

Estimation of the Effect of Grain Boundary Diffusion on Microstructure Development in Magnetite Bi-crystal under Oxygen Chemical Potential Gradient at 823 K

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ABSTRACT

Mass transport near grain boundary in a magnetite bi-crystal has been estimated at 823 K by finite element method. Mass transport near grain boundary strongly depends on the diffusivities along grain boundary. If grain boundary diffusion has the same oxygen activity dependence as lattice diffusion, there is no mass transport between grains and grain boundary. On the other hand, mass transport between grains and grain boundary is observed in the case that grain boundary diffusion has different oxygen activity dependence.

Key words : Microstructure development, Grain boundary diffusion, Mass transport, Chemical potential distribution, Divergence of the ionic flux

1. Introduction

Microstructure development such as formation of excess oxide or void in a growing oxide scale affects scale adherence and exfoliation. These microstructure changes are induced by the divergence of the ionic flux, which is driven by electrochemical potential gradient through the oxide scale. Maruyama and Ueda have been proposed equations for estimating microstructure change in the oxide scales under the constraint of the conservation of sub-lattice sites in ionic crystal.¹⁻³⁾ They have applied this method to magnetite scale formed on iron at 823 K.¹⁾ The position and amount of void can be predicted in 1-dimensional mass transport. The effective diffusion coefficients, which include both lattice and grain boundary diffusions, give more quantitative explanation about microstructure change.²⁾ However, effective diffusion coefficients can be defined based on the assumption that grain boundary diffusion has the same P_{O_2} dependence as lattice diffusion.⁴⁾ Grain boundary diffusion itself has not been taken into account and the calculation could not estimate the actual polycrystalline oxide scale. Thermally grown oxide scale mainly consists of polycrystalline and microstructure change such as void formation may preferentially occur along grain boundary because grain boundary diffusion is much faster than the lattice diffusion. In this study, mass transport near grain boundary was estimated in the magnetite bi-crystal at 823 K by finite element method.

2. Microstructure Development Near Grain Boundary of Magnetite

Fig. 1 shows a schematic illustration of magnetite bi-crystal under oxygen chemical potential gradient. There are two magnetite grains and a grain boundary in between the grains. The grain boundary is located at the center of the cell and it is assumed that grain boundary has finite thickness. Oxygen chemical potential gradient is applied parallel to the grain

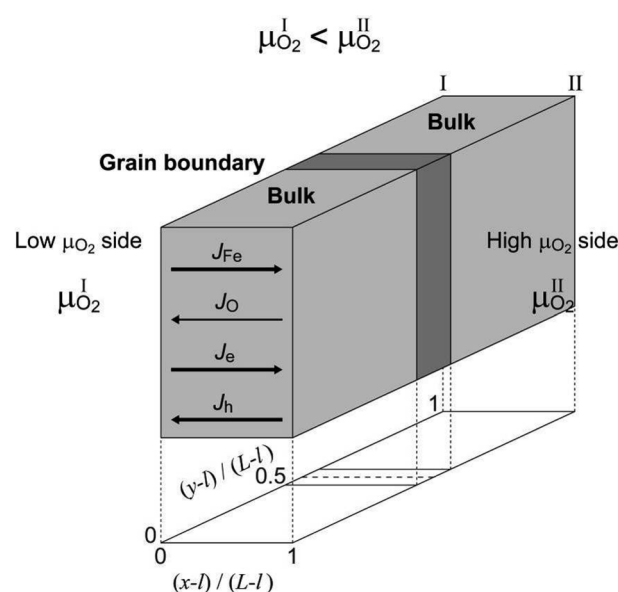


Fig. 1. Schematic illustration of magnetite bi-crystal under oxygen chemical potential gradient.

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boundary. In the magnetite bi-crystal, both iron and oxide ions are driven by electrochemical potential gradient. Electron and hole are also taken into account to keep electro-neutrality during mass transport. Mass transport occurs both in the magnetite grain and in the grain boundary.

The conservation of sub-lattice sites should be maintained during mass transport. The constraint can be expressed as follows,

$$\frac{\partial n_{\text{Fe}_3\text{O}_4}}{\partial t} = -\frac{1}{3}\text{div}(\mathbf{J}_{\text{Fe}}) = -\frac{1}{4}\text{div}(\mathbf{J}_o) \quad (1)$$

where the left-hand term is the change in number of mole of magnetite and \mathbf{J}_i is the flux of a species, i . The flux of a species, i , is expressed by

$$\mathbf{J}_i = -c_i B_i \text{grad}(\eta_i) \quad (2)$$

where c is the concentration, B is the absolute mobility, η is the electrochemical potential. The absolute mobility is directly related to diffusion coefficient.

$$B_i = \frac{D_i}{RT} \quad (3)$$

The electro-neutrality should be maintained throughout the magnetite.

$$z_{\text{Fe}}\mathbf{J}_{\text{Fe}} + z_o\mathbf{J}_o + z_e\mathbf{J}_e + z_h\mathbf{J}_h = 0 \quad (4)$$

Gibbs-Duhem relation can be described by the following equation.

$$c_{\text{Fe}}d\mu_{\text{Fe}} + c_o d\mu_o = 0 \quad (5)$$

Based on eqs. (1) to (5), chemical potential distribution of oxygen in the magnetite can be expressed as follows.

$$\text{div}\left(\frac{\alpha\beta}{\alpha+\beta}\text{grad}(\mu_{o_2})\right) = 0 \quad (6)$$

where α and β are the contributions of ionic and electronic conduction and are defined as follows.

$$\alpha = z_{\text{Fe}}^2 c_{\text{Fe}} B_{\text{Fe}} + z_o^2 c_o B_o \quad (7)$$

$$\beta = c_e B_e + c_h B_h \quad (8)$$

Magnetite has high electrical conductivity so that the term of $\alpha\beta/(\alpha+\beta)$ in eq. (6) can be simplified to be α . Eq. (6) can be expressed as follows.

$$\text{div}(\alpha \text{grad}(\mu_{o_2})) = 0 \quad (9)$$

Chemical potential distribution of oxygen is given by numerically solving eq. (9) with bulk diffusion in magnetite. It is assumed that microstructure change along grain boundary can be also calculated by the same equation with grain boundary diffusion.

The flux of oxide ion in magnetite bi-crystal can be described as follows.

$$\mathbf{J}_o = -c_o B_o \text{grad}(\eta_o) \approx \frac{c_o B_o}{2} \text{grad}(\mu_{o_2}) \quad (10)$$

Moreover, formation or annihilation rate of magnetite in the bi-crystal is also given by the divergence of the flux of oxide ion. The sign and the amount of this rate give information of microstructure change in the bi-crystal.

$$\frac{\partial n_{\text{Fe}_3\text{O}_4}}{\partial t} = -\frac{1}{4}\text{div}(\mathbf{J}_o) \quad (11)$$

3. Diffusivities in Magnetite Grain and Grain Boundary

The calculation requires the diffusivities both lattice and grain boundary of constituent ions as a function of oxygen chemical potential (activity). Ricoult and Dieckmann have estimated the self diffusion coefficient of iron in magnetite at higher temperature from the tracer diffusion coefficient and correlation factor.⁵⁾

$$D_{\text{Fe}}^{\text{Bulk}}/\text{m}^2\text{s}^{-1} = A^{\text{Bulk}} \alpha_{o_2}^{-2/3} + \frac{B^{\text{Bulk}} \alpha_{o_2}^{2/3}}{1 + 2K_V \alpha_{o_2}^{2/3}} \quad (12)$$

where α_{o_2} is the oxygen activity and K_V is the equilibrium constant of iron vacancy formation. The iron interstitial ion is predominant defects at lower oxygen activity and iron vacancy at higher oxygen activity. The parameters of A^{Bulk} , B^{Bulk} and K_V at 823 K were obtained by the extrapolation from the reported values as follows.⁵⁾

$$A^{\text{Bulk}} = 4.3 \times 10^{-35} \text{ m}^2\text{s}^{-1} \quad (13)$$

$$B^{\text{Bulk}} = 5.6 \times 10^{-6} \text{ m}^2\text{s}^{-1} \quad (14)$$

$$K_V = 4.4 \times 10^7 \quad (15)$$

Millot *et al.* reported lattice diffusion coefficient of oxygen in the following manner.⁶⁾

$$D_o^{\text{Bulk}}/\text{m}^2\text{s}^{-1} = C^{\text{Bulk}} P_{o_2}^{-1/2} + F^{\text{Bulk}} P_{o_2}^{1/6} \quad (16)$$

Oxygen vacancy is predominant defects. The second term gives the contribution from anion cation vacancy pairs and it is small enough to be neglected. The parameters of C^{Bulk} at 823 K can be calculated as follows.

$$C^{\text{Bulk}} = 3.1 \times 10^{-34} \text{ m}^2\text{s}^{-1}\text{atm}^{1/2} \quad (17)$$

In this study, diffusion coefficients along grain boundary are assumed in the following two cases because grain boundary diffusion of magnetite has still unknown.

Case 1: Grain boundary diffusion has the same oxygen

activity dependence as the lattice diffusion and its magnitude is three orders of magnitude larger than that of the lattice diffusion. This assumption is based on the paper by Stubican and Carinci describing the experimental observation of the grain boundary diffusion of divalent cobalt ion in polycrystalline magnetite.⁴⁾ Grain boundary diffusion is strongly influenced by the concentration of point defects and is three orders of magnitude larger than the bulk diffusion. The parameters of grain boundary diffusion at 823 K in the case 1 can be described as follows.

$$A^{\text{Gb}} = 4.3 \times 10^{-32} \text{ m}^2\text{s}^{-1} \quad (13')$$

$$B^{\text{Gb}} = 5.6 \times 10^{-3} \text{ m}^2\text{s}^{-1} \quad (14')$$

$$C^{\text{Gb}} = 3.1 \times 10^{-31} \text{ m}^2\text{s}^{-1}\text{atm}^{1/2} \quad (17')$$

Case 2: Grain boundary diffusion is independent of oxygen activity. It is the case that point defects along grain boundary are extremely high because the defects formed by the lattice mismatch or introduced by foreign impurities which are reasonably assumed to be independent of oxygen chemical potential. In this study, it is assumed that diffusion coefficient is constant and three orders of magnitude larger than that of the highest value of lattice diffusion coefficients. Grain boundary diffusions at 823 K are assumed as follows.

$$D_{\text{Fe}}^{\text{Gb}} = 1.7 \times 10^{-13} \text{ m}^2\text{s}^{-1} \quad (18)$$

$$D_{\text{O}}^{\text{Gb}} = 7.9 \times 10^{-18} \text{ m}^2\text{s}^{-1} \quad (19)$$

Fig. 2 shows diffusion coefficients of iron and oxygen at 823 K in each case. Based on the diffusion coefficients, chemical potential distribution of oxygen in magnetite bi-crystal has been calculated to evaluate mass transport near grain boundary.

4. Calculation

Fig. 3 shows a square finite element cell, in which grain boundary is arranged at the center. Chemical potential distribution in the magnetite bi-crystal has been calculated at

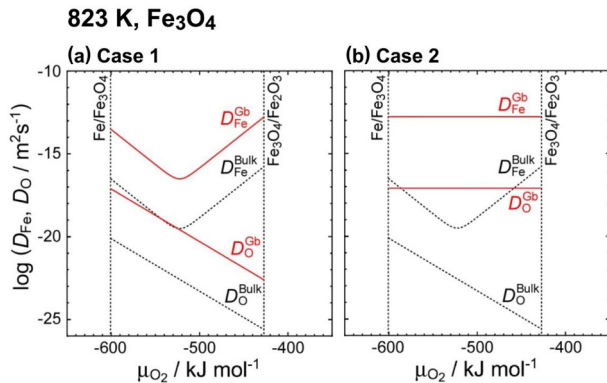


Fig. 2. Diffusion coefficients of iron and oxygen at 823 K.

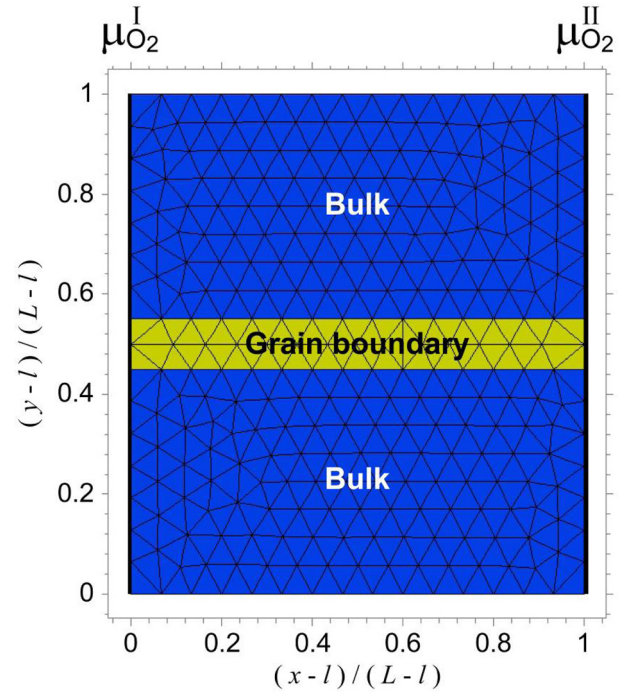


Fig. 3. Square finite element cell for the calculation.

823 K as a functions of the normalized thickness of $(x-l)/(L-l)$ and $(y-l)/(L-l)$ ($0 < (x-l)/(L-l)$, $(y-l)/(L-l) < 1$). The size of the cell ($L-l$) is set to be 2×10^{-7} m (200 nm). Grain boundary is located at the center of the cell ($(y-l)/(L-l) = 0.5$), the thickness of grain boundary is assumed to be 1/10 of the cell size (20 nm). Eq. (9) was numerically solved by using the software of FlexPDE 5.0.9 (PDE Solutions Inc.) with the following boundary conditions and the diffusivities as shown in Fig. 2. Chemical potential of oxygen at the surfaces (I) and (II) are set to be $\text{Fe}/\text{Fe}_3\text{O}_4$ equilibrium and $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ equilibrium, respectively.

$$(x-l)/(L-l) = 0, 0 \leq (y-l)/(L-l) \leq 1, \mu_{\text{O}_2} = \mu_{\text{O}_2}^{\text{I}} = -601 \text{ kJmol}^{-1} \quad (20)$$

$$(x-l)/(L-l) = 1, 0 \leq (y-l)/(L-l) \leq 1, \mu_{\text{O}_2} = \mu_{\text{O}_2}^{\text{II}} = -427 \text{ kJmol}^{-1} \quad (21)$$

Based on the obtained oxygen chemical potential distribution, one can also calculate the flux of oxide ion (J_{O}) and its divergence ($\text{div}(J_{\text{O}})$).

5. Results and Discussion

Fig. 4 shows chemical potential distribution of oxygen in the magnetite bi-crystal at 823 K in the case 1. In this calculation, oxygen activity dependence of the diffusivities is the same in grains and grain boundary. The case 1 is suitable assumption for polycrystalline magnetite scale which formed on iron during high temperature oxidation, because point defects along grain boundary are not influenced by foreign impurities. There is no difference of oxygen chemical potential distribution between grains and grain boundary. Oxygen chemical potential drastically decreases at the position of $(x-l)/(L-l) = 0.15$ in

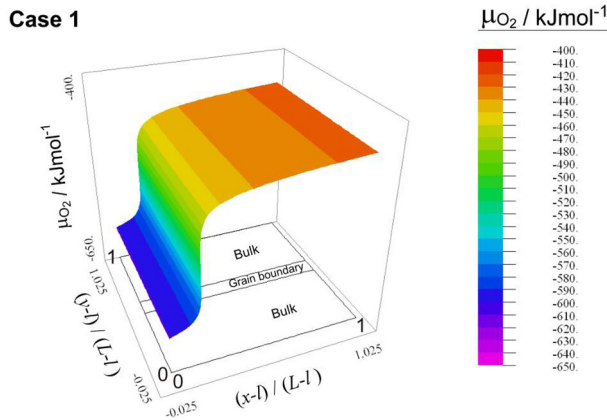


Fig. 4. Chemical potential distribution of oxygen in the magnetite bi-crystal at 823 K in the case 1.

both grains and grain boundary.

Fig. 5 shows the flux of oxide ion at 823 K in the case 1. Figs. 5(a) and (b) are corresponded to the flux of oxide ion in the magnetite grains and along grain boundary, respectively. The flux of oxide ion drastically changes at the position of $(x-l)/(L-l) = 0.15$ in both grains and grain boundary because of the maximum oxygen chemical potential gradient. The flux along grain boundary is three orders of magnitude larger than that in the grains. There is no mass transport between grains and grain boundary.

Fig. 6 shows the negative divergence of the flux of oxide ion ($-\text{div}(J_{O_2})$) in magnetite bi-crystal in the case 1. This value is proportional to the amount of microstructure changes and its sign gives the types of microstructure change. At the position of $(x-l)/(L-l) = 0.15$ in both grains and grain boundary has the negative value, indicating void formation. The amount of void formation in grain boundary can be estimated three orders of magnitude larger than in the grains. It indicates that void preferentially forms in the grain boundary, because grain boundary gives larger mass transport than the grains.

Fig. 7 shows chemical potential distribution of oxygen in the magnetite bi-crystal at 823 K in the case 2. Oxygen chemical potential changes linearly along grain boundary, because grain boundary diffusion is independent of oxygen activity. Chemical potential distribution in the grains drastically changes near grain boundary in the bulk crystal. Fig. 8 shows the flux of oxide ion in the case 2. Figs. 8(a) and (b) show the flux of oxide ion in the magnetite grains and along grain boundary, respectively. Mass transport from the bulk crystal to the grain boundary is observed near grain boundary in this calculation. On the other hand, the flux of oxide ion along grain boundary is constant due to the linear chemical potential gradient. The amount of the flux along grain boundary is three orders of magnitude larger than that in the grains. Fig. 9 shows the negative divergence of the flux of oxide ion in magnetite bi-crystal in the case 2. There is no divergence along grain boundary, indicating no microstructure change. In magnetite grains, it is estimated that void forms not only in the grains but

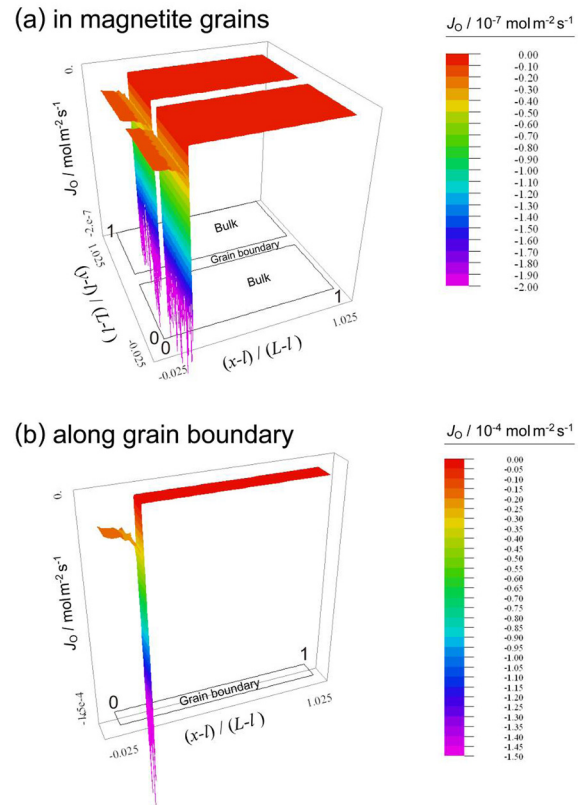


Fig. 5. The flux of oxide ion at 823 K in the case 1. (a) in magnetite grains and (b) along grain boundary.

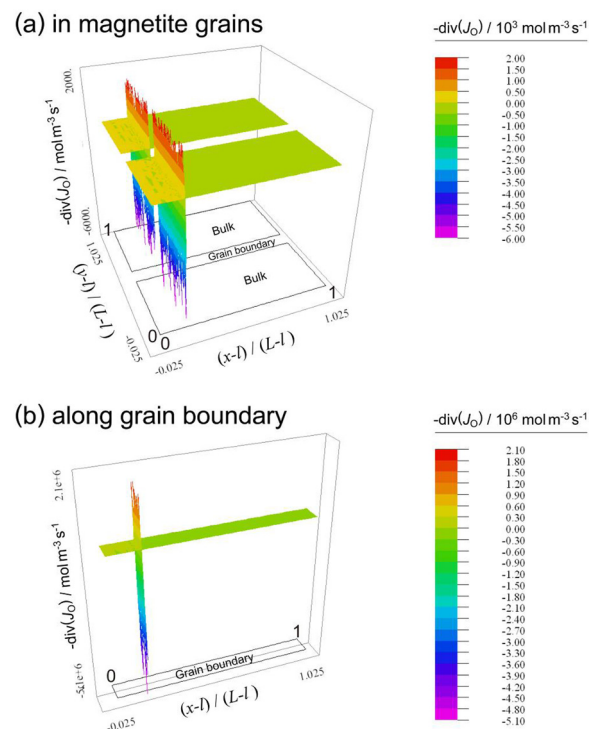


Fig. 6. The negative divergence of the flux of oxide ion at 823 K in the case 1. (a) in magnetite grain and (b) along grain boundary.

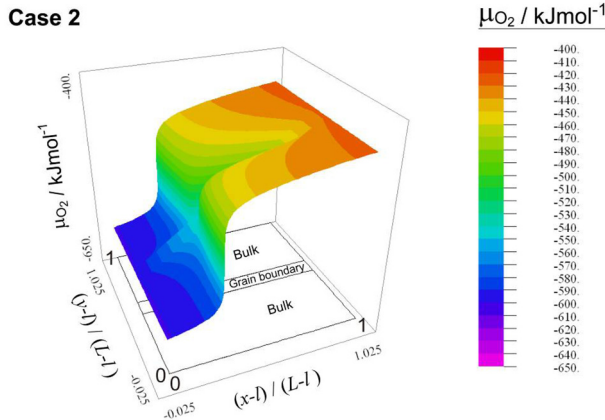


Fig. 7. Chemical potential distribution of oxygen in the magnetite bi-crystal at 823 K in the case 2.

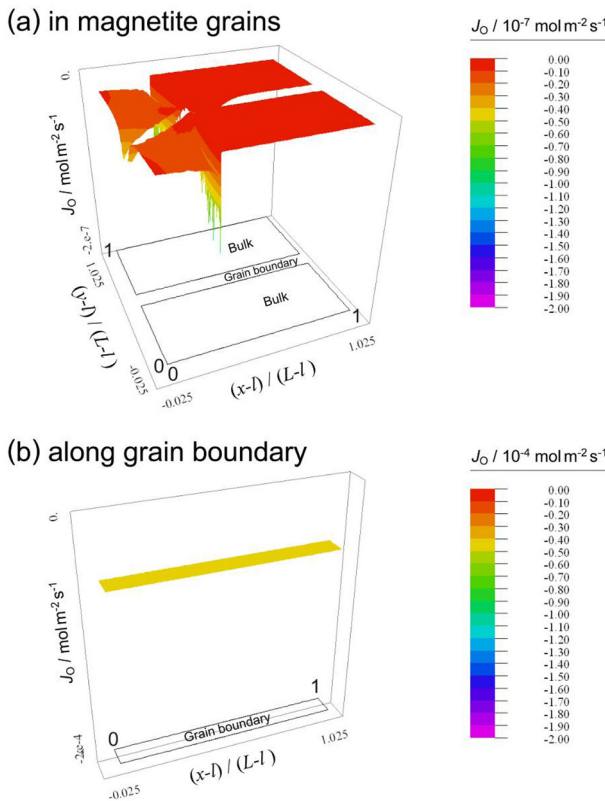


Fig. 8. The flux of oxide ion at 823 K in the case 2. (a) in magnetite grains and (b) along grain boundary.

also near grain boundary. Although the amount of microstructure change is negligible small, the movement of grain boundary may occur in this case.

6. Conclusion

Mass transport near grain boundary in the magnetite bi-crystal at 823 K was calculated by finite element method. Mass transport near grain boundary strongly depend on the diffu-

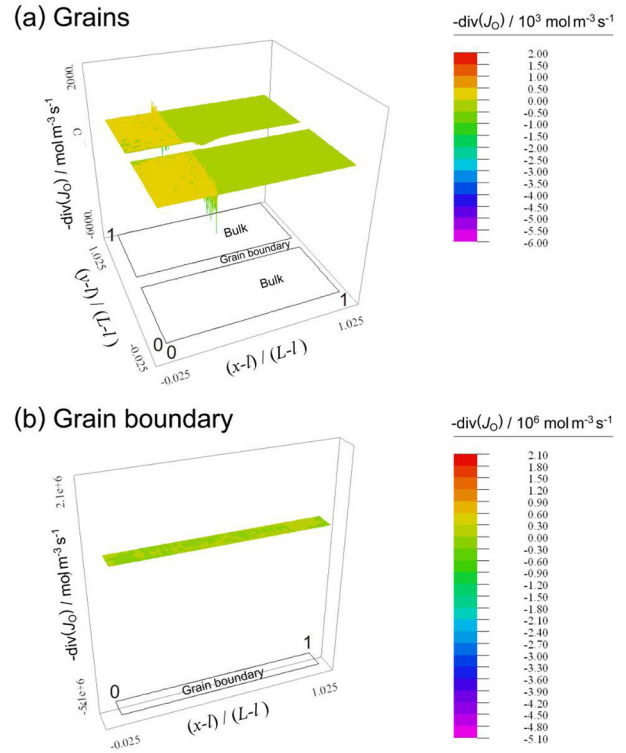


Fig. 9. The negative divergence of the flux of oxide ion at 823 K in the case 2. (a) in magnetite grain and (b) along grain boundary.

sivities along grain boundary. There is no mass transport between grains and grain boundary, if grain boundary diffusion has the same oxygen activity dependence as lattice diffusion. Higher grain boundary diffusion gives the microstructure change preferentially along grain boundary. On the other hand, mass transport between grains and grain boundary was observed in the case that grain boundary diffusion has different oxygen activity dependence. The movement of grain boundary may occur in this case.

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REFERENCES

1. T. Maruyama, N. Fukagai, M. Ueda, and K. Kawamura, "Chemical Potential Distribution and Void Formation in Magnetite Scale Formed in Oxidation of Iron at 823 K," *Mater. Sci. Forum*, **461-464** 807-14 (2004).
2. M. Ueda, K. Kawamura, and T. Maruyama, "Void formation in Magnetite Scale Formed on Iron at 823 K -Elucidation by Chemical Potential Distribution-," *Mater. Sci. Forum*, **522-**

- 523 37-44 (2006).
3. T. Maruyama and M. Ueda, "Void Formation Induced by the Divergence of the Diffusive Ionic Fluxes in Metal Oxides Under Chemical Potential Gradients," *J. Kor. Ceram. Soc.*, **47** [1] 8-18 (2010).
 4. V. S. Stubican and L. R. Carinci, "Point Defects and Grain boundary diffusion in NiO and Fe₃O₄," *Z. Phys. Chem.*, **207** 215-22 (1998).
 5. M. Backhaus-Ricoult and R. Dieckmann, "Defects and Cation Diffusion in Magnetite (VII): Diffusion Controlled Formation of Magnetite During Reactions in the Iron-Oxygen System," *Ber. Bunsenges. Phys. Chem.*, **90**, 690-98 (1986).
 6. F. Millot, J. C. Lorin, B. Klossa, Y. Niu, and J. R. Tarento, "Oxygen Self-diffusion in Fe₃O₄: An Experimental Example of Interactions Between Defects," *Ber. Bunsenges. Phys. Chem.*, **101** [9] 1351-54 (1997).