(a < b\) such as TiO\(_2\), voids may not form but the excess oxide will nucleate within the oxide resulting in stress generation. Fe\(_3\)O\(_4\) and Cr\(_2\)O\(_3\) under the low oxygen pressures belong to this category because both oxides are metal excess with interstitial metal ion as a major defect. In the case of \(a = b\) (\(\frac{N}{J} = 0\)) such as ZnO with divalent metal interstitials as a major defect, the microstructure is stable without formation of void or excess oxides.

5. Void formation in growing magnetite scale formed on iron at 823 K

In this section, high temperature oxidation of iron was carried out at 823 K and the void formation in growing magnetite scale was discussed in comparison of observation and calculation.

5.1. Evaluation of oxidation behavior by calculation with the reported diffusion coefficients

Prior to experiments, a calculation was carried out to evaluate the oxidation behavior at 823 K in the atmosphere with oxygen chemical potential of the Fe\(_3\)O\(_4\)/FeO\(_2\) equilibrium. The calculation requires the diffusivities of constituent ions as a function of chemical potential (activity). Fig. 4 shows the lattice diffusion coefficients of iron.

Table 1. Defect Structure and the Microstructure Development

<table>
<thead>
<tr>
<th>Defect Structure</th>
<th>Schottky Cation Frenkel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major defects</td>
<td>(M^{z_m^<em>}<em>o) (V</em>{M}^{z_m^</em>})</td>
</tr>
<tr>
<td>Oxides</td>
<td>NiO, CoO, FeO</td>
</tr>
</tbody>
</table>

Fig. 4. Lattice diffusion coefficients of iron and oxide ions.
and oxygen in magnetite. The lattice diffusion coefficient of iron was reported by Recoult and Dieckmann in the following manner,

\[ D_{Fe} / \text{m}^2 \text{s}^{-1} = A a_{O_2}^{2/3} + \frac{B a_{O_2}^{2/3}}{1 + 2K_v a_{O_2}^{2/3}} \]

where \( a_{O_2} \) is the activity of oxygen (\( a_{O_2} = \frac{P_{O_2}}{P} \times 10^{9.8} \) Pa) and \( K_v \) is the equilibrium constant of iron vacancy formation. The parameters of \( A, B \) and \( K_v \) at 823 K were obtained by the extrapolation from reported values to be 8.0 \times 10^{16} (\text{m}^2 \text{s}^{-1}), 2.9 \times 10^6 (\text{m}^2 \text{s}^{-1}) and 4.4 \times 10^7, \) respectively. The predominant defects are the iron interstitial ion at lower oxygen pressure and the iron vacancy at higher oxygen pressure.

The lattice diffusion coefficient of oxide ion was reported by Millot et al. \(^{31} \)

\[ D_{O} / \text{m}^2 \text{s}^{-1} = C\beta_{O_2}^{4/3} + F\beta_{O_2}^{4/6} \]

The values of \( C \) and \( F \) at 823 K are 1.3 \times 10^{-4} (\text{m}^2 \text{s}^{-1} \text{atm}^{-2}) and 5.1 \times 10^{-2} (\text{m}^2 \text{s}^{-1} \text{atm}^{-3}) respectively. The predominant defect is oxide ion vacancy. The contribution of the second term in the right hand side of the Eq. (67) is small enough to be neglected.

Magnetite is a highly electronic conductive oxide (\( \beta >> \alpha \)) so that the term of \( \frac{\partial \beta}{\alpha + \beta} \) in Eq. (20) can be described as \( \alpha \).

Fig. 5 shows the value of \( \alpha \) as a function of chemical potential of oxygen. According to Eq. (23), the chemical potential distribution can be calculated as shown in Fig. 6. Around the normal position of \( \bar{X} = 0.15 \), the slope is extremely steep. This position corresponds to the minimum value of \( \alpha \). Fig. 7 shows the flux of oxide ion as a function of position and the value of \( \frac{\partial n_{Fe}}{\partial t} \) (\( -\frac{\partial n_{Fe}}{\partial x} \)). The value of \( \frac{\partial n_{MO}}{\partial t} \) is positive in the region of \( \frac{X}{X_o} < 0.15 \) where the chemical potential of oxygen is lower than that at which \( \alpha \) exhibits its minimum. The positive value of \( \frac{\partial n_{MO}}{\partial t} \) indicates the formation of oxide in the oxide with generation of compressive stress. On the other hand, the value of \( \frac{\partial n_{MO}}{\partial t} \) is negative in the region of \( \frac{X}{X_o} > 0.15 \) where the chemical potential of oxygen is higher than that at which \( \alpha \) exhibits its minimum. The negative value of \( \frac{\partial n_{MO}}{\partial t} \) expects the formation of voids in the oxide.

5.2. Experimental procedure

Iron sheet was cut into coupons in size of 10 \text{cm} \times 20 \times 1 \text{mm}^3 and annealed at 1123 K for 86.4 ks in vacuum. These coupons were ground with abrasive paper up to #2000 and polished with 4 \text{µm} diamond paste. These samples were oxidized at 823 K for up to 172.8 ks in two different atmospheres of Ar-H2-O2 gas mixtures. The oxygen partial pressure in one atmosphere was 2.5 \times 10^{22} Pa (Low \( P_{O_2} \) atmosphere). Voids may not form at this condition, according to the expectation in the section 5.1. The oxygen partial pressure in the other atmosphere was 4.2 \times 10^{23} Pa (High \( P_{O_2} \) atmosphere). In this condition, the void should form. After the oxidation test, samples were fractured in the liquid nitrogen and fractured surface of the cross-section of the magnetite scale was observed by a scanning electron microscope (SEM). The cross-section of the polished magnetite scale was observed by SEM to determine thickness and volume fraction of voids in the magnetite scale. Voids in the magnetite scale were traced from the photograph on transparent papers and the volume fraction was determined by the area ratio of the voids and scale.

5.3. Results

5.3.1. Morphology of the magnetite scale obtained by high temperature oxidation

Fig. 8 shows the fractured surface of the cross-section of magnetite scale formed on iron for 172.8 ks at 823 K. Morphology of the magnetite scale drastically changes in two atmospheres with different oxygen partial pressures. Voids
are not observed in the magnetite scale formed in low $P_{O_2}$ atmosphere ($P_{O_2} = 2.5 \times 10^{-20}$ Pa). On the other hand, many voids are observed through the magnetite scale formed in high $P_{O_2}$ atmosphere ($P_{O_2} = 4.2 \times 10^{-13}$ Pa).

5.3.2. Parabolic rate constants and the ratio of inner and outer scales

Fig. 9 shows the parabolic plot of total scale thickness. The parabolic rate constants are $5.7 \times 10^{-16}$ m$^2$s$^{-1}$ and $1.3 \times 10^{-15}$ m$^2$s$^{-1}$ at low and high atmospheres, respectively. The ratio of inner and outer scales was 0.22 at high $P_{O_2}$ atmosphere.

5.4. Discussion

5.4.1. Comparison of calculation and observation

The behavior of void formation shown in Fig. 8 was qualitatively explained by the calculation. However, the parabolic rate constants obtained in the section of 5.3.2 were one order of magnitude larger than that calculated from the reported diffusion coefficients mentioned in the section 5.1. Although the calculation was carried out with the lattice diffusivities obtained from single crystals, the oxide scale was actually...
polycrystalline. This fact indicates that grain boundary diffusion strongly affects the scale growth. In this study, effective diffusion coefficients are taking into account.

5.4.2. Effective diffusion coefficients of iron and oxygen in magnetite

The oxide scale is actually polycrystalline in most cases. The grain boundary diffusion may play a significant role in the mass transport through scales. Stubican and Carinci measured grain boundary diffusion of divalent cobalt ion in magnetite and showed that the diffusivity was proportional to $P_{O_2}^{1/2}$ at high oxygen pressures and to $P_{O_2}^{-2}$ at low oxygen pressures. These results indicated that the oxygen potential dependence of cation diffusivity is similar both in grain boundary and lattice in magnetite. One can reasonably assume that the oxygen partial pressure dependence of grain boundary diffusion is as same as that of lattice diffusion, and the effective diffusion coefficients of iron and oxygen in magnetite can be described as follows.

$$D_{Fe}^{\text{eff}} \text{ m}^2 \text{s}^{-1} = A_{Fe}^{\text{eff}} a_{O_2}^{3/2} + B_{Fe}^{\text{eff}} a_{O_2}^{-3/2}$$

$$D_{O}^{\text{eff}} \text{ m}^2 \text{s}^{-1} = C_{O}^{\text{eff}} a_{O_2}^{1/2}$$

where $A_{Fe}^{\text{eff}}$, $B_{Fe}^{\text{eff}}$ and $C_{O}^{\text{eff}}$ are constants which include the contribution of both grain boundary diffusion and lattice diffusion. These parameters can be determined by Eqns. (36) and (41) with the kinetic data shown in the section of 5.3.2.

Fig. 10 shows oxygen chemical potential dependence of effective diffusion coefficients of iron and oxygen in magnetite can be described as follows.

5.4.3. Calculation of the chemical potential distribution, the flux of oxide ion and its divergence

Fig. 11 shows calculated oxygen chemical potential and the flux of oxide ion in magnetite scale formed on iron for 172.8 ks at 823 K. The case of low $P_{O_2}$ atmosphere ($P_{O_2} = 2.5 \times 10^{-20}$ Pa), oxygen chemical potential gradually increases from the $Fe/Fe_3O_4$ interface to the $Fe_3O_4/gas$ interface. The flux of oxide ion is negative because its flowing direction is negative. The amount of the flux of oxide ion gradually decreases from the $Fe_3O_4/gas$ interface to the $Fe/Fe_3O_4$ interface. In the case of high $P_{O_2}$ atmosphere ($P_{O_2} = 4.2 \times 10^{-13}$ Pa), oxygen chemical potential drastically increases at the position of about 10 $\mu$m away from the initial surface. The flux of oxide ion has maximum value because of the maximum gradient of oxygen chemical potential.

Fig. 12 shows the mass change from the divergence of the flux of oxide ion for 172.8 ks at 823 K. The mass change is positive through the magnetite scale in low $P_{O_2}$ atmosphere. It indicates that new oxide formed in the growing magnetite scale and voids are expected not to form in the magnetite scale. In high $P_{O_2}$ atmosphere, the mass change is positive at the range from the $Fe/Fe_3O_4$ interface to the position of 10 $\mu$m away from the initial surface. The mass change becomes negative from this position to the $Fe_3O_4/gas$ interface, indicating the void formation. In particular, the void is preferentially formed at this position. The distribution of the divergence in the scale is similar during oxidation so that this position was close to the initial surface at the beginning of oxidation and moved outward during the oxidation. It indicates that voids are observed in the wide range of magnetite scale.

5.4.4. Calculation of volume fraction of voids in the growing magnetite scale

The Eqns. (42) and (43) describe quantitatively the volume of voids and the volume fraction of voids in growing magnetite scale. The important thing is that both the volume of voids and volume of the scale increase in the parabolic manner so that the volume fraction of void in the scale is independent of
time. Fig. 13 shows the volume fractions of voids in the magnetite scale at high $P_{O_2}$ atmosphere as a function of time. The volume fraction is independent of oxidation time to be 0.05. The corresponding calculated value from Eq. (43) is 0.13. The calculated volume fraction is slightly larger than that obtained from experiment probably because of counting loss of voids of which size is too small for SEM observation and voids within grains. The calculation reasonably explains the amount of voids in the magnetite scale.

The void formation in NiO and CoO which exhibit the schottky defect has been reported elsewhere.\textsuperscript{11,12}

6. Conclusion

The divergence of ionic flux is an origin of the void formation in metal oxides under chemical potential gradients. The chemical potential distribution in the oxide is determined by diffusivities which depend on chemical potentials. Defect chemistry in oxides is directly related to the sign of divergence and gives an indication of the void formation behavior. The quantitative estimation on the void formation was successfully applied to a growing magnetite scale in high temperature oxidation of iron at 823 K.

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