Solid State EMF Study of the Equilibrium

Ni(s)+TiO$_2$(s)+1/2O$_2$(g)⇔NiTiO$_3$(s)
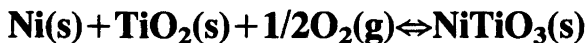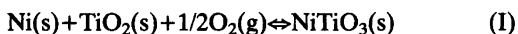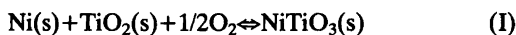
in the Temperature Range 1020−1520 K

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The equilibria

$$Ni(s)+TiO_2(s)+1/2O_2(g)⇔NiTiO_3(s) \quad (I)$$

and

$$Ni(s)+1/2O_2(g)⇔NiO(s) \quad (II)$$
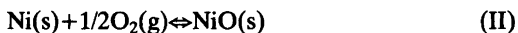
were studied in the temperature range 1020−1520 K by measuring the equilibrium oxygen partial pressures with an oxygen concentration cell involving calcia stabilized zirconia as solid electrolyte. From the measured emf data the following relationships were obtained:

$lg(K/atm^{-1/2})$ (I)=
$-7.722+13280/(T/K)+0.3849 \ln(T/K)$ (±0.0050 at 1300 K)

$lg(K/atm^{-1/2})$ (II)=
$-4.028+12137/(T/K)-0.0492 \ln(T/K)$ (±0.0044 at 1300 K)

In recent years, double oxides of titanium and the transition metals have become the object of emphasized interest due to the search for new materials for many purposes *e.g.* semiconductor, photoelectrolysis and nuclear waste technology. Despite this fact, the access of good basic thermodynamic data (lg K_f) is rather poor.

The emf technique using solid electrolytes has proved to be the most sensitive and accurate method for determining equilibrium constants for reactions involving oxygen. In a recent investigation [1] this method was used to determine the stability of Cu$_3$TiO$_4$. In the present work the equilibria

$$Ni(s)+TiO_2(s)+1/2O_2⇔NiTiO_3(s) \quad (I)$$

and

$$Ni(s)+1/2O_2⇔NiO(s) \quad (II)$$

are studied with calcia stabilized zirconia as solid electrolyte.

Previous work on phase composition and phase relations in the system Ni−Ti−O has recently been reviewed by Armbruster.[2] In addition to the literature mentioned there, the investigations concerning the thermodynamic stability of NiTiO$_3$ by Navrotsky and Muan[3] using gas equilibration technique, and by Taylor and Schmalzried,[4] using the emf technique, could also be mentioned. Although Taylor and Schmalzried[4] used the emf technique, it was considered worthwhile to redetermine lg K(I), since in their work neither the solid electrolyte nor the thermocouple was kept in direct contact with the sample. This could lead to errors in the measured emfs as well as in the thermo emfs.

EXPERIMENTAL

Chemicals. Ni (Merck *p.a.*) and TiO$_2$ (Kebo *puriss.*) were dried at 420 K prior to their use. NiO was synthesized by decomposing NiCO$_3$ (Baker analyzed reagent) for 5 h at 850 K. NiTiO$_3$ was prepared by weighing equimolar amounts of NiO and TiO$_2$, mixing and grinding the mixture in an agate mortar, then heating for 24 h at 1400 K and for 48 h at 1450 K with an intermediate grinding. The formation of NiTiO$_3$

Pt, $O_2(g)$, Ni(s), $NiTiO_3(s)$, $TiO_2(s)$|CSZ|Ni(s), NiO(s), $O_2(g)$, Pt   (A)

Pt, $O_2(g)$, Ni(s), NiO(s)|CSZ|O_2(air), Pt   (B)

Scheme 1. Cell configurations.

was checked with X-ray powder diffraction. The hexagonal unit cell dimensions obtained, $a = 5.0302 \pm 0.00011$ and $c = 13.7861 \pm 0.00049$, were in good agreement with those in JCPDS Powder Diffraction File[5].

Emf cells. The equilibrium oxygen partial pressure for the equilibria (I) and (II) were determined by emf measurements on cells of the configurations given in Scheme 1.
Here CSZ stands for *calcia stabilized zirconia*. The experimental arrangement for cell A can be seen in Fig. 1. The solid sample mixture was placed in the bottom of a 700 mm long closed end zirconia tube (Friedrichsfeld) with an outer diameter of 8 mm and an inner diameter of 5 mm. A platinum wire wound around the lower end of a two hole Al_2O_3 tube inserted in the zirconia tube served as inner electrode. On top of the Al_2O_3 tube a glass tube (pyrex) was glued with epoxy glue. This assembly was evacuated and sealed by melting the glass tube. A platinum wire wound around the lower end of the zirconia tube served as the outer electrode. To isolate the wire connecting the electrode with the voltmeter an Al_2O_3 capillary was used. The zirconia tube was placed in a closed end Al_2O_3 tube containing the reference mixture Ni(s)+NiO(s). This Al_2O_3 tube has an inner diameter of 11 mm and an outer of 16 mm. The outer cell compartment was evacuated and sealed through a glass tube glued on the side of the Al_2O_3. For cell B the experimental arrangement was the same as for cell A apart from the outer Al_2O_3 tube, since air was used as reference.

Furnace, temperature measurements. The cells were heated in a vertical tube resistance furnace. For temperatures 1000 K-1350 K a furnace with kanthal A-1 resistance wire was used and for temperatures 1300 K-1600 K a Pt/40 % Rh resistance furnace was used. The 'measuring zone' was kept in a temperature uniform zone about 50 mm long, where the temperature was maintained constant within ± 1 K by an electronic temperature controller. The temperature was measured with a Pt/Pt (10 % Rh) thermocouple with the reference junction at 273.15 K. Cell emfs as well as thermo emfs were measured with a Solartron 7075 digital voltmeter with a high input impedance (10^{12} Ω).

Cell operations. A typical run was as follows. After the cell was built and placed in the furnace, the temperature was raised during the day to approximately 1200 K. This temperature was maintained over night to ensure equilibrium. The temperature was then changed upwards and downwards in steps of 10–20 K. The emf values obtained when increasing and decreasing the
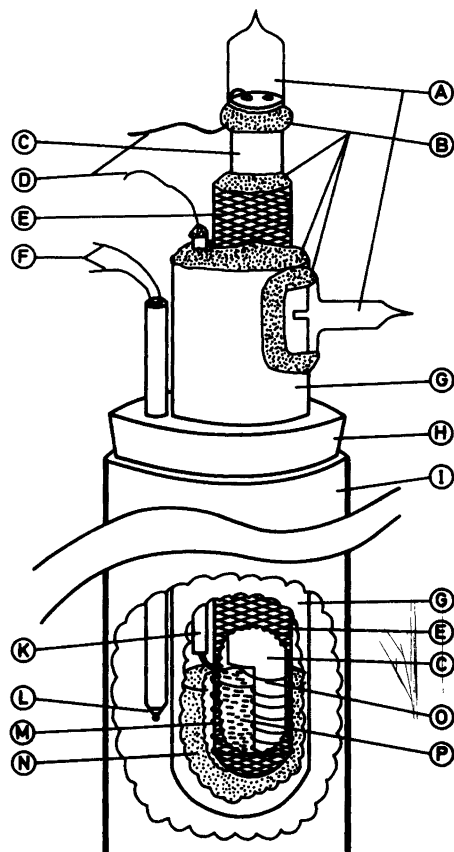

Fig. 1. Sketch of the emf cell assembly. A, pyrex tube. B, epoxy glue. C, two hole Al_2O_3 capillary. D, platinum wires. E, zirconia tube. F, thermocouple wires. G, outer Al_2O_3 tube. H, rubber stopper. I, furnace tube (Al_2O_3). K, Al_2O_3 capillary. L, thermocouple. M, outer platinum electrode. N, reference mixture (Ni+NiO). O, inner platinum electrode. P, sample mixture (Ni+TiO_2+$NiTiO_3$).

Table 1. Basic experimental data, E_{exp} and T, and calculated values $\Delta E = E_{exp} - E$, obtained for the galvanic cell
Pt, $O_2(g)$, Ni(s), $NiTiO_3(s)$, $TiO_2|CSZ|Ni(s)$, NiO(s), $O_2(g)$, Pt

T/K	E_{exp}/mV	ΔE/mV	T/K	E_{exp}/mV	ΔE/mV
1022.9	44.3	0.50	1227.7	39.3	−0.21
1024.0	43.9	0.13	1233.1	39.3	−0.12
1027.8	43.7	0.02	1244.4	39.4	0.17
1030.2	43.6	−0.02	1247.2	39.0	−0.18
1039.1	43.3	−0.10	1248.2	39.0	−0.17
1044.6	43.7	0.43	1250.0	38.9	−0.24
1046.8	43.9	0.68	1258.4	39.1	0.10
1049.5	42.8	−0.35	1259.4	39.1	0.12
1053.9	42.5	−0.55	1267.8	38.7	−0.15
1057.1	42.8	−0.17	1270.0	39.1	0.29
1059.1	42.5	−0.42	1275.1	38.9	0.16
1060.5	42.2	−0.69	1279.7	38.9	0.24
1062.8	42.8	−0.04	1286.1	38.4	−0.17
1068.1	43.1	0.39	1289.9	38.6	0.09
1072.3	42.4	−0.22	1290.6	38.7	0.20
1080.6	42.1	−0.33	1302.1	38.6	0.27
1083.7	43.0	0.64	1309.5	38.1	−0.12
1084.7	42.0	−0.34	1312.4	38.4	0.22
1092.8	42.1	−0.05	1313.5	38.3	0.14
1098.1	42.4	0.36	1319.9	38.2	0.13
1102.2	42.3	0.35	1322.4	38.3	0.26
1102.5	41.8	−0.14	1330.5	37.0	−0.93
1112.4	41.4	−0.33	1332.6	38.2	0.30
1113.4	42.0	0.29	1342.4	38.1	0.33
1119.9	41.4	−0.17	1343.7	37.9	0.15
1124.3	41.6	0.12	1346.8	37.6	−0.11
1128.6	41.0	−0.39	1362.0	37.8	0.29
1136.5	41.4	0.18	1366.2	37.3	−0.16
1140.6	41.5	0.36	1372.7	37.7	0.32
1144.3	40.5	−0.56	1379.6	36.4	−0.89
1146.2	41.1	0.07	1381.8	37.6	0.33
1146.4	40.7	−0.32	1385.3	37.3	0.08
1153.7	40.9	0.02	1394.4	37.4	0.28
1154.1	40.9	0.03	1395.1	37.0	−0.11
1161.3	41.0	0.27	1403.2	36.5	−0.52
1164.4	40.6	−0.07	1412.5	36.9	−0.01
1164.9	40.8	0.14	1420.0	36.3	−0.53
1170.8	40.5	−0.04	1421.2	36.7	−0.12
1176.4	40.5	0.06	1431.5	36.6	−0.11
1182.4	40.4	0.08	1437.9	36.4	−0.24
1184.4	39.9	−0.39	1448.6	36.7	0.17
1186.6	40.4	0.16	1450.3	36.5	−0.01
1196.4	40.2	0.14	1461.7	36.4	0.00
1201.5	39.8	−0.17	1465.3	36.3	−0.07
1208.9	39.9	0.06	1479.7	36.3	0.07
1212.6	40.0	0.23	1488.6	36.2	0.05
1215.4	39.7	−0.02	1500.8	36.3	0.25
1217.7	39.8	0.12	1513.2	36.1	0.16

temperature did not show any systematic disagreement. The time required for equilibration varied with temperature, at 1500 K 1−2 h and at 1000 K up to 24 h.

RESULTS AND CALCULATIONS

Emf values obtained. For equilibrium (I), 96 pairs of emfs and temperatures were obtained in 4 different runs (Table 1). For equilibrium (II) 49 pairs were obtained in 4 different runs, and at each point the total pressure was also measured. The measured values were smoothed by a least-squares treatment to fit the equation $E=a+bT+cT\ln T$, corresponding to a constant but non-zero value of ΔC_p. In the case of equilibrium (II) the emfs were recalculated to correspond to a reference oxygen partial pressure of 0.20946 atm. By doing so, the following relationships were obtained;

$$E(A)/mV =$$
$$113.43-0.36650(T/K)+0.043062(T/K)\ln(T/K)$$
$$(1020\ K<T<1520\ K) \qquad\qquad (1)$$

and

$$E(B)/mV=1204.1-0.43325(T/K)-0.004879(T/K)\ln(T/K)$$
$$(900\ K<T<1460\ K) \qquad\qquad (2)$$

with the calculated standard deviations of the fit, $s_f(A)=\pm0.30$ mV and $s_f(B)=\pm0.57$ mV respectively.

Calculation of oxygen partial pressures. The equilibrium oxygen partial pressure $(p(O_2)/atm)$ is related to the measued emf (E/mV) and temperature (T/K) values and to the oxygen pressure of the reference system $(p^*(O_2)/atm)$, by the equation

$$\lg p(O_2)=\lg p^*(O_2)-(4F/R\ln10)\cdot(E/T) \qquad (3)$$

where R is the gas constant and F is the Faraday constant.

By inserting eqn. (2) and $p(O_2)=0.20946$ atm (1 atm=101.325 kPa) into eqn. (3), the equilibrium oxygen partial pressure for equilibrium (II) is derived

$$\lg(p(O_2)/atm)(II)=8.055-24274/(T/K)+0.0984\ln(T/K)$$
$$(\pm0.0088\ at\ 1300\ K)\ (900\ K<T<1460\ K) \qquad (4)$$

To derive the oxygen partial pressure for equilibrium (I), eqn. (1) is inserted in eqn. (3), and $\lg p^*(O_2)$ is taken from eqn. (4), since a nickel−nickel oxide mixture was used as reference system. On doing this the following expression is derived:

$$\lg(p(O_2)/atm)\ (I)=15.444-26561/(T/K)-0.7698\ln(T/K)$$
$$(\pm0.010\ at\ 1300\ K)\ (1020\ K<T<1520\ K) \qquad (5)$$

lg K values. By applying the law of mass action the following expressions for the equilibrium constants are derived:

$$\lg(K/atm^{-1/2})\ \ (I)=-7.722+13280/(T/K)+0.3849\ln(T/K)$$
$$(\pm0.0050\ at\ 1300\ K)\ (1020\ K<T<1520\ K) \qquad (6)$$

and

$$\lg(K/atm^{-1/2})\ \ (II)=-4.028+12137/(T/K)-0.0492\ln(T/K)$$
$$(\pm0.0044\ at\ 1300\ K)\ (900\ K<T<1460\ K) \qquad (7)$$

DISCUSSION

lg K values. In Table II, lg K(I) values obtained in the present investigation are given together
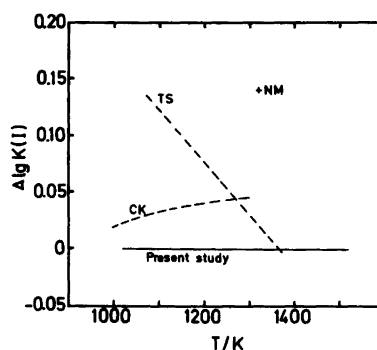
Fig. 2. Differences in lg K values for equilibrium (I) between the present investigation and those of Navrotsky and Muan[3] (NM), Taylor and Schmalzried[4] (TS) and Chattopadhyay and Kleykamp[6] (CK).

Table 2. Calculated lg K values for equilibrium (I) from the present study and from data given in the literature.

T/K	lg(K/atm$^{-1/2}$)			
	Present work	Navrotsky and Muan[3]	Taylor and Schmalzried[4]	Chattopadhyay and Kleykamp[6]
1073	7.340		7.475	7.369
1173	6.320		6.409	6.358
1273	5.462		5.511	5.506
1323	5.082	5.222		
1373	4.731		4.728	

with the corresponding values from Navrotsky and Muan[3], Taylor and Schmalzried[4] and from a very recently published study by Chattopadhyay and Kleykamp.[6] The value from Navrotsky and Muan[3] has been calculated by using lg K_f(NiO)=lg K(II). In Fig. 2, the deviations from the present investigation are visualized.

Navrotsky and Muan's[3] result, obtained from gas equilibration measurements, deviates from that obtained in the present investigation with 0.140 lg units. This deviation is somewhat greater than their given uncertainty of ±300 cal, corresponding to ±0.050 lg units. The temperature relationship given by Taylor and Schmalzried[4] shows a different slope as compared to that of the present study. The differences in lg K are at 1073 K 0.135 lg units and at 1373 K −0.003 lg units. As mentioned before it can be concluded from their paper that the solid electrolyte and the thermocouple were not kept in direct contact with the sample. This could lead to errors in both emfs and thermo emfs. Since air was not forced to circulate within the zirconia tube it seems very likely that the reference p(O$_2$) corresponds to a static air situation. It has been found that in a situation with static air, the oxygen partial pressure does not stay constant with time. Chattopadhyay and Kleykamp[6] also used the emf technique. Their cell was of an open type with argon flowing around and not a closed type as was used in the present investigation. The results from their work agree fairly well with the results of the present study. The deviations are 0.029 lg units at 1073 K and 0.044 lg units at 1273 K. These deviations are somewhat greater than their given uncertainty of about 0.030 lg units.

The measurements on equilibrium (II) were performed to obtain consistent oxygen partial pressures for the reference system Ni−NiO. Comparison of the values obtained with previous results shows a very good agreement. The differences between the values obtained here and the values obtained by Charette and Flengas[7] and by Jacobsson and Rosén[8] are never more than 0.004 and 0.019 lg units respectively.

Temperature range covered. It was suggested by Armbruster[2] that at temperatures above 1530 K, the phase NiTiO$_3$ in contact with TiO$_2$ is enriched in TiO$_2$ yielding the composition Ni$_{1-2x}$Ti$_{1+x}$O$_3$ ($x \leq 0.03$). Assuming this to be correct it would lead to deviations in the measured emf values from what could be expected from extrapolation of such values at temperatures below 1530 K. In this investigation such a deviation could also be observed at temperatures higher than 1520 K, giving higher emfs than expected.

Due to the sluggishness of the reaction at low temperatures the lower limit for this work was set at 1020 K.

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