Thermochimica Acta, 190 (1991) 217–224
Elsevier Science Publishers B.V., Amsterdam

Thermodynamic stabilities of $NiTeO_3$ and Ni_3TeO_6 by solid oxide electrolyte e.m.f. method

C. Mallika and O.M. Sreedharan

Metallurgy Division, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu 603 102 (India)

(Received 4 March 1991)

Abstract

The e.m.f. of the galvanic cells Pt,C,Te(l),$NiTeO_3$,NiO/15 YSZ/O_2 ($P_{O_2} = 0.21$ atm),Pt and Pt,C,$NiTeO_3$,Ni_3TeO_6,NiO/15 YSZ/O_2 ($P_{O_2} = 0.21$ atm),Pt (where 15 YSZ = 15 mass% yttria-stabilized zirconia) was measured over the ranges 833–1104 K and 624–964 K respectively, and could be represented by the least-squares expressions $E_{(I)} \pm 1.48$ (mV) = $888.72 - 0.50427T$ (K) and $E_{(II)} \pm 4.21$ (mV) = $895.26 - 0.81543T$ (K).

After correcting for the standard state of oxygen in the air reference electrode, and by combining with the standard Gibbs energies of formation of NiO and TeO_2 from the literature, the following expressions could be derived for the ΔG_f° of $NiTeO_3$ and Ni_3TeO_6: $\Delta G_f^\circ(NiTeO_3) \pm 2.03$ (kJ mol^{-1}) = $-577.30 + 0.26692T$ (K) and $\Delta G_f^\circ(Ni_3TeO_6) \pm 2.54$ (kJ mol^{-1}) = $-1218.66 + 0.58837T$ (K).

INTRODUCTION

Ternary compounds in the Ni–Te–O system are of interest in solid state chemistry by virtue of their electrical properties [1]. Besides this, tellurium is a deleterious fission product which can attack the stainless steel cladding in fast breeder reactors [2], forming tellurides of Fe, Cr and Ni. Investigation of the Ni–Te system by the solid oxide electrolyte e.m.f. method is limited owing to the lack of Gibbs energy data on the Ni–Te–O system. Further, compounds such as Ni_3TeO_6 can be formed under conditions of reactor accidents [3]. Hence the thermodynamic characterization of the two limiting ternary oxides in the pseudo-binary NiO–TeO_2 and NiO–TeO_3 systems was undertaken.

EXPERIMENTAL

Materials

Reagent grade nickel acetate (purity better than 99.5%, supplied by E. Merck, Germany) and tellurium granules (purity greater than 99.99%, sup-

0040-6031/91/$03.50

plied by BDH, UK) were the starting materials. Tellurium dioxide was obtained by repeated air oxidation of Te granules in the temperature interval 648–698 K for several hours, with intermittent grinding. Reactive powder of NiO was obtained by careful thermal decomposition of nickel acetate in air at 800–1000 K. Intimate mixtures of NiO and TeO_2 in the molar ratios of 1 : 1 and 3 : 1 were compacted into cylindrical pellets of 10 mm diameter and 2 to 3 mm thickness at a pressure of 100 MPa. The pellets of equimolar composition were heated to 973 K in air, gradually followed by raising the temperature to 1123 K, at which they were maintained for 8 h. This procedure was repeated twice after grinding the pellets and recompacting them in order to ensure completion of the reaction. The other set of pellets was heated to 773 K in air for 96 h followed by heating at 925 K for 20 h. The products were checked for the completion of reaction by powder X-ray diffractometry (XRD) within its 5 mass% limit of detection of impurity phases. A mixture of Ni_3TeO_6 and $NiTeO_3$ in the mole ratio 1 : 0.6 was heated in air at 850 K for several hours to confirm their coexistence by XRD. This procedure was repeated again by heating the same mixture with NiO.

Apparatus and procedure

The electrode pellets were made by intimate mixing and compaction of NiO, $NiTeO_3$ and Te in the mass ratio 2 : 6 : 1 at a pressure of 100 MPa into cylindrical pellets of 6 mm diameter and 2 to 3 mm thickness. Likewise, another set of electrode pellets was made from a mixture of $NiTeO_3$, Ni_3TeO_6 and NiO in the mass ratio 1 : 2 : 1 and compacted at a pressure of 100 MPa into cylindrical pellets of 10 mm diameter and 2 to 3 mm thickness. Graphite cups were used to contain the electrode pellets in order to prevent chemical attack of the Pt lead wire by the constituents of the electrode. Both the Pt leads on either side of the cell were located in the isothermal zone of the furnace. The absence of asymmetric potentials due to the graphite cup was verified as discussed in earlier studies [4,5].

The following cell configurations were employed in the present study.

$$\text{Pt,C,Te(l),NiTeO}_3\text{,NiO/15 YSZ/O}_2\ (P_{O_2} = 0.21\ \text{atm}),\text{Pt} \qquad \text{(I)}$$

$$\text{Pt,C,NiTeO}_3\text{,Ni}_3\text{TeO}_6\text{,NiO/15 YSZ/O}_2\ (P_{O_2} = 0.21\ \text{atm}),\text{Pt} \qquad \text{(II)}$$

where 15 YSZ represents a 15 mass% yttria–stabilized zirconia electrolyte tube with one end closed and the closed end flat. This tubular electrolyte was used to separate the gaseous environments of the test electrode and the air–reference electrode compartments. The volatilization of Te was reduced as far as possible by employing a nearly static purified argon atmosphere. The method of purification and other experimental details are described in earlier publications [4,6–8]. The temperature was measured by a Pt–10%

Rh/Pt thermocouple calibrated at the freezing temperatures of high purity metals such as Sn, Zn, Sb and Ag. The e.m.f. readings were taken after equilibrating the galvanic cells at 750 K for at least 24 h. Only those cell voltages which did not drift by more than a fraction of a millivolt per hour and remained reproducible during the subsequent heating cycles were taken into account. The e.m.f. values were tested for reversibility by thermal cycling and by micropolarization [5]. The electrodes were examined by XRD at the end of each experiment to confirm the absence of changes in phase composition.

RESULTS

The e.m.f. results for cells (I) and (II), represented in Tables 1 and 2 and Fig. 1, could be fitted into the following least-squares expressions, which are valid over the ranges 833–1104 K and 624–964 K respectively

$$E_{(\mathrm{I})} \pm 1.48\ (\mathrm{mV}) = 888.72 - 0.50427T\ (\mathrm{K}) \qquad (1)$$

TABLE 1

Experimental e.m.f results for the cell (I). Pt,C,Te(l),$NiTeO_3$,NiO/15 YSZ/O_2 (P_{O_2} = 0.21 atm),Pt, where 15 YSZ denotes 15 mass% yttria-stabilized zirconia

Run	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)	T (K)	E (mV)
1	987.1	389.60	893.8	436.89	1081.9	343.46	1050.7	356.23
	990.6	387.19						
2	918.0	427.29	1050.1	359.81	832.5	469.52	941.7	414.46
	1102.9	336.32						
3	837.6	466.92	1104.1	330.59	1072.4	348.39		

TABLE 2

Experimental results for cell (II). Pt,C,$NiTeO_3$,Ni_3TeO_6,NiO/15 YSZ/O_2 (P_{O_2} = 0.21 atm),Pt

Run	T (K)	E (mV)	T (K)	E (mV)	T(K)	E (mV)	T (K)	E (mV)
1	738.6	291.62	849.3	196.27	697.5	329.78	869.0	185.51
	833.3	209.41	660.1	353.06	707.4	312.47	892.7	174.46
	643.8	368.05						
2	782.8	260.87	879.1	171.24	756.4	280.68	828.4	216.83
	909.6	154.59	624.2	383.86				
3	678.2	344.61	772.1	268.35	870.2	186.16	782.3	264.87
	816.6	225.68	911.9	157.86	706.7	326.15	897.2	158.77
	788.0	256.16	825.9	221.01	804.3	239.27	964.3	109.68
	758.3	278.28						

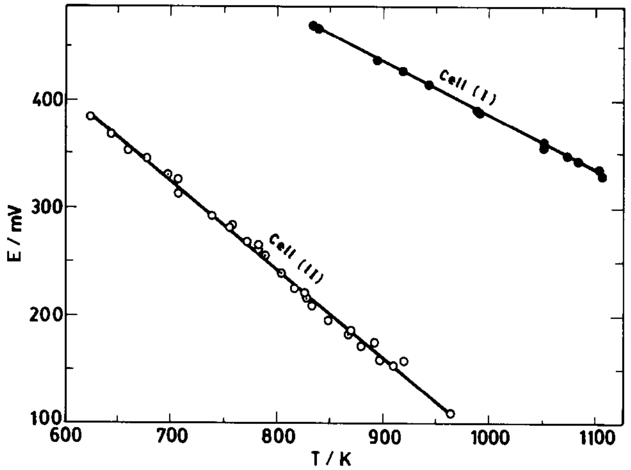

Fig. 1. Experimental e.m.f results for cells (I) and (II) (●) cell (I): Pt,C,Te(l),$NiTeO_3$,NiO test electrode; (o) cell (II): Pt,C,$NiTeO_3$,Ni_3TeO_6,NiO test electrode.

and

$$E_{(II)} \pm 4.21\ (\mathrm{mV}) = 895.26 - 0.81543T\ (\mathrm{K}) \tag{2}$$

DISCUSSION

Equilibrium diagram for Ni–Te–O system

In the pseudo-binary TeO_2–NiO system, three well defined ternary oxides, namely $NiTe_2O_5$, $Ni_2Te_3O_8$ and $NiTeO_3$, have been reported so far [9]. However, only one ternary oxide, Ni_3TeO_6, has been reported which contains Te in the +6 oxidation state, as expected for the NiO–TeO_3 system. Using this information, an isothermal section of the phase diagram for the Ni–Te–O system at 850 K was constructed as shown in Fig. 2. The two three-phase mixtures employed in this present investigation were shown to

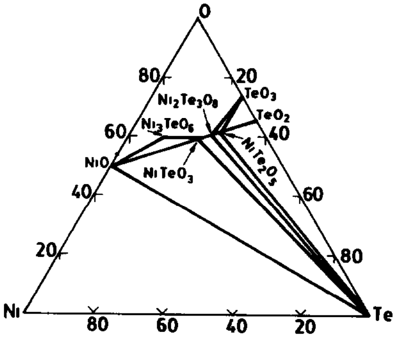

Fig 2 Phase equilibrium diagram of Ni–Te–O system at 850 K

be coexisting phases by XRD analyses of pre-equilibrated samples. The compound $NiTeO_3$ is thus the phase adjacent to NiO in which the activity of TeO_2 (a_{TeO_2}) would be the minimum along the tie line between NiO and TeO_2. Therefore, the biphasic mixture of $NiO/NiTeO_3$ would set the lower limit of the chemical potential of TeO_2. Unless this value is more than one order of magnitude lower than the unit activity of TeO_2, measurement of the standard Gibbs energy of formation of $Ni_2Te_3O_8$ and $NiTe_2O_5$ would not be entirely meaningful within the limits of achievable precision even with e.m.f. measurements.

The higher thermodynamic stability of $NiTeO_3$ expected in accordance with basic thermodynamics could also be corroborated by the reaction of TeO_2 with NiO reported by Sokolov et al. [10]. These workers found that $NiTeO_3$, $NiTe_2O_5$ and $Ni_2Te_3O_8$ were formed at 873, 933 and 973 K, respectively, from TeO_2. Although the thermodynamic order of reactivity was reversed between the second and third compounds, still the lower temperature of formation of $NiTeO_3$ is consistent with the higher thermodynamic driving force. No attempt is made here to construct the temperature–composition phase diagrams for $NiO-TeO_2$ and $NiO-TeO_3$ systems owing to the availability of only partial information in the literature [11]. $NiTeO_3$ and $NiTe_2O_5$ were congruently melting at 1163 and 1123 K respectively, whereas $Ni_2Te_3O_8$ was incongruently melting at 1148 K. Three eutectics in the regions $NiTe_2O_5/TeO_2$, $Ni_2Te_3O_8/NiTe_2O_5$ and $NiTeO_3/Ni_2Te_3O_8$ were reported at 923, 1083 and 1118 K, corresponding to 92.5, 62.5 and 57.5 mol% of TeO_2 respectively.

Gibbs energy of formation of $NiTeO_3$

For the passage of 4 faradays (F) of electricity for cell (I), the half cell reactions could be represented as follows.

$$NiO(s) + Te(l) + 2O^{2-}(g) \rightleftharpoons NiTeO_3(s) + 4e^{-1} \tag{3a}$$

$$O_2\ (P_{O_2} = 0.21\ atm) + 4e^{-1} \rightleftharpoons 2O^{2-}(g) \tag{3b}$$

The overall galvanic cell reaction is given by

$$NiO(s) + Te(l) + O_2\ (P_{O_2} = 0.21\ atm) \rightleftharpoons NiTeO_3(s) \tag{4}$$

The standard Gibbs energy change $\Delta G_r°$, for reaction (4), after correcting for the standard state of oxygen in the air electrode, could be given as

$$\Delta G_r° = -4FE_{(I)} + RT\ \ln(P_{O_2} = 0.21\ atm) = \Delta G_f°(NiTeO_3) - \Delta G_f°(NiO) \tag{5}$$

$$\Delta G_r° = \Delta G_{f,ox}°(NiTeO_3) + \Delta G_f°(TeO_2) \tag{6}$$

i.e.

$$\Delta G_r° \pm 0.57\ (kJ\ mol^{-1}) = -343.00 + 0.18162T\ (K) \tag{7}$$

In eqn. (6) the term $\Delta G^{\circ}_{\mathrm{f,ox}}(\mathrm{NiTeO_3})$ represents the standard Gibbs energy of formation of $NiTeO_3$ from the constituent binary oxides, namely NiO and TeO_2. The following expression was made use of for the $\Delta G_{\mathrm{f}}^{\circ}$ of TeO_2, which was recently reported by Mallika and Sreedharan [12] from precise e.m.f. measurements on a Te(l)/TeO_2(s) electrode employing the same experimental galvanic cell assembly.

$$\Delta G_{\mathrm{f}}^{\circ}(\mathrm{TeO_2}) \pm 0.60\ (\mathrm{kJ\ mol^{-1}}) = -339.31 + 0.19861T\ (\mathrm{K}) \tag{8}$$

Equation (8) is valid over the range 726–898 K and was later shown to be in excellent agreement with independent calorimetric work by Cordfunke et al. [13]. The use of this information would also eliminate systematic errors, if any, which might be inherent in the galvanic cell assembly employed in the present study. By combining eqns. (1) and (5)–(8), the following expression could be derived for $\Delta G^{\circ}_{\mathrm{f,ox}}$ of $NiTeO_3$.

$$\Delta G^{\circ}_{\mathrm{f,ox}}(\mathrm{NiTeO_3}) \pm 1.13\ (\mathrm{kJ\ mol^{-1}}) = -3.69 - 0.01699T\ (\mathrm{K}) \tag{9}$$

The expression (9) was added to eqn. (8) and the $\Delta G_{\mathrm{f}}^{\circ}$ of NiO (from the literature [14]) to derive the following equation for the $\Delta G_{\mathrm{f}}^{\circ}$ of $NiTeO_3$.

$$\Delta G_{\mathrm{f}}^{\circ}(\mathrm{NiTeO_3}) \pm 2.03\ (\mathrm{kJ\ mol^{-1}}) = -577.30 + 0.26692T\ (\mathrm{K})\ (833\text{–}1104\ \mathrm{K}) \tag{10}$$

Gibbs energy of formation of Ni_3TeO_6

For the cell (II), the half cell reactions are taken to be

$$\mathrm{NiTeO_3} + 2\mathrm{NiO} + \mathrm{O^{2-}} \rightleftharpoons \mathrm{Ni_3TeO_6} + 2\mathrm{e^{-1}} \tag{11a}$$

$$0.5\mathrm{O_2}\ \left(P_{\mathrm{O_2}} = 0.21\ \mathrm{atm}\right) + 2\mathrm{e^{-1}} \rightleftharpoons \mathrm{O^{2-}} \tag{11b}$$

Hence the overall cell reaction is

$$\mathrm{NiTeO_3} + 2\ \mathrm{NiO} + 1/2\ \mathrm{O_2}\ \left(P_{\mathrm{O_2}} = 0.21\ \mathrm{atm}\right) \rightleftharpoons \mathrm{Ni_3TeO_6} \tag{12}$$

After correcting for the standard state of oxygen in the reference electrode in eqn. (2), the standard Gibbs energy change $\Delta G_{\mathrm{r}}^{\circ}$ could be subsequently calculated for reaction (12)

$$\Delta G^{\circ}_{\mathrm{r(12)}} \pm 0.81\ (\mathrm{kJ\ mol^{-1}}) = -172.76 + 0.15085T\ (\mathrm{K}) \tag{13}$$

Using eqns. (10), (12) and (13) one can compute the $\Delta G_{\mathrm{f}}^{\circ}$ of Ni_3TeO_6

$$\Delta G_{\mathrm{f}}^{\circ}(\mathrm{Ni_3TeO_6}) \pm 2.54\ (\mathrm{kJ\ mol^{-1}}) = -1218.66 + 0.58837T\ (\mathrm{K})\ (624\text{–}964\ \mathrm{K}) \tag{14}$$

To assess independently the reliability of the standard Gibbs energy data on $NiTeO_3$ and Ni_3TeO_6 determined in this study, precise thermochemical data, such as the standard heats of formation and specific heat measurements from calorimetry, are needed. In the absence of such information, a truly critical assessment is not possible. However, adiabatic vacuum calorimetric studies for the low temperature heat capacities of $Ni_2Te_3O_8$ and $NiTe_2O_5$ have been reported by Zhdanov et al. [15] and values of $\Delta H^\circ_{f,298}$ ($Ni_2Te_3O_8$ and $NiTe_2O_5$) have been reported by Lesar et al. [1] from mass spectrometric studies. These values could not be of much help in assessing the present data. Nevertheless, an examination of eqn. (9) shows that, for the solid–solid reaction between NiO and TeO_2, the value of $\Delta S^\circ_{f,ox}(NiTeO_3)$ is only 16.99 J K^{-1} mol^{-1}, which is in agreement with an expected value of the magnitude of 10 J K^{-1} mol^{-1} for the ideal entropy of mixing. The value of $\Delta G^\circ_{f,ox}$ of $NiTeO_3$ at 900 K works out to be -19 kJ mol^{-1} from eqn. (9); such a small value makes it difficult to make similar measurements on $Ni_2Te_3O_8$ and $NiTe_2O_5$ since the $\Delta G^\circ_{f,ox}$ per TeO_2 would be even smaller in magnitude. The entropy term in eqn. (13) has a value of -150.85 J K^{-1} mol^{-1} for the disappearance of half a mole of oxygen gas, which is rather large compared with the loss of entropy caused by the consumption of half a mole of oxygen gas in the reaction. In the continuing absence of exact information on the possible nonstoichiometry in $NiTeO_3$ and Ni_3TeO_6 and on the defect structure in the relevant crystal lattices, it may not be wholly advisable to assess the entropy changes. In spite of this limitation, the Gibbs energy data derived from e.m.f. values should be quite reliable in the temperature range of measurement, although the same could not be stated regarding the enthalpy and entropy data derived from the e.m.f., according to Kubaschewski [16]. As a cross-check on the reliability of the temperature dependence of the e.m.f. data from cell (II), the temperatures of dissociation of Ni_3TeO_6 in air as well as in oxygen were calculated to be 1098 and 1145 K respectively from eqns. (2) and (13). To verify this, a thermogravimetric analysis was carried out on Ni_3TeO_6, which recorded a weight loss with an inception temperature at 970 K. However, the weight change was compounded by heavy loss of tellurium as tellurium oxide in an atmosphere of ambient air. Nevertheless, the temperature of dissociation in air predicted by extrapolating the e.m.f. data beyond 970 K is not too high. Within acceptable limits of temperature dependent errors, this difference in the observed temperature of weight loss and that predicted from the e.m.f. could be taken as reasonable, considering also the complication arising from the vaporization of tellurium oxide.

CONCLUSION

Precise values of standard Gibbs energies of formation of $NiTeO_3$ and Ni_3TeO_6 over the ranges 833–1104 and 624–964 K respectively with reference to Te(l) could be determined by the solid oxide electrolyte e.m.f. method. These data would also be useful in understanding the oxidation behaviour of $NiTe_x$ ($x = 0.8$–2.0) in the temperature range 573–1223 K, leading to the formation of $NiTe_2O_5$, Ni_3TeO_6 etc. as reported by Drofenik et al. [17].

ACKNOWLEDGEMENTS

The authors express their sincere thanks to Shri J.B. Gnanamoorthy, Head, Metallurgy Division and Dr. P. Rodriguez, Head, Metallurgy and Materials Programme, IGCAR for their keen interest and encouragement throughout the course of this work.

REFERENCES

1 A. Lesar, A. Popovic and J Marsel, J. Less-Common Met, 143 (1988) 151
2 H. Kleykamp, J. Nucl. Mater, 131 (1985) 221.
3 E H.P. Cordfunke, J. Nucl Mater., 130 (1985) 82.
4 O M. Sreedharan, E. Athiappan, R. Pankajavalli and J B Gnanamoorthy, J Less-Common Met., 68 (1979) 143
5 O.M. Sreedharan, M.S. Chandrasekharaiah and M.D. Karkhanavala, High Temp. Sci, 9 (1977) 109.
6 R Pankajavalli, O.M Sreedharan, E. Athiappan and J.B. Gnanamoorthy, J. Electrochem. Soc. India, 30 (1981) 224
7 A M Azad, R Pankajavalli and O M Sreedharan, J. Chem. Thermodyn, 18 (1986) 255
8 C. Mallika and O.M. Sreedharan, J. Chem. Thermodyn, 20 (1988) 769.
9 W F McClune (Editor-in-Chief), Powder Diffraction File, Inorganic Phases, Alphabetical Index, JCPDS International Center for Diffraction Data, PA, 1984
10 Yu. N. Sokolov, K K Samplavskaya and M.Kh. Karapet'yants, Zh Neorg Khim., 22 (1977) 2333.
11 Yu. N Sokolov, K.K. Samplavskaya and M.Kh. Karapet'yants, Neorg. Mater., 14 (1978) 746
12 C. Mallika and O.M. Sreedharan, J. Chem. Thermodyn., 18 (1986) 727.
13 E.H.P. Cordfunke, W. Ouweltjes and G. Prins, J. Chem. Thermodyn, 19 (1987) 369
14 H.H Kellogg, J Chem. Eng Data, 14 (1969) 41.
15 V.M. Zhdanov, V.A. Turdakin, Yu.N Sokolov, K.K. Samplavskaya and M.Kh Karapet'yants, Deposited Doc., VINITI, 1977, 957
16 O Kubaschewski, High Temp. High Press, 4 (1972) 1
17 M Drofenik, D. Kolar, V Marinkovic and T. Porenta, Vestn. Slov. Kem. Drus., 26 (1979) 407