Continuous Monitoring of Oxygen Chemical Potential at the Surface of Growing Oxide Scales during High Temperature Oxidation of Metals

Kojiro Akiba*, Mitsutoshi Ueda, Kenichi Kawamura and Toshio Maruyama

Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Tokyo 152-8552, Japan

The continuous monitoring of the oxygen chemical potential at a surface of a growing oxide surface formed in high temperature oxidation of a metal was developed. During the oxidation of nickel and cobalt at 1373 K in Ar-21%O gas, the oxygen chemical potentials at the surface of formed NiO scale and CoO scale were slightly smaller than that in the atmosphere, because the growths of these oxide scales were mainly rate-limited by the diffusion of the constituent ions in the scales. The difference of the oxygen chemical potential between at the surface of CoO scale and in the atmosphere was larger than that between at the surface of NiO scale and in the atmosphere under the same oxidation condition, since the oxygen consumption rate for the oxidation of cobalt was larger than that of nickel. In the case of the oxidation of iron at 1373 K in Ar-CO-CO gas mixture, the oxygen chemical potential at the surface of formed FeO scale decreased largely from that in the atmosphere, since the growth of FeO scale was very fast and mainly rate-limited by the mass transport from gas phase to the scale surface. The oxygen chemical potential at the surface of FeO scale increased with increment of CO concentration in the atmosphere.

1. Introduction

Solid membranes of ionic crystals are exposed under chemical potential difference at elevated temperatures in applications such as solid oxide fuel cell, gas separation, and so on. The mass transport is driven by the chemical potential gradient in the membrane. The oxide scale being formed in high temperature oxidation of metals is a typical example.

Mechanical properties and performance of the oxide membrane are influenced by the morphology. The microstructure development under mass transport is an important issue to predict the performance and life of the membranes.

Maruyama et al.1) proposed that voids formation in a growing oxide scale in high temperature oxidation of a metal was explained by the evaluation of the divergence of the minor ionic flux under the assumption of the major ionic flux to be responsible to establish the chemical potential distribution, and have demonstrated the validity in FeO scale formed in high temperature oxidation of iron at 823 K. Ueda et al.2) improved this treatment in which all ionic fluxes were taking account into the calculation of the chemical potential gradient and quantitatively explained the position and the volume of voids formed in the FeO scale. Present authors3,4) have demonstrated the prediction of the voids formation in the scales of NiO and CoO formed in high temperature oxidation of nickel and cobalt at 1373 K, and have predicted that the voids in the oxide scale form mainly in the vicinity of the metal/oxide interface in a quantitative manner. These predictions are in good agreement with the morphology that is experimentally observed.

The quantitative prediction requires the diffusivity of constituent ions in the scale, the oxygen chemical potential at the metal/oxide interface and the oxygen chemical potential at the surface of the oxide scale.1–4) Therefore, oxygen chemical potential at the surface of oxide scale is one of the essential parameters for quantitative analyses of the morphological change in the oxide scale.

In the process of high temperature oxidation of a metal, the two possible rate-limiting steps are the chemical (or electrochemical) reaction at the surface of scale, which gives the linear kinetics and the diffusion of constituent ions through the scale, which gives the parabolic kinetics. Figure 1(a) illustrates the distribution of the oxygen chemical potential in the process, which is controlled by diffusion. The oxygen chemical potential at the surface of the scale can be assumed to be identical to that in the atmosphere because diffusion process in the scale is much slower than the mass transport in gas phase. The growth of FeO scale formed on iron is known to be rate-limited by mass transport from gas phase to the scale surface (Fig. 1(b)), the boundary layer is developed and the oxygen chemical potential is much lower than that in the atmosphere. The growth of FeO scale formed in the high temperature oxidation of iron in Ar-CO-CO gas mixtures is known to be rate-limited by mass transport from gas phase.5–10)

For the quantitative prediction of the morphological change under the situation in Fig 1(b), the oxygen chemical potential at the surface should be measured directly.

The purpose of this study is to develop the technique for continuous monitoring of the oxygen chemical potential at the surface of the growing oxide scale during high temperature oxidation of metal. In this study, NiO and CoO scales formed respectively on nickel and cobalt are chosen as examples of the scale whose growth rate is rate-limited by the diffusion of constituent ions and FeO scale formed on iron was as an example for mass transport in gas phase to be rate-limiting.

2. Principle

Calcia-stabilized ZrO2(CSZ) is known as an oxide ion conductor, and is often used as an electrolyte of an
potentiometric oxygen sensor. When CSZ is exposed to a difference of oxygen chemical potential, an electromotive force is generated. In this study, the oxygen concentration cell shown in Fig. 2 is proposed in order to measure the difference of the oxygen chemical potential between at the oxide surface and in the atmosphere during the high temperature oxidation of a metal. A metal sheet welded a platinum lead is placed on a CSZ bar attached with a platinum lead on the other side as shown in Fig. 2(a).

When the cell is exposed to the oxidizing atmosphere at elevated temperatures, the oxide scale is formed on the metal. In the case that the scale growth proceeds inward as shown in Fig. 2(b), the CSZ bar is always attached on the scale surface. On the other hand, when the scale growth proceeds outward (Fig. 2(c)), the CSZ bar is partly embedded in the scale. When the oxide scale is an electronic conductor, the oxide scale itself behaves as an electrode of the cell. The redox reaction of oxygen mostly occurs at the triple phase boundary of CSZ, electrode of the scale and gas phase. The cell is expressed as

\[
(\text{Pt} | \text{gas} (\mu_{\text{Sur}}^{\text{O}_2}), \text{oxide scale} | \text{CSZ} | \text{Pt}, \text{gas} (\mu_{\text{Atm}}^{\text{O}_2}) ) \quad (+) 
\]

where \( \mu_{\text{Sur}}^{\text{O}_2} \) and \( \mu_{\text{Atm}}^{\text{O}_2} \) denote the oxygen chemical potentials at the oxide surface and in the atmosphere, respectively. The electrochemical reaction of the oxide surface is the anode reaction of

\[
2\text{O}^{2-} \rightarrow \text{O}_2 + 4e^- 
\]

and that at the electrode in the atmosphere is the cathode reaction of

\[
\text{O}_2 + 4e^- \rightarrow 2\text{O}^{2-} 
\]

The electromotive force of this cell, \( E_{\text{cell}} \) is expressed as,

\[
E_{\text{cell}} = - (\mu_{\text{Sur}}^{\text{O}_2} - \mu_{\text{Atm}}^{\text{O}_2}) / 4F = (RT / 4F) \ln \left( \frac{p_{\text{Atm}}^{\text{O}_2}}{p_{\text{Sur}}^{\text{O}_2}} \right) 
\]

where \( F \) is the Faraday constant. \( p_{\text{Sur}}^{\text{O}_2} \) and \( p_{\text{Atm}}^{\text{O}_2} \) denote the oxygen partial pressure at the oxide surface and in the atmosphere, respectively. From this equation, the oxygen chemical potential at the oxide surface can be calculated from \( E_{\text{cell}} \) and \( \mu_{\text{Atm}}^{\text{O}_2} \).

The redox reaction of oxygen occurs everywhere the CSZ and the scale are attached. Therefore, the electric potential of the oxide scale (electrode) is a mixed potential. The mixed potential of the oxide scale can be obtained as that which the anodic current and the cathodic current are identical. The anodic reaction occurs much more at the triple phase boundary of CSZ, where the oxygen transport is extremely

Fig. 1 Schematic illustration of chemical potential distribution in and out of the oxide scale whose growth rate is rate-determined by (a) diffusion of constituent ions in the scale and (b) mass transport from gas phase to the scale surface.

Fig. 2 Schematic illustration of the oxidation concentration cell for the measurement of the oxygen chemical potential at the oxide surface (a) before oxidation, (b) during oxidation (the scale grown by inward diffusion of oxide ion) and (c) during oxidation (the scale grown by outward diffusion of metal ion).
higher than the scale interior. Therefore, the mixed potential is just slightly lower than the oxygen potential at the triple phase boundary. However, the difference is considered to be negligibly small.

3. Experiment

3.1 Sample preparation

Three metals of nickel (99.95%), cobalt (99.9%) and iron (99.99%) were purchased and cut into the coupon of $10 \times 10 \times 1$ (mm$^3$) in size. After annealed in vacuum at 1573 K for 36 ks, the samples were polished to a mirror finish with abrasive papers (#600–#2000) and diamond paste of 4 $\mu$m.

3.2 Experimental procedure

Figure 3 shows a schematic illustration of experimental set-up and the oxygen concentration cell. In order not only to support the metal coupon but also to ensure the free gas flow, the CSZ tube was cut into the shape as shown in Fig. 3(c), which has three bars. The platinum electrode detecting the oxygen potential in the atmosphere is attached at the position of 20 mm away from the sample to make the position to be outside of the boundary layer.

A CSZ oxygen sensor is located beneath the cell in order to monitor the oxygen chemical potential in the atmosphere, $\mu_{O_2}^{Atm}$. This sensor monitors the electromotive force generated by the difference of the oxygen chemical potential between the atmosphere and air as shown in Fig. 3(d). The sensor is also a oxygen concentration cell which can be expressed as follows.

\[
(-) \text{Pt|gas($\mu_{O_2}^{Atm}$)|CSZ|Pt, gas($\mu_{O_2}^{Air}$) (+)}
\]
The electromotive force of the oxygen sensor, $E_{\text{sensor}}$, is expressed as,

$$
E_{\text{sensor}} = -(\mu_{\text{Air}, \text{O}_2} - \mu_{\text{Air}, \text{O}_2}^\text{Air})/4F = (RT/4F) \ln(P_{\text{Air}, \text{O}_2}^\text{Air}/P_{\text{Air}, \text{O}_2}^\text{Air})
$$

where $\mu_{\text{Air}, \text{O}_2}$ and $P_{\text{Air}, \text{O}_2}^\text{Air}$ denote the oxygen chemical potential and the oxygen partial pressure in air. Both the cell and the CSZ oxygen sensor should be located in the isothermal zone of the furnace to minimize errors caused by thermo-electromotive force of CSZ\(^{11}\) and temperature dependence of gas phase equilibrium. The isothermal zone was determined to be 30 mm before the experiments. The temperatures at the metal coupon and at the oxygen sensor were monitored during oxidation experiments by thermocouples (T. C.) of type -R that were placed as shown in Fig. 3(a).

The cell was heated with a flowing Ar-1%H\(_2\) gas up to 1373 K at the heating rate of $8.3 \times 10^{-2}$ Ks\(^{-1}\) so that the metal coupon was not oxidized during the heating process. When the temperature reached at 1373 K, the oxidizing gas was introduced into the chamber. Ar-21%O\(_2\) gas ($P_{\text{O}_2} = 9.3 \times 10^{-7}$ Pa at 1373 K, the low $P_{\text{CO}_2}$ atmosphere) and Ar-1%CO-10%CO\(_2\) gas ($P_{\text{O}_2} = 3.8 \times 10^{-6}$ Pa at 1373 K, the high $P_{\text{CO}_2}$ atmosphere). Since the oxygen partial pressure of Fe/FeO equilibrium and FeO/Fe\(_2\)O\(_4\) equilibrium is $P_{\text{O}_2} = 5.1 \times 10^{-6}$ Pa and $P_{\text{O}_2} = 1.5 \times 10^{-6}$ Pa at 1373 K respectively,\(^{12}\) the oxygen partial pressure of the low $P_{\text{CO}_2}$ atmosphere is in the region that FeO is stable, and that of the high $P_{\text{CO}_2}$ atmosphere is in the region that Fe\(_2\)O\(_4\) is stable thermodynamically. When the oxidation was terminated, argon gas was introduced into the chamber and the furnace was cooled down to room temperature at the cooling rate of $8.3 \times 10^{-2}$ Ks\(^{-1}\).

At the beginning of oxidation, the Ar-1%H\(_2\) gas is exchanged by the oxidizing gas. During this exchange process, some electromotive force is expected to be generated temporarily in the cell. A blank test using platinum foil instead of metal coupon was carried out in the low $P_{\text{CO}_2}$ atmosphere of the oxidation of iron.

Determination of the oxygen chemical potential distribution in the gas boundary layer is important to assure the platinum electrode on CSZ to be located outside the gas boundary layer. The oxidation of iron in the low $P_{\text{CO}_2}$ atmosphere was carried out with a CSZ which has three platinum electrodes as shown in Fig. 4, and the electromotive forces were measured between the surface of the scale and each platinum electrode of 1, 2 and 3.

### 4. Results

#### 4.1 Blank test using platinum foil

Figure 5 shows the electromotive forces generated in the cell, $E_{\text{cell}}$ and the oxygen sensor, $E_{\text{sensor}}$, and the temperatures during the blank test using platinum foil as a sample, which is carried out in Ar-1%CO-5%CO\(_2\) (the low $P_{\text{CO}_2}$ atmosphere of the oxidation of iron) for 18 ks. The time of zero (start) represents the time when the gas is changed from Ar-1%H\(_2\) into Ar-1%CO-5%CO\(_2\). The temperature difference between at the surface of the sample and at the oxygen sensor is at most 3 K during the experiment. The electromotive force of the sensor, $E_{\text{sensor}}$ is stable at about 703 mV during the experiment. The oxygen partial pressure in the atmosphere calculated from this $E_{\text{sensor}}$ with the eq. (4) is $1.0 \times 10^{-6}$ Pa. This oxygen partial pressure is almost the same to that of the oxidizing gas, Ar-1%CO-5%CO\(_2\) ($P_{\text{O}_2} = 9.3 \times 10^{-7}$ Pa at 1373 K). This result proves the CSZ oxygen sensor can monitor the oxygen partial pressure (oxygen chemical potential) in the atmosphere correctly.

The electromotive force of the cell is generated only in the period in which the gas is being changed because of nonuniformity of the oxygen chemical potential in the ambient gas. When the oxygen chemical potential in the atmosphere is stable, the electromotive force of the cell is...
almost 0 mV. From the result, it can be confirmed that the electromotive forces caused by the thermo-electromotive force and temperature dependence of gas phase equilibrium are negligibly small.

4.2 High temperature oxidation experiment

Figure 6 shows the electromotive forces generated in the cell and the oxygen sensor, and the temperatures during the oxidation of nickel at 1373 K in Ar-21 %O$_2$ for 172.8 ks. The time of zero (start) represents the time when the gas is changed from Ar-1 %H$_2$ into Ar-21 %O$_2$. The temperature difference between at the surface of the sample and at the oxygen sensor is at most 2 K during the experiment. When the gas is changed from Ar-1 %H$_2$ to Ar-21 %O$_2$, the electromotive force of the cell is largely positive, and quickly decreases to about 20 mV.

Figure 7 shows the electromotive forces generated in the cell and the oxygen sensor, and the temperatures during the oxidation of cobalt at 1373 K in Ar-21 %O$_2$ for 172.8 ks. The temperature difference between at the surface of the sample and at the oxygen sensor during the experiment is at most 2 K during the experiment. The electromotive force generated in the cell is largely positive just after the oxidation starts, and then, decreases with time as well as the result of the oxidation of nickel.

Figure 8 shows the electromotive forces generated in the cell and the oxygen sensor, and the temperatures during the oxidation of iron at 1373 K in Ar-1 %CO-5 %CO$_2$ (the low P$_{CO}$ atmosphere) for 176.4 ks. The temperature difference between at the surface of the sample and at the oxygen sensor during the experiment is at most 2 K. Just after the gas is changed from Ar-1 %H$_2$ to Ar-1 %CO-5 %CO$_2$, the electromotive force of the cell exhibits constant value of around 140 mV. After about 82 ks, the electromotive force in the cell drastically decreases and...
reaches to about 0 mV. The temperatures and the electromotive force of the oxygen sensor during the oxidation have no significant differences comparing with those of the blank experiment shown in Fig. 5. Therefore, both the temperatures and the oxygen chemical potential in the atmosphere are not affected by the consumption of oxygen and the exothermic heat caused by the oxidation of iron.

Figure 9 shows the electromotive forces generated in the cell and the oxygen sensor, and the temperatures during the oxidation of iron at 1373 K in Ar-1 %CO-10 %CO$_2$ (the high P$_{CO_2}$ atmosphere) for 18 ks. The electromotive force of the cell is about 170 mV during the oxidation, and is larger than that in the low P$_{CO_2}$ atmosphere.

4.3 Measurement of thickness of gas boundary layer formed in oxidation of iron in Ar-1 %CO-5 %CO$_2$

Figure 10 shows the electromotive forces generated in the cell and the oxygen sensor, and the temperatures during the oxidation of iron at 1373 K in Ar-1 %CO-5 %CO$_2$ (the low P$_{CO_2}$ atmosphere) for 18 ks. The electromotive force of the cell is about 170 mV during the oxidation, and is larger than that in the low P$_{CO_2}$ atmosphere.

5. Discussion

5.1 The oxygen chemical potential at the surface of the oxide scale formed in high temperature oxidation of nickel and cobalt

Figure 12 shows the oxygen chemical potentials in the atmosphere, $\mu^{\text{Amn}}_{O_2}$, and at the surface of the NiO scale, $\mu^{\text{Sur}, \text{NiO}}_{O_2}$, and of the CoO scale, $\mu^{\text{Sur}, \text{CoO}}_{O_2}$ calculated from the
electromotive forces generated in the sensor and the cell shown in Fig. 6 and Fig. 7 during the oxidation of nickel and cobalt. The oxygen chemical potentials of Ni/NiO equilibrium, \( \mu_{\text{Sur, NiO}} \) and of Co/CoO equilibrium, \( \mu_{\text{Sur, CoO}} \) are also shown in the figure. Both \( \mu_{\text{Sur, NiO}} \) and \( \mu_{\text{Sur, CoO}} \) rapidly reach values a little smaller than \( \mu_{\text{Atm}}^{\text{O}_2} \), and the difference of each oxygen chemical potential decreases with time.

The difference between \( \mu_{\text{Sur, NiO}} \) and \( \mu_{\text{Sur, CoO}} \) is larger than that between \( \mu_{\text{Sur, NiO}}^{\text{Am}} \) and \( \mu_{\text{Sur, CoO}}^{\text{Am}} \) especially in the initial stage of the oxidation. Figure 13 shows the parabolic plots of the scale thickness of both NiO scale and CoO scale formed on nickel and cobalt in Ar-21 \% O\(_2\) at 1373 K, which was reported by the present authors.\(^3,4\) The growth rate of CoO scale on cobalt is larger than that of NiO scale on nickel. This indicates that the oxygen consumption rate for the oxidation of cobalt is larger than that of nickel. This fact may result in the decrease of the oxygen consumption rate for the oxidation, and result in the increase of \( \mu_{\text{Sur}}^{\text{O}_2} \) of both scales with time.

5.2 The oxygen chemical potentials at the surface of the oxide scales formed in high temperature oxidation of iron

Figure 14 shows the oxygen chemical potentials in the atmosphere, \( \mu_{\text{Atm}}^{\text{O}_2} \), and at the surface of FeO scale, \( \mu_{\text{Sur, FeO}} \), calculated from the electromotive forces generated in the sensor and the cell shown in Fig. 8 during the oxidation of iron in Ar-1 \% CO-5 \% CO\(_2\) for 176.4 ks. The oxygen chemical potentials of Fe/FeO equilibrium, \( \mu_{\text{Fe/FeO}}^{\text{Am}} \) and of FeO/Fe\(_3\)O\(_4\) equilibrium reported by Darken and Gurry\(^12\) are also shown in the same figure. \( \mu_{\text{Sur, FeO}} \) drops more than 2 orders of magnitude down from \( \mu_{\text{Atm}}^{\text{O}_2} \) after about 82 ks, \( \mu_{\text{Sur, FeO}}^{\text{Am}} \) increases drastically. When a metal is oxidized for a very long time, the supply of the metal ion for the formation of the oxide scale should decrease with time since the area at which the scale contacts to the substrate decreases by the consumption of the substrate. This may cause the decrease of the oxygen consumption rate for the oxidation, and result in the increase of the oxygen chemical potential at the surface of the oxide scale. When the
iron substrate is totally oxidized, $\mu_{\text{FeO}}^{\text{Sur}}$ reaches to $\mu_{\text{O}_2}^{\text{Atm}}$, because the oxygen consumption for the oxidation does not occur any more.

Figure 15 shows the oxygen chemical potential in the atmosphere, $\mu_{\text{O}_2}^{\text{Atm}}$, and at the surface of FeO scale, $\mu_{\text{O}_2}^{\text{Sur}}$, calculated from the electromotive forces generated in the sensor and the cell shown in Fig. 9 during the oxidation of iron in Ar-1 %CO-10 %CO$_2$ (the high $P_{\text{CO}_2}$ atmosphere) for 18 ks. They are compared with those of the low $P_{\text{CO}_2}$ atmosphere shown in Fig. 14. $\mu_{\text{O}_2}^{\text{Sur}}$ of the high $P_{\text{CO}_2}$ atmosphere is larger than that of the low $P_{\text{CO}_2}$ atmosphere. This result elucidates that $\mu_{\text{O}_2}^{\text{Sur}}$ depends on the concentration of the oxidant, CO$_2$ in the atmosphere.

5.3 Thickness of gas boundary layer formed in oxidation of iron in Ar-1 %CO-5 %CO$_2$

As shown in Fig. 11, the gradient of the electromotive force generated in the cell which has three electrodes during the high temperature oxidation of iron decreases with increasing the distance between the oxide surface and the platinum electrode on CSZ. The electromotive force is generated by the difference of the oxygen chemical potential between the surface of the oxide scale and the platinum electrode on the CSZ tube. Therefore, the distribution of the electromotive force shown in Fig. 11 follows the oxygen chemical potential in the atmosphere including the gas boundary layer. There is almost no gradient of the electromotive force around electrode 3. It indicates that the electrode 3 is located out of the gas boundary layer.

Therefore, when the distance between the metal surface and the platinum electrode on CSZ tube is 2 cm, the electromotive force generated by the oxygen chemical potential difference between the surface of the oxide scale and the atmosphere out of the gas boundary layer can be measured correctly. This fact proves the validity of the obtained results in this study, since the distance between the metal surface and the platinum electrode on CSZ tube was 2 cm.

6. Conclusion

Oxygen chemical potential at the surface of growing oxide scales formed in high temperature oxidation of metals was monitored continuously by the oxygen concentration cell constructed with Calcia-Stabilized ZrO$_2$. The oxygen chemical potential at the surface of growing NiO scale and CoO scale in the oxidation of nickel and cobalt at 1373 K in Ar-21 %O$_2$ gas was slightly smaller than that in the atmosphere. In the case of FeO scale formed at 1373 K in Ar-CO-CO$_2$ gas mixture, the oxygen chemical potential at the surface decreased more than 2 orders of magnitude comparing with that in the atmosphere. Furthermore, the oxygen chemical potential at the surface of FeO scale increased with increment of CO$_2$ concentration in the atmosphere.

The proposed method to monitor the oxygen chemical potential at the surface of a growing oxide scale will enable to demonstrate more quantitative analyses of the morphological change in the scale.

Acknowledgements

This research was financially supported in part by the Grant-in-Aid for Scientific Research on Priority Area, “Nanoionics (439) by the Ministry of Education, Culture, Sports, and Technology”.

REFERENCES