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Standard Gibbs energy of formation of tellurium dioxide measurement by a solid-oxide electrolyte EMF technique

M. Aspiala, D. Sukhomlinov, P. Taskinen*

Aalto University School of Chemical Technology, Department of Materials Science and Engineering, The Research Group for Thermodynamics and Modelling, Vuorimiehentie 2K, P.O. Box 16200, FI-00076 Aalto, Finland

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ABSTRACT

The standard Gibbs energy of formation of TeO_2 in the temperature range 369–795 °C was measured by the EMF method involving solid-oxide electrolyte galvanic cells of the type:

$$(-)\mathrm{Pt},\ \mathrm{Ir},\ \mathrm{Te(s,\ l)},\ \mathrm{TeO_2(s,\ l)}|\mathrm{YSZ}|\mathrm{O_2},\ \mathrm{Pt}(+),$$

where YSZ denotes stabilized zirconia with 8.5 mass percent of yttrium oxide. The standard Gibbs energies of formation obtained from the above cells are linear functions of temperature as:

$$\Delta_f G^\circ(\mathrm{kJ/mol}) = -317.09 + 0.180\,T\,(\mathrm{K}) \pm 0.307 \quad (642\text{–}722.15\,\mathrm{K})\ \text{both phases are solid.}$$

$$\Delta_f G^\circ(\mathrm{kJ/mol}) = -318.01 + 0.181\,T\,(\mathrm{K}) \pm 0.308 \quad (722.15\text{–}1005.8\,\mathrm{K})\mathrm{Te\text{–}liquid;\ TeO_2\text{–}solid.}$$

$$\Delta_f G^\circ(\mathrm{kJ/mol}) = -256.26 + 0.120\,T\,(\mathrm{K}) \pm 0.226 \quad (1005.8\text{–}1068\,\mathrm{K})\ \text{both phases are liquid.}$$

1. Introduction

Anode slimes of copper electrorefinery process frequently contain significant levels of tellurium. Its recovery in particular may have positive impact on the overall profitability of an integrated copper smelter. The recovery is possible in various stages of the anode slime treatment process, including the Doré smelting where it is oxidized from crude silver to the slag. Against this background, the thermodynamic stability of TeO_2 was studied [1].

Te and TeO_2 melt at 722.15 ± 0.3 K [2] and at 1005.8 ± 0.1 K [3,4], respectively. TeO_2 has been determined to be the most stable oxide in the tellurium–oxygen system [4]. TeO_2 has been found to exist in three polymorphic forms; α-TeO_2, β-TeO_2 and TeO_2II. The last crystallographic structure is an orthorhombic phase formed in high pressures (0.9 GPa at room temperature) [5,6]. In addition to TeO_2, tellurium–oxygen system includes also stable β-TeO_3 and Te_2O_5 high temperature compounds [7]. The invariant transformation temperatures of the compounds are for TeO_2 the α–β-equilibrium at 723.15 K and for Te_2O_5 (α–β) between 773.15 K and 793.15 K [7], respectively.

The electrochemical cell arrangements for the standard Gibbs energy of formation studies of TeO_2 used previously in the literature are presented in Table 1, together with that of this study.

The aim of this study is to re-examine and improve the accuracy and reliability of the literature values for the standard Gibbs energy of formation of TeO_2 as a function of temperature. The measurements were done by using a solid electrolyte EMF technique. Several improvements in the experimental technique and the data processing have been done in order to increase the reliability when comparing to the previous studies in the literature.

2. Experimental

2.1. Materials

A mixture of TeO_2 (Alfa Aesar, purity 99.99%) and Te (Alfa Aesar, purity 99.999%) in a weight ratio of 1:5 was used as the unknown electrode. The same ratio was successfully employed earlier in the studies of Mallika and Sreedharan [11]. The mixture was melted inside a zirconia electrolyte tube before the measurements, in order to homogenize the sample and improve the electrical conductivity. The solid-electrolyte tube (Friatec, Degussit YSZ with

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* Corresponding author. Tel.: +358 405017411.
E-mail addresses: markus.aspiala@aalto.fi (M. Aspiala), dmitry.sukhomlinov@aalto.fi (D. Sukhomlinov), pekka.taskinen@aalto.fi (P. Taskinen).

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Table 1
The cell arrangements of previous experiments.

Arrangement			Temperature range (K)	Reference
Anode	Electrolyte	Cathode		
Te + TeO_2, Ir, Pt	Zirconia(+yttria)	O_2, Pt	642–1068	This study
Te + TeO_2, W	Zirconia(+calcia)	Air, Pt	787–990	[8]
Te + TeO_2, Re, Kanthal	Zirconia(+calcia or yttria)	Air, Pt	748–973	[9]
Te + TeO_2, Pt	Zirconia(+yttria)	Air, Pt	733–873	[10]
Te + TeO_2, Pt	Zirconia(+yttria)	Air, Pt	586–898	[11]

8.5 wt% of Y_2O_3) was used to separate gaseous oxygen (AGA-Linde, 99.95%) reference electrode and the argon atmosphere (AGA-Linde, 99.999%) of the test electrode compartment. The lead wire contact to the sample was made using 12 mm long Ø 0.5 mm iridium wire (Alfa Aesar, 99.9%), which was welded to a platinum lead wire (Johnson-Matthey Noble Metals, 99.99%), because of an insignificant solubility of iridium to tellurium [12]. Anode Pt lead wire was protected by an alumina sheath (Friatec, Degussit Al23) to prevent reactions with the gaseous species of tellurium and tellurium oxides and the platinum lead wire.

2.2. EMF measurements

The schematic picture of the used cell is presented in Fig. 1. The Te–TeO_2 sample was located inside the solid-electrolyte tube and the closed end of it was pressed towards a circular platinum contact by steel springs. The contact between the anode lead wire and the sample was formed by inserting the tip of the iridium wire into the molten Te–TeO_2 sample. The sample was located in the isothermal zone of a vertical Lenton LTF 16/-/450 tube furnace, where the temperature difference over the length of the cell was verified to be within 1 K, by measuring the temperature on both sides of the cell with calibrated S-type thermocouples (Johnson-Matthey Noble Metals, accuracy ±1 K). The thermovoltages of the thermocouples were measured by a Keithley 2010 DMMs and the cold junction compensation was accomplished by a Pt100 resistance thermometer (SKS-Group, accuracy class 1/10 B), with a Keithley 2000 DMM voltmeter.

The pure oxygen reference electrode was generated by a steady oxygen flow outside the solid-electrolyte tube. Since the prevailing pressure of oxygen in the reference electrode corresponds to the ambient pressure outside the furnace, the pressure measurements were accomplished by measuring the ambient atmospheric pressure with a Vaisala PTU300 barometer, a combined pressure, humidity and temperature transmitter. Purified argon was used to provide an inert atmosphere inside the zirconia electrolyte tube. Argon was purified with titanium chips at 600 °C for removing traces of oxygen from the gas.

The cell EMF values were measured with a Keithley 6517B electrometer with an internal impedance of 10^{14} Ω and it was stated to be stabilized after at least a 10 min period, when the variation of EMF was within 0.1 mV. The EMF values reported are averages of at least 100 data points collected after the system equilibration at each temperature. Two different cells were measured by cooling and heating the furnace in order to prove the repeatability of the results obtained. The used temperature values are respectively averages of the measured values of thermocouples. The readings were collected from all the measurement devices every 5 s and stored in a laptop computer.

3. Results

The measured EMF values of this study for the cells

$$(-)\text{Pt, Ir, Te(s, l), TeO}_2\text{(s, l)}|\text{YSZ}|\text{O}_2\text{, Pt}(+) \quad (1)$$

are presented together with corresponding temperature of the cell and oxygen pressure of the reference electrode in Table 2. The presented values are averages of at least 100 data points collected after the stabilization of the cell in each temperature. Presented

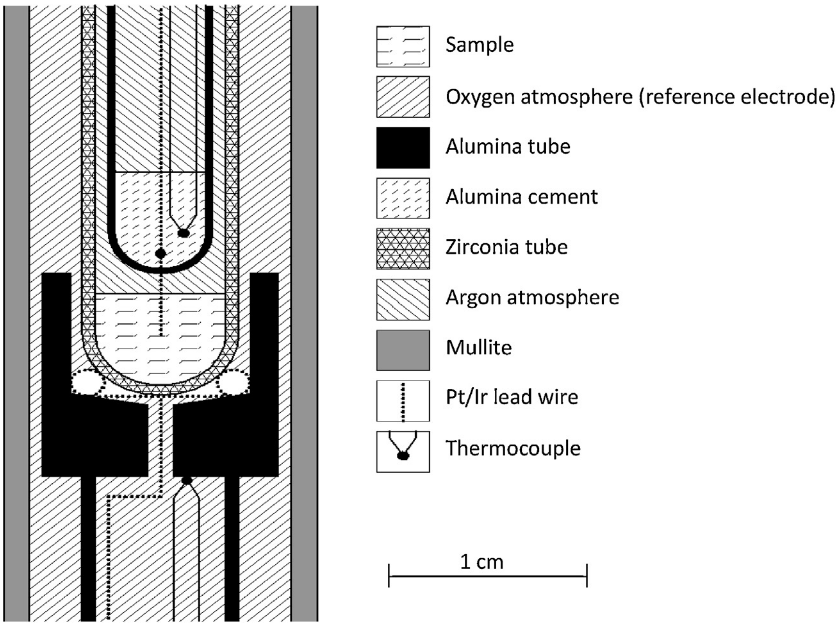

Fig. 1. The cell arrangement used for measuring oxygen potential of the tellurium–tellurium dioxide equilibrium, the scale of the schematic is suggestive.