Influence of Trace Impurities on Oxygen Activity for High Purity Nitrogen Gas Processed by Zirconia Oxygen Pump

Shumpei OZAWA[1], Yuki KAWANOBE[1], Kazuhiko KURIBAYASHI[1] and Toru NAGASAWA[2]

Abstract

Oxygen activity ($a_{\mathrm{O_2}}$) of high purity nitrogen gas was controlled and monitored by a zirconia oxygen pump and sensors operated at 600 °C. It was confirmed that the oxygen pump and sensors can control the $a_{\mathrm{O_2}}$ at 600 °C precisely. Solid metal samples of copper, nickel and iron were actually oxidized under the processed gas when the indicated value of the $a_{\mathrm{O_2}}$ is higher than the equilibrium oxygen activity for formation of the metal oxides. When the indicated value of $a_{\mathrm{O_2}}$ is lower than the equilibrium oxygen activity for formation of the oxides, the samples were reduced. The processed gas showed a temperature reliance induced from the gas phase equilibrium between the H_2 and H_2O gases, which were contained in the source gas as an impurity.
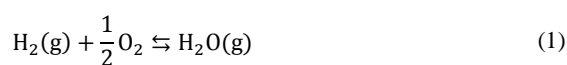
1. Introduction

Space provides optimal conditions to measure thermophysical properties of high temperature melts because a container being chemically reactive with the sample at high temperature is not required to hold a high temperature melt. The measurement can be free from convection and hydrostatic pressure which generally deteriorate the accuracy of ground based measurements. An international collaboration called OXYTHERM is planned for inclusion on the International Space Station (ISS), and one of the purposes of the project is to obtain a benchmark for the thermophysical properties, such as density, viscosity, and surface tension [1] by oscillating droplet method using electromagnetic levitation. In this project, it is essential that oxygen activity of atmospheric gas ($a_{\mathrm{O_2}}$) is controlled and monitored during the measurement under extended periods of microgravity conditions. The $a_{\mathrm{O_2}}$ influences the surface tension of metallic melt because oxygen is strong surfactant [2-5]. Since the viscosity is calculated from the damping time of surface oscillations of the levitated droplet [6], it would be also influenced by $a_{\mathrm{O_2}}$ during the measurement.

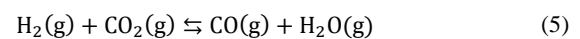The $a_{\mathrm{O_2}}$ of atmospheric gas is often controlled by the gas phase equilibrium using buffer gases such as H_2-H_2O, CO-CO_2, and H_2-CO_2 mixtures in terrestrial experiments.

$$H_2(g) + \frac{1}{2}O_2 \leftrightarrows H_2O(g) \qquad (1)$$

$$K_{\mathrm{H_2O}} = \frac{a_{\mathrm{H_2O}}}{a_{\mathrm{H_2}} \cdot a_{\mathrm{O_2}}^{1/2}} \qquad (2)$$

$$CO(g) + \frac{1}{2}O_2 \leftrightarrows CO_2(g) \qquad (3)$$

$$K_{\mathrm{H_2O}} = \frac{a_{\mathrm{CO_2}}}{a_{\mathrm{CO}} \cdot a_{\mathrm{O_2}}^{1/2}} \qquad (4)$$

$$H_2(g) + CO_2(g) \leftrightarrows CO(g) + H_2O(g) \qquad (5)$$

$$K_{\mathrm{CO+H_2O}} = \frac{a_{\mathrm{CO}} \cdot a_{\mathrm{H_2O}}}{a_{\mathrm{CO_2}} \cdot a_{\mathrm{H_2}}} \qquad (6)$$

where K is the equilibrium constant for the reactions and a_i is the activity of the gases. When a sufficiently large activity of these gases has been achieved, the temperature dependence of $a_{\mathrm{O_2}}$ can be calculated thermodynamically from the equilibrium constant of the reactions and the standard Gibbs energy for formation of H_2O and CO_2, assuming that the mixing ratio of the gases such as $a_{\mathrm{H_2}}/a_{\mathrm{H_2O}}$, $a_{\mathrm{CO}}/a_{\mathrm{CO_2}}$, and $a_{\mathrm{H_2}}/a_{\mathrm{CO_2}}$ is constant regardless of temperature. The influence of the formation and decomposition of the H_2O and CO_2 induced from the temperature variation under the gas phase equilibrium is negligible on the mixing ratios of these gases.

However, the use of these gases is unacceptable under the safety regulations on the ISS. An oxygen sensing and control

1 Department of Mechanical Science and Engineering, Chiba Institute of Technology, 2-17-1, Tudanuma, Narashino, Chiba275-0016 Japan.
2 Canon Machinery INC, Kusatsu, Shiga525-8511 Japan.
(E-mail: shumpei.ozawa@it-chiba.ac.jp)

device (OSC) using a solid stabilized-zirconia electrolyte is proposed to control and monitor the oxygen activity of an inert gas in OXYTHERM on the ISS. A solid electrolyte is known to be able to transport oxygen ions at a temperature high enough for the experiment but low enough to suppress electronic conduction. A voltage put across a dividing wall of a solid electrolyte works as an oxygen pump because oxygen ions migrate through the wall from the cathode to the anode according to the Nernst equation [7]. This can also work as an oxygen sensor when the voltage difference induced by the a_{O_2} between the process gas and reference gas is monitored at the dividing wall.

However, it is important to note that even if a high purity inert gas is used to control the a_{O_2} by the OSC, a small amount of H_2, H_2O, CO, and CO_2 gases will be present as potential impurities. Comparatively large amounts of H_2O are usually physically-adsorbed by all surfaces such as the insides of a chamber wall and a gas flow path. When the a_{O_2} of the inert gas is reduced significantly lower than the activities of these impurity gases (a_{H_2}, a_{H_2O}, a_{CO}, and a_{CO_2}) by the OSC, the gas phase equilibrium between these impurity gases may influence the a_{O_2} of the processed gas. Since the absolute values of a_{H_2}, a_{H_2O}, a_{CO}, and a_{CO_2} in the processed gas are quite small, these may not work as sufficient buffers to control the a_{O_2}; it might not be appropriate to calculate the temperature reliance of a_{O_2} of the gas thermodynamically on the assumption that the mixing ratio of these gases is constant regardless of temperature. Nevertheless, the zirconia oxygen sensor cannot measure the temperature dependence of a_{O_2}, instead it detects the a_{O_2} of the gas introduced into the oxygen sensor maintained at certain temperature. Therefore, it is crucial to confirm and calibrate the temperature dependence of a_{O_2} for the processed gas by the OSC.

In this study, the a_{O_2} of high purity commercial nitrogen gas was decreased and controlled by a zirconia oxygen pump and sensor. A solid metal, such as copper, iron, and nickel, was heated in the processed gas at high temperature in order to oxidize and reduce it. The purpose of this investigation was to confirm and estimate the temperature reliance of a_{O_2} on nitrogen gas processed by a zirconia oxygen pump and sensor.

2. Experimental procedure

Figure 1 depicts a schematic diagram of the experimental set up, which consists of the zirconia oxygen pump system (ULOCE-500, Canon Machinery Inc), and a gold image furnace. Cylindrical samples of high purity copper (99.999 %), nickel (99.998 %) and iron (99.998 %) were put on the W/Re thermocouple sheathed with quartz glass, and then placed at the center of a quartz glass chamber inside the gold image furnace. The quartz glass chamber and gas flow path were evacuated and
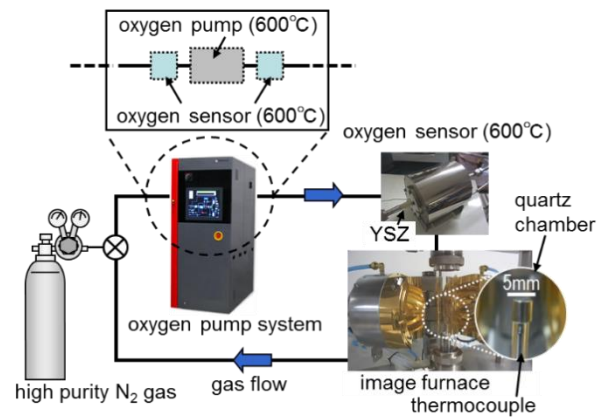

Fig. 1 Schematic of experimental setup

Table 1 Nominal composition of N_2 gas used in this study

(vol. ppm)

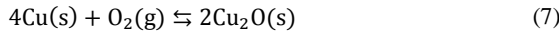| O_2	CO	CO_2	THC*	NO_x	SO_2	H_2O	N_2
<0.1	<0.1	<0.1	<0.05	<0.01	<0.01	<2.7	Val.

*Total hydrocarbon

then backfilled with a high purity commercial nitrogen gas. The nominal composition of the nitrogen gas is shown in **Table 1**. The a_{O_2} of the circulating gas with a flow rate of 2L/min was controlled by the oxygen pump and sensors maintained at 600 °C. The target value of a_{O_2} was selected to be slightly above and below the equilibrium oxygen activity for forming the metal oxide at 600 °C. After the indicated a_{O_2} in the oxygen sensors had stabilized, the sample was heated and maintained at 600 °C for several hours to several tens of hours for calibrating the oxygen pump and sensors; whether the a_{O_2} prepared by the oxygen pump and sensors was actually higher or lower than the equilibrium oxygen activity for forming the metal oxide was evaluated by observing the oxidation and reduction of the sample.

The sample temperature was elevated to various values under the same a_{O_2} conditions to evaluate the temperature reliance of the a_{O_2} from the oxidation/reduction behavior of the sample as in the case of the sample maintained at 600 °C.
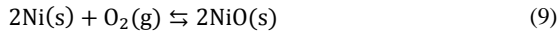
3. Results and discussion

The zirconia oxygen pump and sensors can control the a_{O_2} of the atmospheric gas at 600 °C which is the working temperature of these devices used in this study. In order to calibrate the zirconia oxygen pump and sensors, the oxidation and reduction behavior was confirmed for metallic samples of high purity copper, nickel, and iron at 600 °C under circulating nitrogen gas in which the a_{O_2} was controlled at slightly higher and lower values than the equilibrium oxygen activity for forming metal
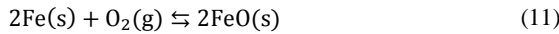
oxides. The results are shown in **Fig. 2**. The equilibrium oxygen activity in the following reactions for forming Cu_2O, NiO, and FeO were calculated thermodynamically from the standard Gibbs energy, ΔG° [8].

$$4Cu(s) + O_2(g) \leftrightarrows 2Cu_2O(s) \tag{7}$$

$$\Delta G^{\circ}_{2Cu_2O} = -338300 + 146.63T \tag{8}$$

$$2Ni(s) + O_2(g) \leftrightarrows 2NiO(s) \tag{9}$$

$$\Delta G^{\circ}_{2NiO} = -468580 + 169.44T \tag{10}$$

$$2Fe(s) + O_2(g) \leftrightarrows 2FeO(s) \tag{11}$$

$$\Delta G^{\circ}_{2FeO} = -528860 + 129.46T \tag{12}$$

When the indicated value of a_{O_2} in the oxygen sensors is controlled to be slightly higher than the equilibrium oxygen activity for forming the metal oxide within an increment of less than an order of magnitude, oxidation of all the samples is actually confirmed from the disappearance of metallic luster. When the indicated value of the oxygen sensors is controlled to be slightly lower than the equilibrium oxygen activity for forming the metal oxide, a metallic luster appears on all samples due to reduction. These results indicate that the zirconia oxygen

pump and sensors used in this study can control and monitor the a_{O_2} of the nitrogen gas accurately within the tolerance of at least an order of magnitude at 600 °C.

Even when the a_{O_2} of atmospheric gas is precisely controlled by the oxygen pump and sensors at 600 °C, there may be a temperature dependence due to the gas phase equilibrium induced from the potential impurities of H_2, H_2O, CO, and CO_2 gases contained in the source gas. In order to confirm a temperature dependence of the a_{O_2} processed by the oxygen pump and sensors, the nickel samples were heated at 800, 1000, and 1300 °C. The results are shown in **Fig. 3**, in which the temperature dependence of the a_{O_2} is calculated under the assumption that the activities of the potential impurities of H_2, H_2O, CO, and CO_2 gases contained in the source gas are large enough to work as buffers. The calculated results are almost the same under the CO-CO_2 and H_2-CO_2 buffers in this calculation condition (dotted lines). When the a_{O_2} of atmospheric nitrogen gas is controlled to 6.5×10^{-19} atm at 600 °C by the oxygen pump and sensors, the nickel sample is oxidized between 600-1300 °C. If the a_{O_2} of the nitrogen gas processed by oxygen pump is not temperature reliant, the nickel sample should not be oxidized between 800-1300 °C because the a_{O_2} of 6.5×10^{-19} atm is lower than the equilibrium oxygen activity for forming nickel oxide. This result confirms that the a_{O_2} of nitrogen gas processed by oxygen pumps is temperature dependent.

When the a_{O_2} of atmospheric nitrogen gas is controlled to 5.2×10^{-21} atm at 600 °C, reduction of the sample is observed between 800-1300 °C. This oxidation/reduction behavior of the nickel sample is in good correspondence with the calculated
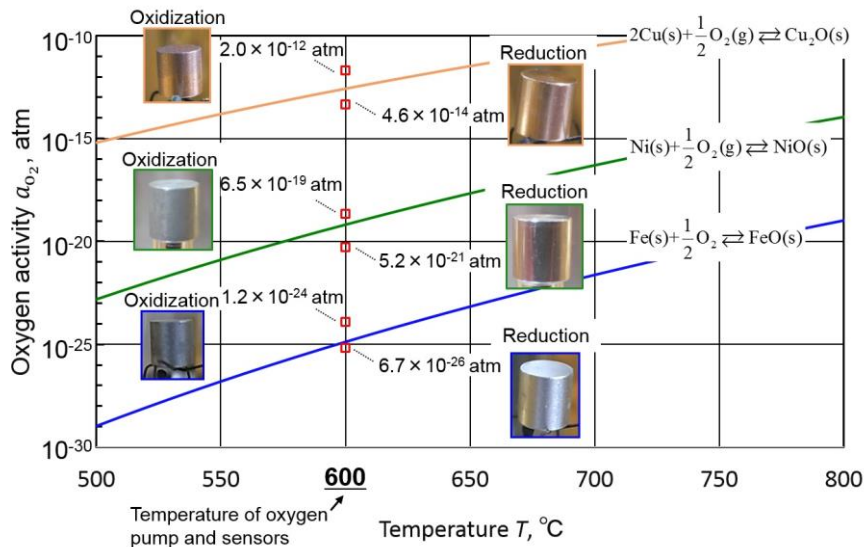

Fig. 2 Behaviors of oxidation and reduction of solid copper, nickel, and iron, under the nitrogen gas processed by the oxygen pump and sensors at 600 °C. The solid lines correspond to the equilibrium oxygen activities for formation of the metal oxides. The square plots are indicated values of the oxygen activity of the atmospheric gas prepared by the oxygen pump and sensors.
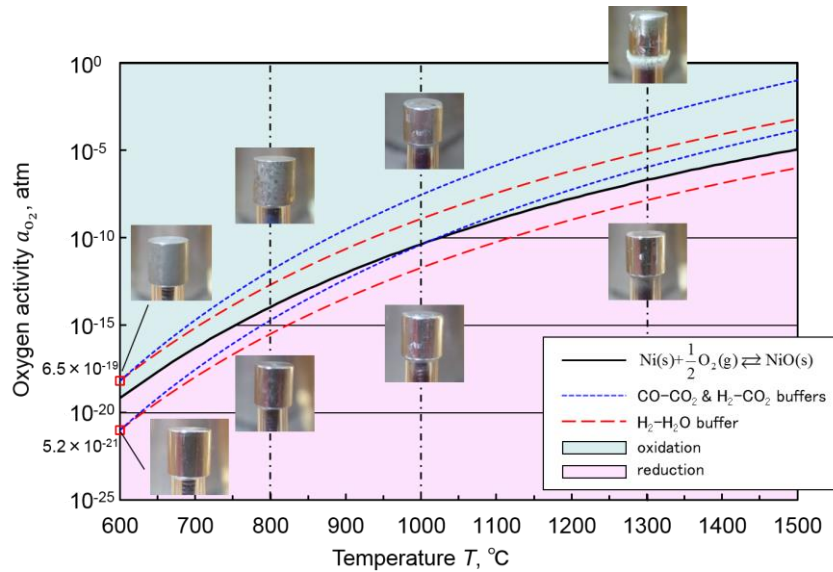
Fig. 3 Behaviors of oxidation and reduction of solid nickel at 800, 1000, and 1300 °C, at which the a_{O_2} of the atmospheric nitrogen gas was controlled at 6.5×10^{-19} and 5.2×10^{-21} atm by oxygen pump and sensors maintained at 600 °C.

temperature reliance of a_{O_2} that is assumed to be controlled by gas phase equilibrium of the H_2-H_2O buffer indicated by the dashed lines: the oxidized sample is reduced when the calculated a_{O_2} is changed from a higher value to a lower value compared with the equilibrium oxygen activity for the formation of nickel oxide. If the temperature dependence of a_{O_2} is controlled by the gas phase equilibrium of CO-CO_2 or H_2-CO_2 buffers, the nickel sample should be oxidized at 1300 °C because a_{O_2} becomes higher than the equilibrium oxygen activity for forming nickel oxide. The nominal quantities of CO and CO_2 contained in the source gas as potential impurities are much smaller than that of H_2O as shown in **Table 1**. Thus, the temperature dependence of the nitrogen gas processed through the zirconia oxygen pump would be controlled not by the gas phase equilibrium of CO-CO_2 and H_2-CO_2 but by that of the H_2-H_2O buffer.

As mentioned above, even if the a_{O_2} of a high purity inert gas is reduced by a zirconia oxygen pump and sensors, it shows a temperature dependence induced from the gas phase equilibrium of the H_2-H_2O buffer. Therefore, in order to make the OXYTHERM project at the ISS succeed, it is essential to clarify the quantities of potential impurities, such as H_2, H_2O, CO, and CO_2, in the source gas to evaluate the temperature reliance of the a_{O_2} of gas.

4. Summary

The a_{O_2} of high purity nitrogen gas was controlled and monitored by a zirconia oxygen pump and sensors operated at 600 °C. When solid copper, nickel and iron were heated at 600 °C under the controlled a_{O_2} condition by the oxygen pump and sensors, the samples were oxidized and reduced depending on the indicated a_{O_2} as expected. The temperature dependence of the a_{O_2} was confirmed by oxidation/reduction reaction of nickel sample at various temperature. It was well agreement with that induced from the gas phase equilibrium of H_2-H_2O mixtures.

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