



Oxygen partial pressure control for microgravity experiments

Michał Schulz^{a,*}, Jürgen Brillo^b, Christian Stenzel^c, Holger Fritze^a

^a Clausthal University of Technology, Institute of Energy Research and Physical Technologies, Am Stollen 19B, 38640 Goslar, Germany

^b German Aerospace Center (DLR), Institute of Materials Physics in Space, Linder Höhe, 51170 Cologne, Germany

^c Astrium-Space Transportation, Department: TO 5, 88039 Friedrichshafen, Germany

ARTICLE INFO

Article history:

Received 9 September 2011

Accepted 9 April 2012

Available online 5 May 2012

Keywords:

Oxygen pump

Yttrium-stabilized zirconia

Electromagnetic levitation

ABSTRACT

A system consisting of a high-temperature yttrium-stabilized zirconia (YSZ) based oxygen ion pump and potentiometric sensor enables precise measurement and control of oxygen partial pressure, p_{O_2} , at elevated temperatures within 0.2 to 10^{-20} bar. The principle of operation as well as the influence of temperature and gas buffers like H_2/H_2O on the p_{O_2} is discussed. The ion pump is controlled by a microcontroller system and adjusts the oxygen partial pressure with an uncertainty of $\Delta \log(p_{O_2}/\text{bar}) < 0.02$ and response times between 5 and 90 s over the entire p_{O_2} range.

The oxygen ion pump is tested in combination with the electromagnetic levitation. Here, the surface tension of molten Ni at 1720 °C as a function of oxygen partial pressure is determined. A good agreement of this measurement with calculated value confirms the applicability of the system for high-temperature measurement and control of p_{O_2} . The developed hardware is suitable for the electromagnetic levitation facility onboard the international space station (ISS).

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The investigation of the material properties in the liquid phase at elevated temperatures requires often precise knowledge of the oxygen partial pressure. Surface oxidation and oxygen dissolution may affect the properties significantly. Depending on the considered substance, its oxidation may occur even at extremely low p_{O_2} , such as 10^{-24} bar. Therefore, it is required to control the p_{O_2} with range depending on the specific experiment.

Measurement of O_2 concentration at elevated temperatures using e.g. optical or photoacoustic methods is not applicable for systems, where oxidation at elevated temperatures takes place at very low p_{O_2} . The sensitivity of such devices is hardly better than 10^{-6} bar. Further, the information about the oxygen content does not necessarily correspond to the oxygen activity which is the property of interest. Also, resistive and amperometric methods offer either a narrow range of measurement or a sensitivity only of about 10^{-7} bar, respectively. Therefore, potentiometric systems are most favorable. They allow measurements of the p_{O_2} in the range from 10^0 to 10^{-24} bar and exhibit very short response times.

Control of oxygen partial pressure in such wide range is not possible using conventional gas mixing systems. Gas buffers, like H_2/H_2O and CO/CO_2 enable relatively precise adjustment of p_{O_2} below 10^{-15} bar. The oxygen partial pressures above 10^{-7} bar may be obtained using cascades of conventional mass flow controllers. Around the

equilibrium composition, where stoichiometric amounts of gases are reacting, smallest fluctuations in gas composition shift the p_{O_2} by several orders of magnitude. In order to overcome this difficulty, an oxygen ion pump based on yttrium-stabilized zirconia (YSZ) is applied. In contrast to conventional mass flow controllers which adjust the oxygen flow with an uncertainty of about $50 \text{ mm}^3/\text{min}$, the oxygen ion pump can control oxygen flow with a resolution of at least $0.001 \text{ mm}^3/\text{min}$. In combination with a potentiometric sensor, it enables precise transport of oxygen into and out from the system and thus allows precise control of the p_{O_2} within the 10^{-24} to 0.2 bar range.

One of the applications, where oxygen partial pressure must be known, is the determination of the surface tension of liquid metals and alloys at elevated temperatures. Even under high-purity conditions, undefined atmospheres may lead to oxidation of the samples which impacts the surface tension by 10 to 30%. Depending on the sample, the oxygen partial pressure has to be below 10^{-24} bar to avoid oxidation.

As the contact based techniques, such as sessile drop technique [1–4], can often lead to erroneous results, in particular due to chemical reactions between the sample and the substrate, contactless techniques such as the electromagnetic levitation are indicated for investigation of high-purity materials. Here, a molten sample is levitating in an electromagnetic field, giving an oscillating drop [5]. Even though the oscillations are influenced by the environment, like gas perturbations in the vicinity of the sample or drop rotations, mathematical treatment is developed which enables extraction of the surface tension from this data [6]. Since any contact between sample and crucible is avoided with this technique, it is a highly

* Corresponding author. Tel.: +49 5321 6855 172; fax: +49 5321 6855 159.
E-mail address: michal.schulz@tu-clausthal.de (M. Schulz).

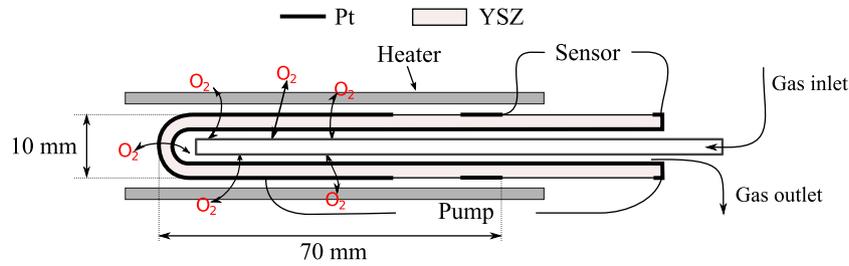


Fig. 1. Schematic view of a YSZ based oxygen ion pump. The carrier gas is delivered through the inlet into the active area, where an electric current I is applied. Depending on the polarity, the pump enriches or depletes the oxygen concentration in carrier gas. An additional reference electrode is provided, where Nernst potential and, therefore, oxygen partial pressure is measured.

suitable approach for determination of material data for high-purity materials. In order to reduce the perturbations introduced by strong electromagnetic field as required to levitate the sample under 1 g, the conduction of this experiments in microgravity conditions on-board the international space station (ISS) is mostly favorable.

2. Operation principle

2.1. Oxygen ion pump

The oxygen ion pump is based on an ionic conductor operated at a temperature sufficiently high to enable the transport of O^{2-} through an electrolyte, but low enough to suppress the electronic conduction. In case of dominant ionic conductivity, the flux of oxygen is defined as [7–9]:

$$J_{O_2} = \frac{I}{4F}, \quad (1)$$

whereas I and F correspond to the electric current and Faraday constant, respectively. Using a pumping current of 40 mA a transfer of about $8 \text{ cm}^3 \text{ O}_2$ per hour occurs. If the oxygen flow J_{O_2} is low with respect to the total gas flow, the resulting oxygen partial pressure depends on the total pressure p_{tot} , total gas flow J_{tot} and the initial oxygen partial pressure in the carrier gas $p_{O_2}^0$:

$$p_{O_2} = p_{O_2}^0 + p_{\text{tot}} \frac{J_{O_2}}{J_{\text{tot}}}. \quad (2)$$

The scheme of the oxygen ion pump is shown in Fig. 1 and explained in detail in Section 3.1. Here, the large electrode is used to transport oxygen from the reference gas (ambient air) to the carrier gas. The small electrode is used to monitor the electromotive force which is given by the Nernst equation

$$E_{\text{cell}} = \frac{RT}{4F} \ln \left(\frac{p_{O_2}}{p_{O_2}^{\text{ref}}} \right), \quad (3)$$

where R and T are the universal gas constant and the temperature,¹ respectively. The oxygen partial pressure in the reference gas, $p_{O_2}^{\text{ref}}$, equals 0.209 bar. The error introduced by regarding this value as constant is negligible.

2.2. Oxygen equilibrium in buffer gas mixtures

In case of the presence of buffer gas mixtures, Eq. (2) describing oxygen partial pressure does not apply. Here, the gas equilibrium

has to be taken into account. In hydrogen-containing atmospheres, the formation of water vapor takes place:



with the equilibrium constant

$$K(T) = \frac{(p_{H_2O}^0 + \Delta p_{H_2O})}{(p_{H_2}^0 + \Delta p_{H_2})(p_{O_2}^0 + \Delta p_{O_2})^{1/2}}. \quad (5)$$

Here, $p_{H_2}^0$, $p_{H_2O}^0$ and $p_{O_2}^0$ correspond to the initial partial pressures of hydrogen, water vapor and oxygen, respectively, before the reaction takes place. The temperature dependent equilibrium constant is defined as [10]:

$$K(T) = 1.423 \cdot 10^{-3} \exp \left(\frac{2.56 \text{ eV}}{k_B T} \right). \quad (6)$$

Combining Eqs. (1), (2), (5) and (6), the oxygen partial pressure adjusted by an oxygen ion pump $p_{O_2} = p_{O_2}^0 + \Delta p_{O_2}$ is calculated numerically for given initial partial pressures and temperatures and shown in Fig. 2. As carrier gas, Ar (99.999%, $p_{O_2} = 1.6 \cdot 10^{-4}$ bar) mixed with H_2 ($p_{H_2} = 0.005$ bar) flowing at $20 \text{ cm}^3/\text{min}$ is used.

Based on Fig. 2 three different regions are discussed:

Low p_{O_2} region. Hydrogen and nearly all oxygen form water vapor resulting in p_{O_2} s as low as 10^{-25} bar at $600 \text{ }^\circ\text{C}$ and a pump current $I = 0$ mA (see Fig. 2). Due to very high excess of H_2 , further titration of oxygen ($I < 8$ mA) results in slight increase of oxygen partial pressure.

Stoichiometric point. Here, a nearly stoichiometric composition of H_2 and O_2 to form water is reached. Only very slight changes in the pumping current ($I \approx 8$ mA) and thus in the amount of oxygen provided, result in p_{O_2} changing by several orders of magnitude.

High p_{O_2} region. Nearly all hydrogen reacts with oxygen and forms water vapor. Further introduction of oxygen into the system ($I > 9$ mA) leads to a slight shift of equilibrium and to a steady increase of oxygen partial pressure, only. The control of p_{O_2} using conventional gas mixing systems is feasible.

The amount of electric current applied to the oxygen ion pump causing a change of p_{O_2} by one order of magnitude at the stoichiometric point is shown in Fig. 3. As shown there, at low flow and low temperatures, the pumping current has to be controlled precisely in a range of 10^{-9} A. If such expectation cannot be fulfilled, either higher temperature or, according to Eq. (2), higher flow rates are required.

2.3. Correction of the oxygen partial pressure

If the temperature of the sample differs from the operating temperature of the oxygen sensor, the p_{O_2} must be corrected. The

¹ The calculations are done using the temperature in Kelvin. The plots show the results in degree Celsius.

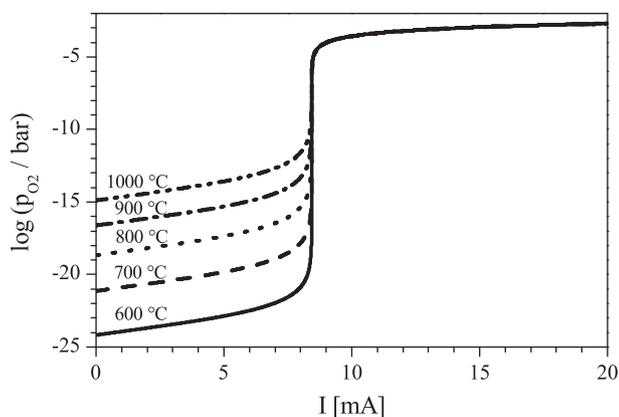


Fig. 2. Oxygen partial pressure as a function of pumping current I and temperature, adjusted by the zirconia titration pump at different temperatures. Calculations for 0.5% H_2/Ar gas flowing through the oxygen pump at rate of $20 \text{ cm}^3/\text{min}$.

total amounts of hydrogen and oxygen present in the reaction chamber before a reaction takes place are expressed again by $p_{\text{H}_2}^0$ and $p_{\text{O}_2}^0$, respectively. For further discussions, the amounts of hydrogen and oxygen bound in water are added to $p_{\text{H}_2}^0$ and $p_{\text{O}_2}^0$, respectively. The approach is used to define a reference gas composition and to calculate subsequently the partial pressures of oxygen, hydrogen and water after completing the reaction according to Eq. (4) as a function of temperature. Those properties are denoted again by p_{O_2} , p_{H_2} and $p_{\text{H}_2\text{O}}$, respectively. Similar considerations can be done for gas mixtures containing O_2 , CO and CO_2 . However, the following application examples base on atmospheres which contain very little amounts of CO and CO_2 with respect to H_2 and H_2O . Therefore, the occurrence of carbon containing gases is ignored for the further discussion.

The gases used for experiments contain a fixed amount of hydrogen $p_{\text{H}_2}^0$. The amount of oxygen $p_{\text{O}_2}^0$ required to adjust a certain p_{O_2} is provided by an oxygen pump. As explained in more detail in Section 3, two cases are realized:

1. Intentional insertion of 0.5% H_2/Ar
2. Use of highly pure argon with $p_{\text{H}_2} < 1 \text{ ppm}$.

In order to calculate the temperature dependence of the p_{O_2} , Eq. (5) is solved for $p_{\text{O}_2} = p_{\text{O}_2}^0 + \Delta p_{\text{O}_2}$. In a first step $p_{\text{O}_2}^0$ is varied until a certain $p_{\text{O}_2} = p_{\text{O}_2}^{600}$ at $600 \text{ }^\circ\text{C}$, i.e. at the sensor temperature, is adjusted. In a second step, the temperature is varied using fixed values for $p_{\text{H}_2}^0$ and $p_{\text{O}_2}^0$.

Fig. 4 shows the result for $p_{\text{H}_2}^0 = 10^{-7} \text{ bar}$ and different $p_{\text{O}_2}^{600}$. It becomes obvious that changes in temperature have a minor impact on the p_{O_2} as long as $p_{\text{O}_2}^{600} \gtrsim 10^{-7} \text{ bar}$. Below that value there is a

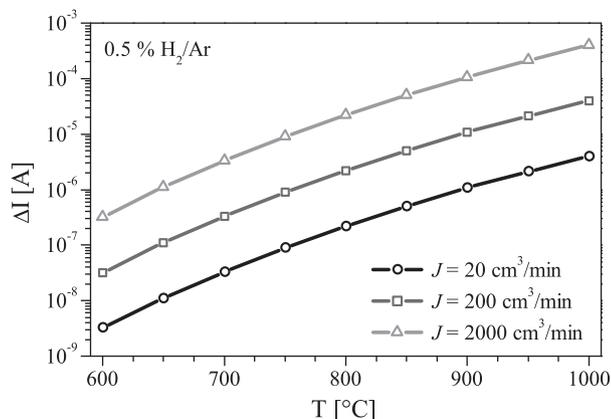


Fig. 3. Electric current required to change the p_{O_2} at the stoichiometric point by one order of magnitude calculated for different temperatures and total gas flows.

strong temperature dependence which must be regarded while discussing experiments where the temperature of the oxygen sensor and the sample are different.

It should be noted that the p_{O_2} below which corrections are necessary strongly depends on $p_{\text{H}_2}^0$. Higher total hydrogen concentrations shift this p_{O_2} to higher values.

3. Experimental

The oxygen loading system (OLS) consisting of ion pump, potentiometric sensor and mechanical gas circulation pump is tested in two different environments. Laboratory conditions, free of strong electromagnetic fields and dust particles in carrier gas due to evaporation of liquid samples, enable precise determination of oxygen pump's performance, response time and signal stability. In case of the experiments, where the oxygen partial pressure is adjusted during levitation, strong electromagnetic fields impact potentially the stability of the control system. The experimental results are correlated with theoretical considerations on surface tension as a function of oxygen partial pressure.

3.1. Oxygen control system

The p_{O_2} is controlled using two YSZ tubes which are operated as oxygen pump and sensor, respectively. The approach enables to measure the p_{O_2} independent of the pump at positions in the experimental setup which are defined by the actual application. In general, the sensor should be installed in the close vicinity of the sample to be investigated. It must be noted, that the pump is equipped with an additional oxygen sensor whose signal is used to improve the stability of the control algorithm.

The one-side closed, 8 mol% Y_2O_3 -doped ZrO_2 tubes with platinum electrodes are purchased at Metrotec GmbH, Kirchheim, Germany. The scheme and the dimensions of the first tube used primarily as oxygen pump are shown in Fig. 1. Since the device is also designed to measure the p_{O_2} , the outer face is covered with platinum paste in two regions, i.e. there is a large pumping area of about 125 cm^2 and a small sensor area of about 3 cm^2 . Due to the large distance between the pumping and sensor electrode, no impact of the pumping current on the Nernst potential is observed. The inner face is coated with a common platinum electrode. The second tube is operated as oxygen sensor. The device is coated with a small outer electrode of 3 cm^2 and a large inner electrode. The general design corresponds to that of the oxygen pump.

Both, the oxygen ion pump and the sensor are operated at $600 \text{ }^\circ\text{C}$. This temperature ensures sufficiently high oxygen ion mobility and long-term stability of the system. The YSZ tubes are enclosed in

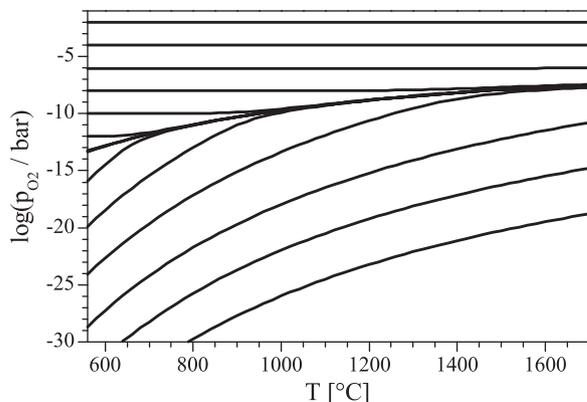


Fig. 4. Calculated temperature dependence of oxygen partial pressure for a gas consisting of a total amount of hydrogen which corresponds to $p_{\text{H}_2}^0 = 10^{-7} \text{ bar}$.

large thermal insulation blocks to minimize the temperature gradients. It should be noted that the temperature is monitored very close to the oxygen sensors. The temperature of those small areas is expected to be very uniform and is used to calculate the p_{O_2} according to Eq. (3). Potential temperature fluctuations in the larger pumping area do not impact the p_{O_2} control since the applied electrical current is the property of interest.

Since the system is operated in an environment, where strong electromagnetic noise occurs, commercial temperature controllers do not fulfill the stability requirements under such conditions. Therefore, a robust custom device is built. In order to reduce the crossfeed between the power supply and monitored temperature, commonly used thermocouples are replaced with resistive temperature sensors. Further, EMI shielding for control electronics and for entire OLS is provided.

The pumping current I of at most 40 mA is adjusted by a pulse width modulation control based on a PID algorithm. Thereby the polarity of the current can be changed. The controller achieves a resolution of about 1 μ A.

Because of a strong nonlinearity of the $p_{O_2}(I)$ curve (see Fig. 2), classical PID algorithm cannot be used. The necessary modifications include i.a. dynamic adjustment of PID parameters at different oxygen partial pressures. Additionally, the system features a cascade PID controller, which enables p_{O_2} adjustment at two different potentiometric sensors.

3.2. Levitation facility

In order to confirm the applicability of the oxygen control system for electromagnetic levitation experiments, it is integrated at the levitation facility. The entire system is mounted on top of the experimental chamber (EC). The carrier gas with oxygen content adjusted by the pump is directed to the sample, whereas an additional potentiometric sensor monitors the oxygen partial pressure in gas leaving the EC.

4. Results and discussion

4.1. Control of oxygen partial pressure in buffer gases

The performance of the oxygen ion pump using the aforementioned 0.5% H_2 /Ar buffer gas is shown in Fig. 5. Here, the oxygen partial pressure is adjusted stepwise between 10^{-3} and 10^{-20} bar over several days. Throughout all oxygen partial pressures a signal stability of $\Delta\log(p_{O_2}/\text{bar}) < 0.02$ is achieved.

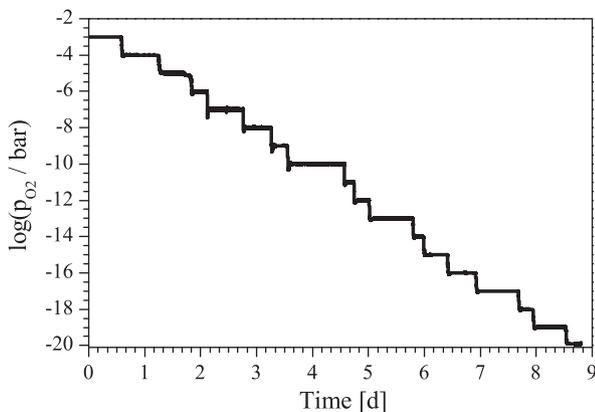


Fig. 5. Oxygen partial pressure regulated stepwise between 10^{-3} and 10^{-20} bar in a 0.5% H_2 /Ar at 600 °C.

4.2. Control of oxygen partial pressure without buffer gases

The result of oxygen ion pump controlling p_{O_2} at the nominally buffer-free carrier gas (Ar 99.999%) is shown in Fig. 6. Here, the oxygen partial pressure is varied stepwise between 10^{-7} and 10^{-3} bar. Remarkable is the very short response time of less than 90 s and signal stability of $\Delta\log(p_{O_2}/\text{bar}) < 0.02$. Since the oxygen control system features switching of the pumping current polarity, it is possible to control p_{O_2} below and above oxygen's partial pressure in the carrier gas.

4.3. Application example

Several pure metal samples are melted in the levitation facility at different oxygen partial pressures. At the same time the oscillations of the surfaces are observed with a high-speed camera. Based on this data, a p_{O_2} -dependent surface tension is determined [11]. According to theoretical considerations, in case of dilute solution of oxygen in a liquid metal, the surface tension γ is expressed by the Belton equation [12]:

$$\gamma = \gamma^{\text{pure}} - RT\Gamma_0 \ln(1 + Ka), \quad (7)$$

where γ^{pure} , R and T are the surface tension of pure liquid, universal gas constant and temperature, respectively. Γ_0 , K and a are the surface excess coefficient, adsorption coefficient and bulk activity of oxygen, respectively.

Exemplarily, a result of these tests is shown in Fig. 7. Here, a 99.999% Ni sample is molten and levitated at 1720 °C. An Ar gas (99.9999%) with adjusted p_{O_2} at flow rate of about 7000 cm^3/min is supplied directly at the sample. Major residual components of the Ar used are hydrogen and water ($p_{H_2} < 0.5$ ppm, $p_{H_2O} < 0.5$ ppm). For the following discussion a totality $p_{H_2}^0 = 10^{-7}$ bar is assumed. Taking the related results from Fig. 4, a scale for the p_{O_2} at 1720 °C is generated and added to Fig. 7. Again, the influence of temperature on p_{O_2} above 10^{-7} bar is negligible. As a consequence, no correction of the p_{O_2} is required in the range, where the surface tension undergoes its major changes. Below that p_{O_2} , of course, corrected values at 1720 °C have to be considered.

The measured oxygen partial pressure dependent surface tension is compared with the value calculated with Eq. (7) and the previous measurement of pure Ni annealed at the same temperature in nominally oxygen-free atmosphere [11]. The experimental result shows a good agreement with the Belton equation. A slightly lower surface tension compared to the previous measurement may be a result of a statistical error.

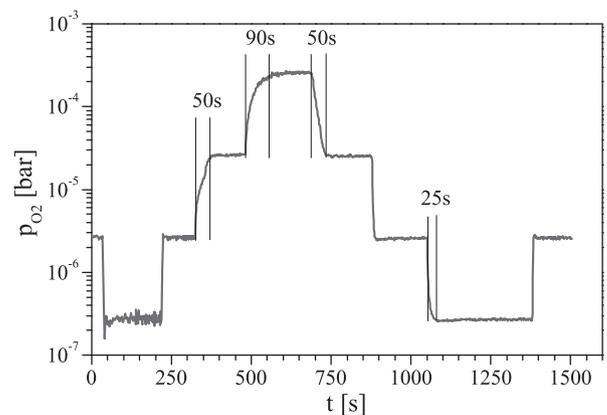


Fig. 6. Oxygen partial pressure adjusted by the pump operated at 600 °C. Here, the response time is determined by the amount of oxygen to be transferred through the electrolyte.

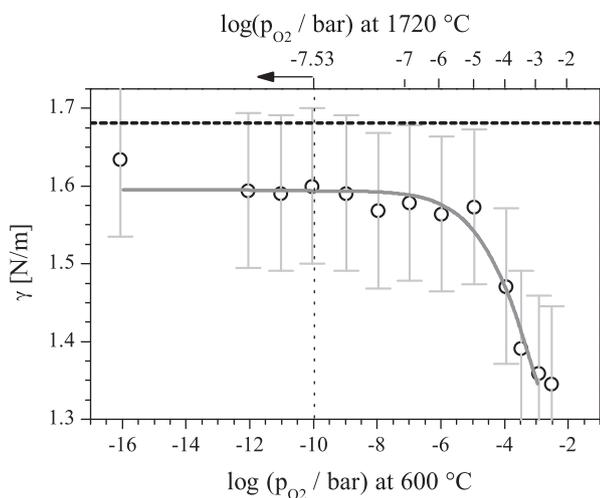


Fig. 7. The surface tension γ of 99.999% Ni as a function of p_{O_2} . The dotted line corresponds to the previous measurement in nominally oxygen-free atmosphere [11] whereas the gray line corresponds to the Belton Eq. (7). A good agreement of the measurement with the calculated curve is clearly visible.

5. Conclusions

A standalone system for oxygen partial pressure measurement and control is developed. It controls the p_{O_2} within 0.2 to 10^{-20} bar range with an uncertainty of $\Delta \log(p_{O_2}/\text{bar}) < 0.02$. The response time of the system is determined predominantly by the total volume of the experimental chamber. The developed hardware and electronics are thereby principally suited for later implementation into the EML (Electro-Magnetic-Levitator) facility onboard the ISS.

The system is successfully tested in the vicinity of high-power sources of electromagnetic fields, like e.g. power supply for

electromagnetic levitation facility. The surface tension of molten Ni determined as a function of oxygen partial pressure shows a good agreement with the Belton Equation. It confirms the correct operation of OLS set-up as well as the impact of p_{O_2} on the metal's surface properties at elevated temperatures. The test series have revealed that the developed OLS can be employed and successfully operated even under the harsh environmental conditions of a high-temperature levitation facility.

Since the temperature of the sample differs from the operating temperature of the oxygen sensor, the p_{O_2} must be potentially corrected. For the conditions here, no correction of the p_{O_2} is required in the range above $p_{O_2}^{600} \approx 10^{-7}$ bar, where the surface tension undergoes its major changes. Below that p_{O_2} corrected values at 1720 °C have to be considered.

Acknowledgment

The authors thank European Space Agency (ESA) and German Research Foundation (DFG) for financial support.

References

- [1] W. Kingery, M. Humenik Jr., *J. Phys. Chem.* 57 (1953) 359–363.
- [2] D. Staicopolus, *J. Colloid Sci.* 17 (1962) 439–447.
- [3] J. Butler, B. Bloom, *Surf. Sci.* 4 (1966) 1–17.
- [4] E. Ricci, E. Arato, A. Passerone, P. Costa, *Adv. Colloid Interface Sci.* 117 (2005) 15–32.
- [5] H. Lamb, *Hydrodynamics*, University Press, 1916, p. 443.
- [6] I. Egry, *J. Mater. Sci.* 26 (1991) 2997–3003.
- [7] A. Caneiro, M. Bonnat, J. Fouletier, *J. Appl. Electrochem.* 11 (1981) 83–90.
- [8] J. Fouletier, E. Siebert, A. Caneiro, *Adv. Ceram.* 12 (1984) 618–628.
- [9] J. Fouletier, E. Mantel, M. Kleitz, *Solid State Ionics* 6 (1982) 1–13.
- [10] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, 1997.
- [11] J. Brillo, I. Egry, *J. Mater. Sci.* 40 (2005) 2213–2216.
- [12] G. Belton, *Metall. Mater. Trans. B* 7 (1976) 35–42.