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Journal of Nuclear Materials 301 (2002) 183–186

journal of nuclear materials

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Gibbs energy of formation of solid Ni_3TeO_6 from transpiration studies

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Received 19 September 2001; accepted 17 November 2001

Abstract

The thermodynamic stability of nickel tellurate was established by studying the heterogeneous equilibrium $Ni_3TeO_6(s) = 3NiO(s) + TeO_2(g) + \frac{1}{2}O_2(g)$. Using the transpiration technique, the equilibrium constant of the reaction was obtained from the vapor pressure measurement of $TeO_2(g)$ over the biphasic mixture of $Ni_3TeO_6(s)$ and NiO(s) under 1 bar oxygen pressure. From the equilibrium data the second-law value of $\Delta_f H^\circ$ ($Ni_3TeO_6(s)$, 298.15 K) was found to be $-1216(\pm 14)$ kJ mol^{-1}. The energy change of the heterogeneous reaction derived from the equilibrium constant was used to calculate the Gibbs energy of formation of Ni_3TeO_6 as could be expressed by $\Delta_f G^\circ$ ($Ni_3TeO_6(s)$) (± 13 kJ mol^{-1}) $= -1307 + 0.64 \cdot T$, (1122 K $\leqslant T \leqslant$ 1202 K). The above Gibbs energy data were found to be consistent with the available thermodynamic information of the Ni–Te–O ternary system.

1. Introduction

The volatile fission product tellurium, following its formation inside the nuclear fuel pin, has the tendency to diffuse out under a steep radial temperature gradient in the pin. The outward diffusion results in its release from the fuel and settlement at the fuel–clad interface. Tellurium accumulation on the inner surface of the clad can be detrimental [1]. In fast breeder reactors based on mixed oxide fuels the clad of the alloy steel containing nickel can react with the tellurium forming nickel tellurite and tellurate at a very high burn up where the oxygen potential builds up significantly within the fuel pin. The tellurites such as $Ni_2Te_3O_8$ and $NiTe_2O_5$ [2,3], and tellurate such as Ni_3TeO_6 [4] have large molar volumes. Their precipitation at the grain boundaries of the clad can result in its stress corrosion cracking. The data on the thermodynamic stability of these nickel compounds are thus important for the assessment of performance of such clad at high burn up.

There is little information on the thermodynamic stability of the nickel tellurate $Ni_3TeO_6(s)$. The reported stability data of the compound [5] were derived from an effusion study measuring the mass loss due to the reaction $Ni_3TeO_6(s) = 3NiO(s) + TeO_2(g) + 0.5O_2(g)$ occurring in a boron nitride cell. The derived data, however, suffer from the assumption that the cell wall was inert to $O_2(g)$ and that the mass loss due to oxygen was according to the stoichiometry of the reaction. However, this assumption used in their data evaluation need not be correct as the thermodynamic key data of the boron compounds [6] suggest that the cell wall can readily take part in oxidation reactions such as $4BN(s) + 3O_2 = 2B_2O_3(liq) + 2N_2(g)$. The oxidation lowers not only $p(O_2)$ in the cell but also the mass loss as the reaction product $N_2(g)$ then takes over the effusion of $O_2(g)$. The reported data of the tellurate [5] are indeed found to be inconsistent with the information that $Ni_3TeO_6(s)$ remains in ternary equilibrium with the tellurites $Ni_2Te_3O_8(s)$ and $NiTe_2O_5(s)$ at 873 K under 1 bar oxygen pressure [3].

To get more reliable thermodynamic data from the vaporization of the tellurate, it is necessary to control the oxygen atmosphere accurately. This was achieved in

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0022-3115/02/$ - see front matter
PII: S0022-3115(01)00754-1

the present study by the measurements of the $TeO_2(g)$ vapor pressure under flowing oxygen at 1 bar pressure in the transpiration technique.

2. Experimental

Ni_3TeO_6 was prepared by mixing NiO and TeO_2 in the molar ratio of 3:1 and heating the mixture in a platinum boat in air at 1073 K for 24 h with intermittent grinding. The formation of the compound was confirmed from XRD studies which showed the presence of Ni_3TeO_6 (JPCD file no. 20-794) lines and the absence of NiO and TeO_2 lines as shown in Fig. 1(a). The compound was subjected to thermogravimetric analysis in a simultaneous TG-DTA apparatus (SETARAM-model 92-16.18) under flowing oxygen and argon atmospheres at a heating rate of 10 K min^{-1}. The weight loss in argon started at a lower temperature and its rate was higher as compared to that in oxygen gas. The differential TG signals exhibited the weight loss peaks at 1173 K in $O_2(g)$ and 1133 K in Ar(g). The TG run was intercepted in between, and X-ray diffraction of the decomposing mixture was taken, which indicated lines due to the compound and NiO(s) as shown in Fig. 1(b). These observations corroborate to the reported information [5] that the volatilization of the compound takes place through the following chemical reaction involving $O_2(g)$ as one of the gaseous products

$$Ni_3TeO_6(s) = 3NiO(s) + TeO_2(g) + \tfrac{1}{2}O_2(g). \qquad (1)$$

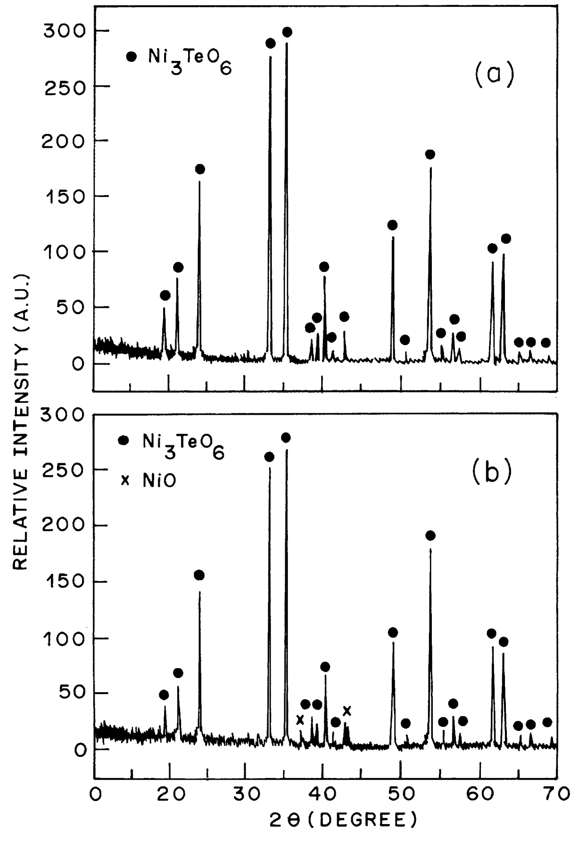

Fig. 1. XRD pattern of a $Ni_3TeO_6(s)$ sample as prepared (a), and after partial evaporation in oxygen atmosphere (b).

For the incongruent volatilization of the compound under 1 bar of oxygen pressure the equilibrium constant of the above reaction can be written as $K_p = p(TeO_2)$, $p(TeO_2)$ being the partial pressure of TeO_2 over the biphasic mixture of Ni_3TeO_6 and NiO under equilibrium condition. Pressure $p(TeO_2)$ remains invariant at a given temperature.

After establishing the phase equilibrium and thus the invariance of $p(TeO_2)$ during volatilization of the tellurate, TeO_2 vapor pressure measurements were carried out by the transpiration technique. In the transpiration apparatus, the powder sample was taken in a two-tier platinum boat suspended from a micro-thermobalance and heated at fixed temperatures under a controlled flow of the carrier gas oxygen at 1 bar pressure. The temperature was controlled with an overall uncertainty of ±1 K. The details of the apparatus and the procedure for temperature and flowmeter calibrations were described elsewhere [7,8]. The mass loss from the sample under the carrier gas flow was recorded by the automatic recording micro-thermobalance. As a prerequisite for the dynamic measurement, the region of flow rate independence of the mass loss, m_T, per unit flow volume of the carrier gas was established by recording the loss from the compound at 1103 K with the flow rates varying from 3.3 to 3.9 l h^{-1}. The mass loss was found to be independent of the flow rate in the region of 3.5–3.7 l h^{-1}. The plateau in the evaporation could be established with a precision of 1% as shown in Fig. 2, where the

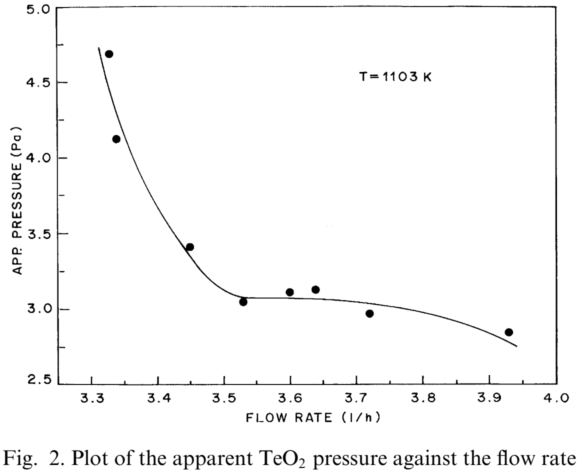

Fig. 2. Plot of the apparent TeO_2 pressure against the flow rate of the carrier gas.

mass loss is expressed as apparent pressure of TeO_2(g) at the different flow rates. The region of saturation of the carrier gas by the vapor generated from the sample was thus established, the vapor pressure measurement was carried out at a flow rate of 3.6 l h^{-1} at 1 bar oxygen pressure in the temperature range of 1122–1202 K.

3. Results and discussion

The vapor pressure of TeO_2(g) over the nickel tellurate was calculated at different temperatures from the observed mass loss of the sample m_T, per unit flow volume of O_2(g) evaluated at STP under the dynamic equilibrium in transpiration. As the loss was due to the volatilization of both TeO_2 and O_2, m_T values were apportioned for the contributions of TeO_2 and then the vapor pressures were calculated as

$$p_{TeO_2}(\text{bar}) = (m_{TeO_2}/M_{TeO_2})RT_c, \quad (2)$$

where

$$m_{TeO_2} = m_T M_{TeO_2}/(M_{TeO_2} + 0.5M_{O_2}). \quad (3)$$

The quantity m_{TeO_2} thus represents the mass of TeO_2 present in unit volume of the carrier gas. T_c is the ambient temperature at which the carrier gas was collected for the measurement of its flow volume, M_{TeO_2} and M_{O_2} are the molecular weights of TeO_2 and O_2 respectively and R is the gas constant.

From the vapor pressure values of TeO_2 over the sample the values of the equilibrium constant at the different temperatures were obtained as $K_p = p(TeO_2)$, which are tabulated in Table 1. The temperature dependence of the evaluated constant could be expressed as

$$\ln K_p(\pm 0.08) = -63050.04/T + 44.23 \quad (1122\ \text{K} \leqslant T \leqslant 1202\ \text{K}). \quad (4)$$

From the slope of the above linear fit, shown in Fig. 3, the value of the enthalpy of sublimation of Ni_3TeO_6(s) following reaction (1) was obtained as 524(±1) kJ mol^{-1}. Considering the value of the enthalpy so obtained and also the reported thermodynamic data of the products [9] of reaction (1), the enthalpy of formation of Ni_3TeO_6(s) was evaluated to be −1307(±14) kJ mol^{-1} at the mean working temperature of 1170 K of this study. The second-law data were then extrapolated to 298.15 K with the help of the thermal functions of the reactant and products of the evaporation given in reaction (1). Thermal functions of the products were taken from the literature [9]. In the absence of any reported data of the thermal function of Ni_3TeO_6(s) its molar heat capacity was estimated following Kopp's rule [10] with the consideration that the C_p value is made up of contributions from 3NiO(s) and the hypothetical TeO_3(s) components. For the C_p value of the TeO_3 component, the estimation considered a contribution from $TeO_2(s) + 0.5O_2(g)$ together with the correction factor derived from the difference of C_p values of MoO_3(s) and MoO_2(s) [9]. The value of $\Delta_f H°$ (Ni_3TeO_6(s), 298.15 K) was thus worked out to be −1216(±14) kJ mol^{-1}. From the vaporization data, the Gibbs energy of formation of Ni_3TeO_6(s) was also obtained in the following way.

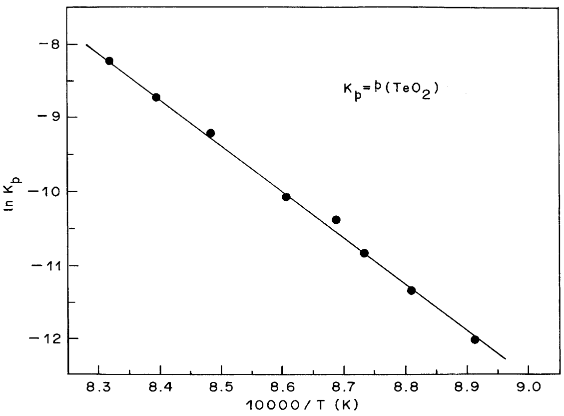

Fig. 3. Plot of $\ln K_p$ against the reciprocal temperature.

The standard Gibbs energy change for reaction (1), $\Delta_r G°$ is given by

Table 1
Vapor pressure data and the Gibbs energy of formation of Ni_3TeO_6(s)

Serial no.	Temperature (K)	Weight loss for TeO_2 (mg l^{-1})	$p(TeO_2)$ (Pa)	$K_p \times 10^6$	$\Delta_f G°$ Ni_3TeO_6 (kJ mol^{-1})
1	1122	0.039	0.605	5.968	−589.05
2	1135	0.078	1.213	11.97	−580.73
3	1145	0.127	1.985	19.59	−574.33
4	1151	0.199	3.111	30.71	−570.49
5	1162	0.271	4.238	41.83	−563.45
6	1179	0.651	10.172	100.40	−552.57
7	1191	1.031	16.109	159.00	−544.89
8	1202	1.710	26.723	263.7	−537.85

$$\begin{aligned}\Delta_r G^\circ &\equiv -RT\ln K_p \\ &= 3\Delta_f G^\circ(\mathrm{NiO(s)}) + \Delta_f G^\circ(\mathrm{TeO_2(g)}) \\ &\quad - \Delta_f G^\circ(\mathrm{Ni_3TeO_6(s)}).\end{aligned}$$

Therefore,

$$\Delta_f G^\circ(\mathrm{Ni_3TeO_6(s)}) = 3\Delta_f G^\circ(\mathrm{NiO(s)}) + \Delta_f G^\circ(\mathrm{TeO_2(g)}) + RT\ln K_p. \quad (5)$$

Considering Eqs. (4) and (5), $\Delta_f G^\circ$ (Ni_3TeO_6(s)) could be expressed as

$$\begin{aligned}&\Delta_f G^\circ(\mathrm{Ni_3TeO_6(s)})(\pm 13\,\mathrm{kJ\,mol^{-1}}) \\ &\quad = -1307 + 0.64T \quad (1122\ \mathrm{K} \leqslant T \leqslant 1202\mathrm{K}). \quad (6)\end{aligned}$$

The value of $\Delta_f H^\circ$ (Ni_3TeO_6(s), 298.15 K) of this study was compared with that of the Knudsen effusion mass loss study of the tellurate [5]. The present value is seen to be 78.6 kJ mol^{-1} higher than the corresponding value of −1295(±10) kJ mol^{-1} obtainable from the result of the reported study. The difference in the enthalpy values could be attributed to the improper control on the oxygen pressure within the Knudsen cell of the study [5] due to the involvement of the reaction $4BN(s) + 3O_2(g) = 2B_2O_3(liq) + 2N_2(g)$. As the reaction leads to the lower mass loss from the cell, the K_p values for reaction (1) evaluated from this mass loss would be lower than the actual one with an altered temperature dependence.

The Gibbs energy data of the nickel tellurate, Ni_3TeO_6 obtained from this study were used to calculate the onset temperature for the reported oxidation reaction of tellurite $Ni_2Te_3O_8$(s) [3] as

$$\begin{aligned}&5\ \mathrm{Ni_2Te_3O_8(s)} + 0.5\mathrm{O_2(g)} \\ &\quad = \mathrm{Ni_3TeO_6(s)} + 7\mathrm{NiTe_2O_5(s)}. \quad (7)\end{aligned}$$

Thus Eq. (6) together with the available stability data of the two tellurite phases $Ni_2Te_3O_8$(s) and $NiTe_2O_5$(s) [5] yields the condition for the oxidation reaction at one bar pressure of oxygen as

$$\Delta G^\circ_{\mathrm{oxidation}} = 155.5 - 0.18T \leqslant 0 \quad \text{i.e. } T \geqslant 864\ \mathrm{K}. \quad (8)$$

It may be noted that the Gibbs energy data of the tellurites used in the above analysis were taken again from the mass loss study [5] with a BN Knudsen cell, for the evaporation reactions of the tellurites do not involve oxygen. The tellurite data [5] thus do not suffer from the problem of oxygen pressure control. The temperature limit for the oxidation reaction of Eq. (7) analyzed employing the thermodynamic data of the tellurate from the present study and expressed in Eq. (8) is in good agreement with the reported value of 873 K for the ternary equilibrium [3]. On the other hand, if the reported stability data of the tellurate are used instead, the above analysis leads to a much lower value for the onset temperature implying the incorrectness of the data [5].

4. Conclusion

From the transpiration study of the vaporization of the nickel tellurate Ni_3TeO_6(s), the standard Gibbs energy of formation of the compound was obtained and also, the value of $\Delta_f H^\circ$(Ni_3TeO_6(s), 298.15 K) was derived as −1216(±14) kJ mol^{-1}.

Acknowledgements

The authors thank Dr J.P. Mittal, Director, Chemistry and Isotope Group, BARC and Dr N.M. Gupta, Head, Applied Chemistry Division, BARC for their support and encouragement during this work.

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