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Thermodynamic activity measurements in nickel-base industrial alloys and steels by Knudsen cell – Mass spectrometry

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ABSTRACT

The first activity measurements of nickel, copper, chromium and iron in industrial nickel-base alloys (Monel®400, Monel®K-500, Nicorros®400, Nicorros®K-500, Hastelloy-X®, Hastelloy-C2000®, model alloy 1181) and steels (Uranus®65 and Uranus®45N) were performed using multiple Knudsen effusion Cell Mass Spectrometry in the temperature range 1483–1593 K. For each constituent, the activity is expressed as: $\ln(a_i) = (A \pm \delta A)/T + (B \pm \delta B)$. The experimental results were compared with calculated data using the SSOL2 database from Thermo-Calc.

1. Introduction

In France, the isotopic enrichment of natural uranium is performed by an ultracentrifugation process using uranium hexafluoride, UF_6, which is fabricated by fluorination of uranium tetrafluoride, UF_4, at high temperature (T > 1500 °C) in a flame reactor. In such environment, corrosion phenomena are important and the choice of the material of the reactor vessel is fundamental to improve its lifetime. Nickel and nickel alloys (like copper-nickel) are known to have a better resistance in fluorine and uranium hexafluoride atmosphere than other types of materials [1,2] and are thus potential candidates for the flame reactor vessel. In fact, Ni-base alloys are known to develop a protective NiF_2 layer on their surface. To predict the surface reactivity of a material exposed to a corrosive atmosphere, chemical activity data are useful [3,4].

As an example, solid Cu-Ni alloys were investigated thermodynamically within the whole range of composition by Knudsen cell mass spectrometry [5]. Thermodynamic activities in this system show positive deviations from Raoult's law.

Only few activity measurements in industrial alloys are available in the literature. Vapour pressure measurements on inconel 617, nimonic alloy PE 13 and IN-643 alloys were performed using high-temperature mass spectrometry in the frame of advanced gas-cooled high temperature reactor and thermonuclear fusion devices. Partial pressure data of nickel, chromium, iron (1350–1510 K) and cobalt (1215–1505 K) over IN-643 [6], nickel, chromium (1355–1527 K) and cobalt (1214–1517 K) over inconel 617 as well as of nickel, chromium, iron (1349–1493 K) and cobalt (1279–1500 K) over nimonic PE 13 [7] were obtained. An electromotive force (emf) technique was used for the determination of thermodynamic activities of metallic constituents of commercial grade AISI 316 (Cr, Ni, Fe, Mn, Mo) [8], 304 (Mn, Cr, Fe, Ni) [9] and 316LN (Cr, Mn, Fe, Ni, Mo) [10] stainless steel of approximately 800–1200 K. These data were used to study the corrosion behaviour of the stainless steels in liquid sodium.

Owing to their good corrosion resistance in spent nuclear fuel reprocessing plant, nickel-base alloys (Monel®400, Monel®K-500, Nicorros®400, Nicorros®K-500, Hastelloy-X®, Hastelloy-C2000®, model alloy 118) and steels (Uranus®65 and Uranus®45N) were selected [11]. Measurements of the major constituents thermodynamic activity in these alloys by Knudsen cell-mass spectrometry are presented in this work. These thermodynamic data are fundamental to interpret the corrosion behaviour of the alloys under fluorine and uranium hexafluoride atmosphere.

2. Experimental method

Multiple Knudsen cell mass-spectrometry is a standard method for measuring thermodynamic activity data in multi-components systems at high temperature. Our apparatus was previously described in [12–14]. The mass spectrometer used in this work is a Nermag R10-10C quadrupole. The ionization is performed by electron impact. The emission current is about 0.2 mA with a 15 V ionizing potential for all species. For detection, the electron

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multiplier is a 21-dynodes one and the tension applied on first dynode is 2 kV. We measure the ionic current for a given mass. The samples are heated using a tungsten resistor in which a molybdenum block holds the four effusion cells. These four Knudsen cells (crucible and lid) are made of dense alumina (99.7% from High Tech Ceram) for the pure iron reference and alloys, of dense graphite (PT 2114 from Mersen) for the pure copper reference and of hypostoichiometric yttria, Y_2O_{3-x} for the pure chromium and nickel references. A W-Re thermocouple located at the bottom of the isothermal molybdenum block is used to monitor and regulate temperature of the furnace. During the experiment, the temperature of the sample is measured in the Knudsen cell using a calibrated optical bicolour pyrometer (Impac) through the hole of the analysed crucible. The resulting accuracy is of ±6 K for the optical pyrometer. The real temperature of the sample given by the optical pyrometer is taken.

In our experimental conditions, the gaseous phase is in equilibrium with the condensed phase. This vapour phase is rarefied and can be considered as ideal. The thermodynamic activity a_i of the component i of the mixture can be defined as the ratio of the partial vapour pressure p_i^m of component i above the mixture to the vapour pressure p_i^0 of the pure element, at the same temperature. The mass spectrometer allows us to measure the ionic intensity of component i which is related to the partial pressure as follows: $p_i = (I_iT)/S_i$. Use of restricted collimation [14] increases the quality of the measurements by elimination parasite vapour contributions. As the sensitivity S_i of component i and temperature are the same in all effusion cells [15], at a given temperature, the activity is directly equal to the ratio of the ionic intensities of component i measured respectively above the mixture I_i^m and over the pure element I_i^0:

$$a_i = p_i^m/p_i^0 \cong I_i^m/I_i^0 \quad (1)$$

On one hand, our technique requires the formation of a properly collimated molecular vapour beam which corresponds to a pressure in the cell $<10^{-4}$ bar. On the other hand, the vapour pressures of the components have to be high enough to reach measurable ion currents. Considering these two conditions, the resulting temperature range of the measurements in the present study is small: 1483 K–1593 K.

The chemical compositions of the industrial alloys selected in the present work are listed in Table 1. Depending on the major elements in these different alloys, Ni, Cr, Fe or Cu activities were measured (as indicated in bold in Table 1). Natural copper, nickel, chromium and iron have respectively two, five and four isotopes (Table 2). For these elements, the ionic intensities were measured using the mass of the major isotopes, i.e. ^{63}Cu, ^{52}Cr, ^{58}Ni and ^{56}Fe.

Table 2
Abundance ratio, melting temperature and vapour pressure data of the pure elements.

Elements	Isotopes and abundance ratio supress [08Del]	Melting T/K	Pressure at the melting/Pa
Cu	**^{63}Cu 69.17%** ^{65}Cu 30.83%	1357	5.73×10^{-2}
Cr	^{50}Cr 4.4% **^{52}Cr 83.7%** ^{53}Cr 9.5% ^{54}Cr 2.4%	2148	546
Ni	**^{58}Ni 68.1%** ^{60}Ni 26.2% ^{61}Ni 1.2% ^{62}Ni 3.6% ^{64}Ni 0.9%	1728	0.45
Fe	^{54}Fe 5.8% **^{56}Fe 91.8%** ^{57}Fe 2.1% ^{58}Fe 0.3%	1808	3.36

The mass spectrometer resolution was optimized in order to avoid the overlap between iron ^{56}Fe and manganese ^{55}Mn signals, manganese being very volatile.

For each run, the good reproducibility of the measurements was checked by comparing the intensity data on both heating and cooling. In fact, a good agreement between intensities measured on heating and cooling is an indication that there is no significant deviation of the sensitivity of the mass spectrometer or of the alloy composition (Fig. 1). In addition, at the end of each run, we finally checked that the intensity value remained at a constant value at a given temperature. The difference did not exceed 3%.

3. Results

3.1. Enthalpy of sublimation and vaporisation of pure elements

From 1483 to 1593 K, pure nickel, chromium and iron are in solid state and copper is in liquid state. The heat of sublimation at room temperature of pure nickel, chromium and iron, and of vaporisation of pure copper, were calculated from the measured intensities using the second-law and the increment enthalpy data given by Pankratz [16]. Our results are reported in Table 3. To decrease the uncertainty on our results, the temperature range has been chosen as large as possible considering the possible

Table 1
Nominal composition (wt%) of the industrial alloys investigated in the present work. The elements analysed are **in bold**.

Alloy	Composition (wt%)										Supplier
	Ti	C	Si	Mn	S	Al	Co	Cu	Fe	Ni	
Monel® 400		0.14	0.25	0.99	0.001	<0.01	0.13	**33.1**	2.10	**63.2**[b]	Rolled alloys
Monel® K-500	0.6	0.11	0.16	0.78	0.001	2.96	0.01	**30.28**	0.63	**64.2**	Rolled alloys
Nicorros® 400	0.61	0.13	0.14	0.62	<0.001	2.93	0.004	**30.06**	0.71	**64.7**[b]	Jacquet (Thyssen Krupp)
Nicorros®K-500	0.02	0.14	0.14	0.99	<0.002	0.18	0.04	**32.39**	1.86	**64.15**	Jacquet (Thyssen Krupp)

Alloy	Composition (wt%)											Supplier
	Cr	C	W	Si	Mn	S	Mo	Co	Cu	Fe	Ni	
Uranus®45 N	22.54	0.022		0.31	1.41	0.001	3.20	0.08	**0.17**	**66.31**[b]	**5.77**	Jacquet (Industeel)
Uranus®65	25.4[a]			0.10[a]	0.60[a]		<0.1[a]			**53.4**[a]	**20.5**[a]	CEA
Hastelloy®C-2000	**23.02**	0.006		0.03	0.23	0.001	15.59	<0.05	**1.49**	1.23	**58.2**[b]	Haynes International
Hastelloy®X	**21.49**	0.084	0.72	0.40	0.67	<0.002	8.38	1.82		**19.34**	**47.1**[b]	Haynes International
1181 alloy	**22**	0.1	14								**63.9**[b]	CEA

[a] Chemical analysis performed in SEARS/LISL by ICP-AES (Perkin Elmer Optima 2000).
[b] Balance.