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Determination of chemical activities of Fe, Cr, Ni and Mn in stainless steel 316 by Knudsen effusion cell mass spectrometry

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Abstract

Cold-worked austenitic stainless steel of the type AISI 316 is being used as the cladding and wrapper materials in fast reactor fuel pins. Knowledge of the thermodynamic activities of the steel constituents is necessary to predict the possibility of fuel–cladding, coolant–cladding or fission product–cladding chemical reactions. The thermodynamic activities of Fe, Cr, Ni and Mn for stainless steel 316 were determined by measuring their partial pressures in the temperature range 1293–2120 K, using Knudsen effusion cell mass spectrometry. High purity Ag was used as an internal calibrant. The chemical activities of Fe (a_{Fe}), Cr (a_{Cr}), Ni (a_{Ni}) and Mn (a_{Mn}) were evaluated using literature data for the vapour pressures of pure metals.

$$\log a_{Fe} \pm 0.18 = -1.586 + 2074/T \quad (T = 1293\text{–}1872\ \text{K})$$

$$\log a_{Cr} \pm 0.30 = -2.350 + 2612/T \quad (T = 1293\text{–}2120\ \text{K})$$

$$\log a_{Ni} \pm 0.20 = -2.140 + 1794/T \quad (T = 1468\text{–}1974\ \text{K})$$

$$\log a_{Mn} \pm 0.23 = -2.041 - 5478/T \quad (T = 1302\text{–}1894\ \text{K})$$

Keywords: Chemical activities; Stainless steel; Knudsen cell mass spectrometry

1. Introduction

Austenitic type 316 stainless steels are used as the cladding and wrapper materials for a liquid metal-cooled fast breeder reactor (LMFBR). The American Iron and Steel Institute (AISI) has given the common designation of austenitic-structured stainless steels, and the type 316 steel has the following composition (in weight per cent): 0.08; Mn, 2; Mo, 2; Si, 1.00; Cr, 16–18; Ni, 10–14; Fe balance [1].

Knowing the chemical activities of steel constituents such as Fe, Cr, Ni, Mn and Mo is necessary to predict the possibility of reactions with the fuel, cladding and coolant under different oxygen and carbon potential gradients. Some thermodynamic information on stainless steels with 18 wt.% Cr and 8 wt.% Ni is reported in the literature [2–7]. Azad et al. [2,3] directly determined the chemical activities of all the steel constituents in type 316 stainless steel by employing a metastable e.m.f. method using a CaF_2 electrolyte galvanic cell in the temperature range 800–1200 K. In this method, the transient e.m.f. developed as a result of the metastable equilibrium between the less noble metal and the fluoride of the more noble metal was measured before a direct chemical reaction could arise. Other references [4–7] mainly report on the chemical activity of Cr in stainless steel.

Recently, Lee [8] used Knudsen effusion cell mass spectrometry (KEMS) to determine the partial pressures of the constituents in stainless steel containing different composition of Fe, Cr and Ni in Fe–Ni–Cr–Al and Fe–Ni–Cr–Al–Si alloys in the temperature range 1613–2000 K. Lee's data indicated that additions of Ni, Cr, Al and Si have no effect on the activity of Fe.

In the present study, the equilibrium partial pressures of various constituents were determined simultaneously over the commercial 316 stainless steel used in our fast breeder test reactor (FBTR), using KEMS.

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Table 1
Composition of AISI 316 steel

	Fe	Cr	Ni	Mo	Mn	Si	Cu	Zn	Co	V
wt.%	62.62	19.67	10.01	3.98	3.52	0.14	0.067	<DL[a]	<DL[a]	<DL[a]
at.%	61.91	22.52	9.41	2.29	3.54	0.27	0.058			

[a] DL, detection limit.

Table 2
Ion intensities of Cr^+, Fe^+ and Ni^+ after correcting for isotopic abundance and multiplier efficiencies

T(K)	$I_{Fe}\times10^{15}$	$I_{Ni}\times10^{15}$	$I_{Cr}\times10^{15}$
(Pressure calibration constant, 1.11×10^{11} Pa A^{-1} K^{-1})			
1293	9.7×10^{-3}	–	4.14×10^{-3}
1338	1.6×10^{-2}	–	1.66×10^{-2}
1402	6.9×10^{-2}	–	9.58×10^{-2}
1468	2.4×10^{-1}	1.47×10^{-2}	2.74×10^{-1}
1529	8.5×10^{-1}	3.42×10^{-2}	8.22×10^{-1}
1603	2.71	1.30×10^{-1}	2.19
1657	6.51	3.00×10^{-1}	5.34
1709	13.8	6.35×10^{-1}	9.62
1751	25.4	1.26	17.5
1788	43.9	2.28	29.2
1835	73.8	3.85	45.9
1872	112	6.14	66.6
(Phase transition)			
1916	170	9.62	91.5
1947	239	13.9	116
1985	306	18.5	130
2011	394	23.1	164
2034	487	28.6	222
2060	619	35.0	298

Table 3
Ion intensities of Mn^+ after correcting for multiplier efficiency

T(K)	$I_{Mn}\times10^{15}$	T(K)	$I_{Mn}\times10^{15}$
(Pressure calibration constant, 6.56×10^{9} Pa A^{-1} K^{-1})			
1414	6.42×10^{-2}	1635	2.64
1451	1.18×10^{-1}	1671	4.46
1497	2.86×10^{-1}	1699	6.73
1536	5.32×10^{-1}	1727	9.86
1564	9.42×10^{-1}	1758	15.3
1600	1.69	1777	19.4

2. Experimental details

2.1. Materials

A commercial austenitic stainless steel (AISI 316) tube used as the cladding material for the FBTR was cut into small pieces, acid pickled and then introduced into the Knudsen cell. The chemical composition of the steel was determined by induction-coupled plasma–atomic emission spectrometry (ICP–AES). The results of the analysis are given in Table 1.

Table 4
Values of multiplier gain Γ, isotopic abundance H and ionization cross-sections σ used for different gaseous atomic species

Species	H	σ	Γ[a]
^{56}Fe	0.9172	6.1088	25709
^{52}Cr	0.8379	4.4480	28837
^{58}Ni	0.6827	6.4930	25001
^{55}Mn	1.0000	5.3854	21454

[a] Experimentally measured.

2.2. Knudsen effusion cell mass spectrometry measurements

The steel sample weighing about 0.5–1 g, together with approximately 2–3 mg of high purity Ag, was loaded into a Ta crucible kept inside a Ta Knudsen cell with a circular orifice 1 mm in diameter at the centre of the lid. This cell was contained in another Ta cell with a circular orifice of diameter 2.5 mm in line with the inner cell orifice. Fresh samples were used for each run, so that composition change resulting from volatility was minimized.

At each isothermal temperature of the Knudsen cell, the ion intensities of all the ions were measured by changing the magnetic field. The temperature was then increased by 15–20 K and similar measurements were made. Thus, a run consisted of measuring the ion intensities of all the gaseous ionic species, such as Fe^+, Cr^+ and Ni^+, simultaneously at different temperatures. Each run lasted about 2–3 h, depending upon the temperature. Mn is the most volatile among the steel constituents, so the ion intensities of Mn^+ were measured separately. For Mn^+, ion measurements could be performed down to 1302 K, where its partial pressure was around 10^{-6} Pa.

The design of the cell, the differential pumping system and the detector system are described in detail in an earlier publication [9]. However, a brief description is given here for clarity. The mass spectrometer used in the present study was a single-focusing, normal geometry, 90° sector, magnetic-type instrument. Turbomolecular pumps and ion pumps produced a vacuum of the order of 10^{-5} Pa in the Knudsen cell compartment and in the ion source chamber, while ion pumps produced 10^{-6} Pa in the analyzer compartment. This type of differential pumping was found to be necessary to

Table 5
Partial pressures of Fe, Cr, Ni and Mn over AISI 316 stainless steel in different runs [a]

	Temperature range (K)	a	b	p(Pa) at 1800 K
Fe	1293–1872	10.33 ± 0.17	18.287 ± 0.246	1.5
	1431–2128	10.19 ± 0.09	17.884 ± 0.140	1.8
Mean	1293–2128	10.26 ± 0.26	18.086 ± 0.280	(1.6 ± 0.3)
Cr	1293–1872	10.04 ± 0.22	17.780 ± 0.315	1.5
	1431–2128	9.15 ± 0.05	16.476 ± 0.087	1.0
Mean	1293–2128	9.60 ± 0.32	17.128 ± 0.455	(1.2 ± 0.4)
Ni	1468–2128	9.24 ± 0.12	18.563 ± 0.198	0.1
	1468–1985	9.62 ± 0.12	19.217 ± 0.198	0.1
	1373–1974	9.64 ± 0.14	19.040 ± 0.215	0.1
Mean	1373–2128	9.50 ± 0.25	18.941 ± 0.320	(0.1 ± 0.03)
Mn	1302–1894	8.24 ± 0.08	18.322 ± 0.126	0.01
	1414–1777	8.63 ± 0.08	17.949 ± 0.110	0.04
Mean	1302–1894	8.44 ± 0.28	18.136 ± 0.280	(0.02 ± 0.005)

[a] Log $p(\mathrm{Pa}) = a - (b \times 10^3)/T(\mathrm{K})$.

The overall probable errors are evaluated on the basis of assuming an error of ±3 K in absolute temperature, i.e. +3 K and −3 K as differential errors at the highest and lowest temperatures, and an error of ±10% in cross-sections and ion intensities.

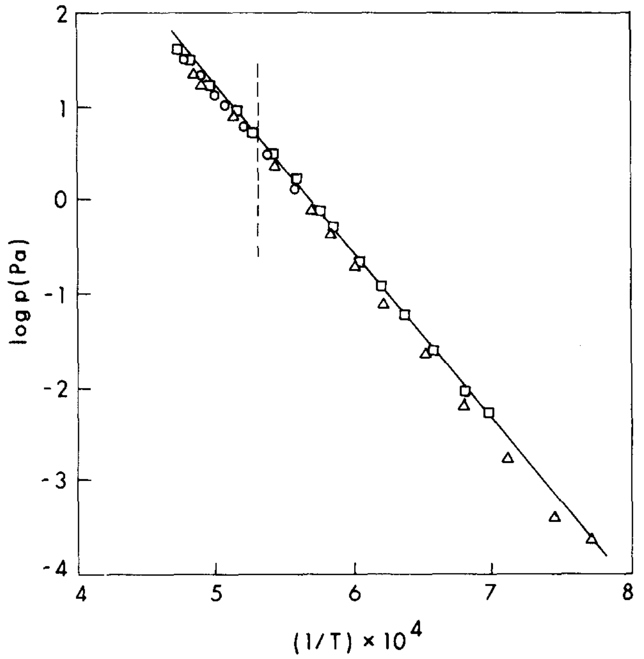

Fig. 1. Dependence of partial pressure of Fe(g) on reciprocal temperature for type 316 stainless steel: ○; △, □, different experimental runs; – – –, solidus temperature; ——, mean over entire temperature range.

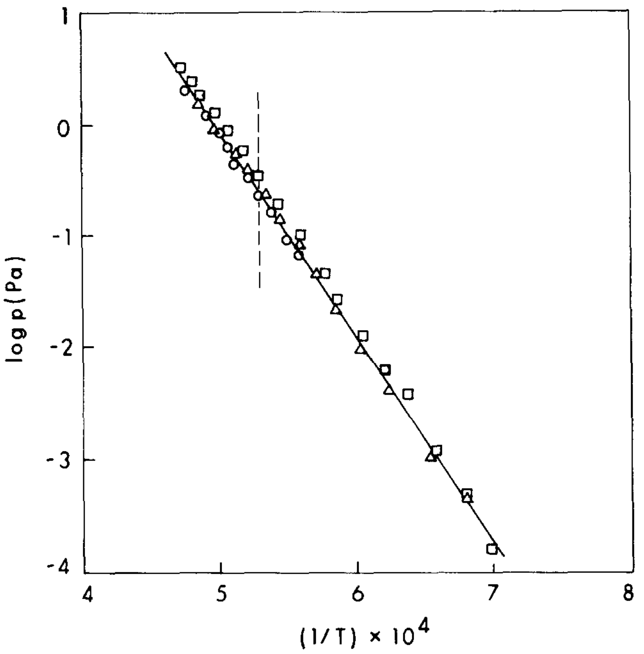

Fig. 2. Dependence of partial pressure of Ni(g) on reciprocal temperature for type 316 stainless steel: ○; △, □, different experimental runs; – – –, solidus temperature; ——, mean over entire temperature range.

obtain a high signal-to-noise ratio. The ionization chamber was separated from the Knudsen cell compartment by a shutter with an aperture of diameter 2 mm, through which passed the molecular beam originating in the Knudsen cell. The aperture could be closed by a metal-sealed ultrahigh vacuum valve, so shuttering the molecular beam. The cell temperature was monitored using a disappearing filament-type optical pyrometer which was calibrated by means of the melting temperatures of Ag, Au and Ni given in Ref. [10]. The temperatures could be reproduced within ±3 K. After the experiments, the stainless steel sample came out easily from the crucible and no perceptible erosion could be seen on the inner surface. This indicated that no chemical reaction took place between the liquid steel and Ta.

Table 6
Vapour pressure data reported for pure elements [a]

Ref.	1500–1900 K				1520–1800 K			
	Fe(s)		Cr(s)		Ni(s)		Mn(l)	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
[12]	11.85	20.160	11.95	19.740	11.64	20.735	10.48	12.658
[14]	11.18	19.514	11.89	19.740	12.22	21.816	10.26	12.239
[8]	11.69	20.160	12.05	19.950	11.84	20.94		

[a] $\log p\ (\mathrm{Pa}) = a - (b \times 10^3)/T\ (\mathrm{K})$.

Table 7
Comparison of chemical activity values with those of Lee [8]

Ref.	1550 K		1429 K		1667 K		1500 K	
	a_{Fe}	Γ_{Fe}	a_{Cr}	Γ_{Cr}	a_{Ni}	Γ_{Ni}	a_{Mn}	Γ_{Mn}
[8] [a]	0.78	1.04	0.28	2.9	0.19	1.29	–	–
[8] [b]	0.50	0.66	0.34	3.5	0.26	1.76	–	–
This work	0.56	0.92	0.29	1.3	0.09	0.95	2×10^{-6}	6×10^{-5}

[a] Using equations for pressures of pure Fe, Cr and Ni reported by Lee.

[b] Using pressure values for pure Fe, Cr and Ni reported by Hultgren et al.

The synthetic sample used by Lee contained 75.38 at.% Fe, 14.90 at.% Ni and 9.72 at.% C.

Table 8
Comparison of chemical activities of stainless steel constituents with those of Azad et al. [1]

	Present study		Azad et al. [2]	
	1150 K [a]	1600 K	1150 K	1600 K [a]
a_{Fe}	1.6	0.5	0.9	1.0
a_{Cr}	0.8	0.2		0.3
a_{Ni}	0.3	0.1	0.8	1.0
a_{Mn}	2×10^{-7}	3×10^{-6}	0.03	0.1

[a] Extrapolated.

A constant ion acceleration voltage of 3 kV and electron current of 100 μA with 40 eV electron energy were used throughout the experiments for the ionization of neutral gaseous atoms. The ion intensities of ^{52}Cr, ^{56}Fe, ^{58}Ni and ^{55}Mn produced by ionization were measured using a Faraday cup, as well as by a secondary electron multiplier. The Faraday cup was used for measurement of strong ion intensities and also to determine the multiplier efficiencies for different mass numbers. The contribution of the ion intensity from ^{58}Fe in the measurement of the intensity of ^{58}Ni was corrected to obtain the partial pressure of Ni.

The partial pressure p of gas was evaluated from the measured ion intensity I, multiplier efficiency Γ, isotopic abundance H and ionization cross-section σ, using the relationship

$$p = \frac{(kIT)}{(\sigma H \Gamma)} \qquad (1)$$

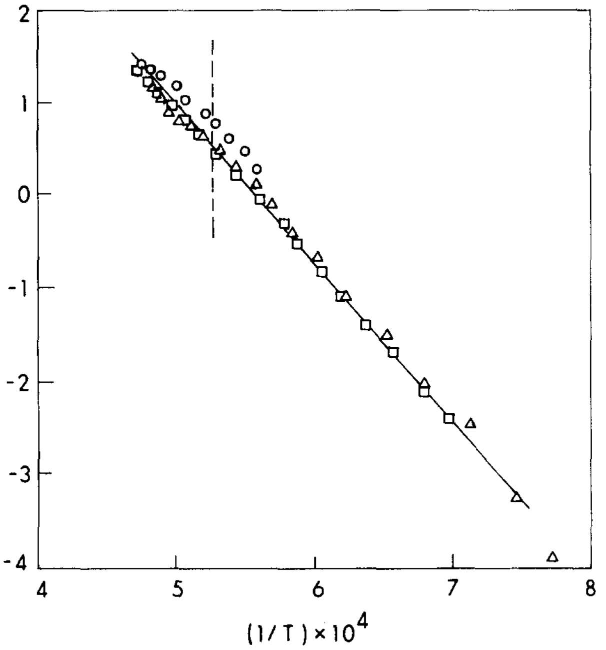

Fig. 3. Dependence of partial pressure of Cr(g) on reciprocal temperature for type 316 stainless steel: ○; △, □, different experimental runs; – – –, solidus temperature; ——, mean over entire temperature range.

where k is the calibration constant obtained by vaporizing pure Ag in situ or by a separate experiment, and T is the temperature of the Knudsen cell in kelvin.

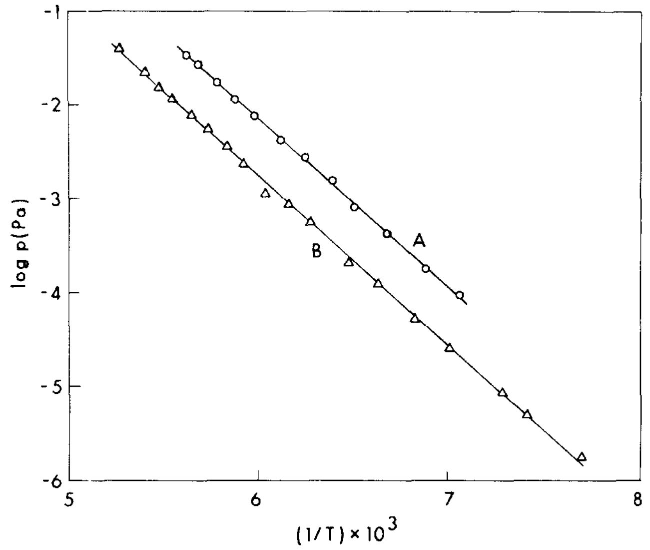

Fig. 4. Dependence of partial pressure of Mn(g) on reciprocal temperature for type 316 stainless steel: A, runs with fresh samples; B, runs with used samples; —–, least-squares fit of the datum points.

3. Results and discussion

Several sets of experimental runs were performed, in which the ion intensities of all the gaseous species were simultaneously determined, except for Mn. Fresh stainless steel samples were used for each run, because the composition was expected to change as a result of vaporization loss. The composition change was kept to a minimum during the vapour pressure measurement of Mn by measuring the ion intensity corresponding to Mn^+ only, and limiting the temperature to 1900 K. The chemical analysis before and after the experiment indicated that the concentration change of the different constituents was within ±5%. However, for Mn, the concentration change was up to ±10%. The values of the multiplier efficiency, ionization cross-section and isotopic abundance necessary for the conversion of measured ion intensities into corrected intensity values are given in Tables 2 and 3. The corrected ion intensities for one set of measurements is given in Table 4.

The partial pressures for different constituents were evaluated using the ion intensity data and relative ionization cross-section values at 40 eV reported by Mann [11], using (1). The partial pressure data are given in Table 5. The partial pressures obtained from different sets of measurements agreed well with one another, and this can be seen from Figs. 1–3.

The solidus temperature indicated in the figures was ascertained from the abrupt change in ion intensity when the molten steel was cooled. In the solid range, all the ion intensities were measured during heating and cooling. The ion intensities were measured over the liquid range in the heating mode only. The ion intensities did not remain constant in the liquid range. This may be because of the thin oxide layer cover over the liquid metal decreasing the metal's vaporization rate, so decreasing the ion intensity.

The dependence of the partial pressure of Mn on temperature is given in Fig. 4. As can be seen from the figure, the partial pressures of Mn were lower when the Mn^+ intensities were measured simultaneously with other ion intensities. Hence, the measurements should be performed over a short time, with a fresh sample for each run.

From the partial pressures calculated in this way, the chemical activities of Fe, Cr, Ni and Mn were evaluated using the vapour pressures of the pure elements. The available literature data on the vapour pressures of pure elements are given in Table 6. The data reported by Hultgren et al. [12] were used to evaluate the activities.

In the present study, partial pressures were obtained over both solid and molten steel. In the temperature range over solid steel, pure Mn exists in a liquid state. For the calculation of the chemical activities, solid standard states were assumed for Fe, Ni and Cr, and a liquid state for Mn.

The chemical activities evaluated are respectively given by the following equations:

$$\log a_{Fe} \pm 0.18 = -1.586 + 2074/T \quad (T = 1293\text{–}1872\ K)$$

$$\log a_{Cr} \pm 0.30 = -2.350 + 2612/T \quad (T = 1293\text{–}2120\ K)$$

$$\log a_{Ni} \pm 0.20 = -2.140 + 1794/T \quad (T = 1468\text{–}1974\ K)$$

$$\log a_{Mn} \pm 0.23 = -2.041 - 5478/T \quad (T = 1302\text{–}1894\ K)$$

The present results for the partial pressures and activities could not be compared, because of the non-availability of literature data on type 316 stainless steel in the temperature range of the present study. However, the data are compared in Table 7 with the KEMS-measured values of Lee [8] for synthetic stainless steel alloys containing mainly Fe, Cr and Ni. The present values are found to be in reasonable agreement wtih the steel alloys of Lee. The small difference in the chemical activities may be attributed to differences in the compositions of the alloy constituents. However, the differences may be more due to the minor components, such as Mo and Mn, present in the commercial stainless steel used in the present study. The present value of a_{Cr} at 1472 K (0.297) is in very good agreement with the mean activity value reported by Slough et al. [13] for the 18-8 stainless steel (0.293), determined by radiometry using tracer ^{51}Cr.

The activities of commercial type 316 stainless steel determined from the present study by KEMS in the temperature range 1293–2120 K are compared in Table 8 with the values of Azad et al. [1,2], determined in the temperature range 800–1200 K by a solid state metastable e.m.f. technique. The activities from both the measurements were extrapolated for comparison.

Azad et al. used type 316 stainless steel with the following composition (in weight per cent): Cr, 16.85; Ni, 12.15; Mo, 2.36; Mn, 1.86; Fe, 66.78. Though the composition is close to that of the steel composition used in the present study, there is quite a large difference in the activity values. The disagreement between the two studies may be because of the non-validity of extrapolation between the two temperature ranges of measurement. However, the good agreement with Lee [8] seems to indicate the reliability of the present data for type 316 stainless steel in the high temperature region, though the compositions of the steels used are different.

It is suggested from the present study that the chemical activities for type 316 stainless steel required for any evaluation purpose can be taken from Azad et al., for temperatures between 800 and 1200 K, and from the present study between 1300 and 2200 K.

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