Activities of Iron in Liquid Copper-Iron Alloys Saturated with Copper-Iron Solid Solutions[1]

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ABSTRACT

In order to elucidate the activities of Fe in {Cu-Fe} liquid alloys saturated with <Cu-Fe> solid solutions, the equilibrium oxygen partial pressures of the following mixtures were determined by employing an electrochemical technique at temperatures between 1473K and 1613K.

(i) "pure" FeO + {Cu-Fe} + <Cu-Fe>
(ii) <CaO> + <Ca_3SiO_5> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>
(iii) <Ca_3SiO_5> + <Ca_2SiO_4> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>
(iv) <Ca_2SiO_4> + <$Ca_3Si_2O_7$> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>
(v) <$Ca_3Si_2O_7$> + <$CaSiO_3$> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>

The electrochemical cell used for the measurements involved magnesia-stabilized zirconia as electrolyte and Mo + MoO_2 mixture as reference electrode. The activities of Fe in liquid {Cu-Fe} alloys saturated with <Cu-Fe> solid solutions could be expressed by a formula:

$\log a_{Fe} = -(0.58 \pm 0.07) + (0.083 \pm 0.011) \times 10^4 / (T/\mathrm{K})$

INTRODUCTION

During a course of studies directed toward elucidating the thermodynamic properties of the system CaO + P_2O_5 + FeO, it became necessary to know the activities of Fe in {Cu-Fe} liquid alloys saturated with <Cu-Fe> solid solutions. The activities of Fe in such two-phase regions can be determined by equilibrating the subject alloys with ferrous oxide of known activities, and measuring the equilibrium oxygen partial pressures. For this purpose, in this study, the following mixtures were employed.

(i) "pure" FeO + {Cu-Fe} + <Cu-Fe>
(ii) <CaO> + <Ca_3SiO_5> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>
(iii) <Ca_3SiO_5> + <Ca_2SiO_4> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>
(iv) <Ca_2SiO_4> + <$Ca_3Si_2O_7$> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>
(v) <$Ca_3Si_2O_7$> + <$CaSiO_3$> + {CaO-SiO_2-FeO} melt + {Cu-Fe} + <Cu-Fe>

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Figure 1 shows the isothermal section of the phase diagram of the system CaO + SiO_2 + FeO in equilibrium with pure solid <Fe>, at 1573K. The FeO apex and the regions A, B, C and D, respectively, correspond to mixtures (i), (ii), (iii), (iv) and (v), respectively. In this study, the equilibrium oxygen partial pressures were measured by means of solid-oxide galvanic cells incorporating Mo + MoO_2 as reference electrode and MgO-stabilized zirconia as solid electrolyte. The cells used in this study can be formulated as

Mo/ Mo+MoO_2 / ZrO_2(MgO) / <FeO> + {Cu-Fe} +
<Cu-Fe> / Fe cell (I)
Mo/ Mo+MoO_2 / ZrO_2(MgO) / *C* + *C3S* + *L* +
{Cu-Fe} + <Cu-Fe> / Fe cell (II)
Mo/ Mo+MoO_2 / ZrO_2(MgO) / *C3S* + *C2S* +
{Cu-Fe} + <Cu-Fe> / Fe cell (III)
Mo/ Mo+MoO_2 / ZrO_2(MgO) / *C2S* + *C3S2* +
L + {Cu-Fe} + <Cu-Fe> / Fe cell (IV)
Mo/ Mo+MoO_2 / ZrO_2(MgO) / *C3S2* + *CS* +
L + {Cu-Fe} + <Cu-Fe> / Fe cell (V),

where *C*, *C3S*, *C2S*, *C3S2*, *CS* and *L* denote, respectively, <CaO>, <Ca_3SiO_5>, <Ca_2SiO_4>, <$Ca_3Si_2O_7$>, <$CaSiO_3$> and {CaO-SiO_2-FeO} liquid slag.

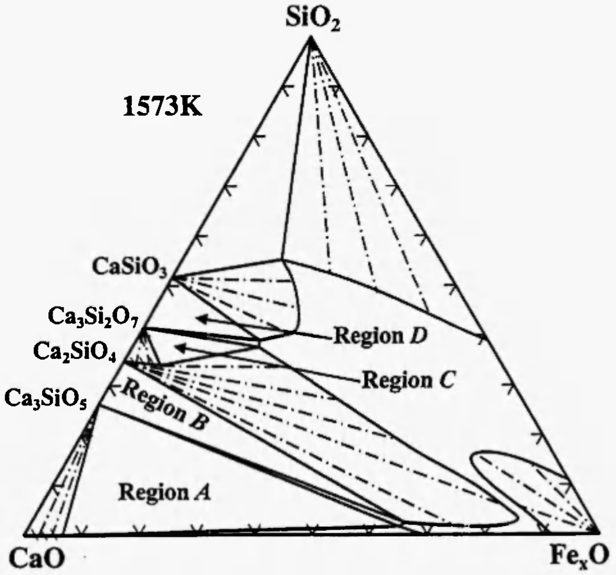

Fig. 1: Iso-thermal section of the system CaO + SiO_2 + FeO at 1573K. Compositions are given in per cent by weight.

EXPERIMENTAL ASPECTS

The apparatus, as shown in Figure 2, and experimental procedure have been reported elsewhere /1/. Hence only a brief description is given in this paper. A SiC resistance furnace was equipped with a mullite reaction tube of 70 mm O.D., 60 mm I.D. and 1000 mm in length. The electrochemical half-cell, Mo / Mo + MoO_2 / ZrO_2(MgO), consisted of a zirconia tube, a molybdenum rod and a two-phase mixture of Mo+MoO_2. Iso-statically pressed zirconia tubes, closed at one end and stabilized by 9 mol % MgO, were supplied by Nikkato Corp. These tubes had an i.d. of 4mm, an o.d. of 6 mm and a length of 50 mm. A molybdenum rod of 3 mm in diameter was used as an electrical lead to the reference electrode, which consisted of four parts Mo and one part of MoO_2 by weight. The molybdenum rod was fixed at the top of the zirconia tube by means of zirconia cement (SUMICERAM S-301, Asahi Chemical Co., Ltd.). The electrical contact to the outer electrode of the zirconia probe was made by a steel rod soldered to the iron crucible. Temperatures were measured with a Pt-PtRh13 thermocouple and controlled to ±1 K by using a control thermocouple and a proportional-integral-differential-

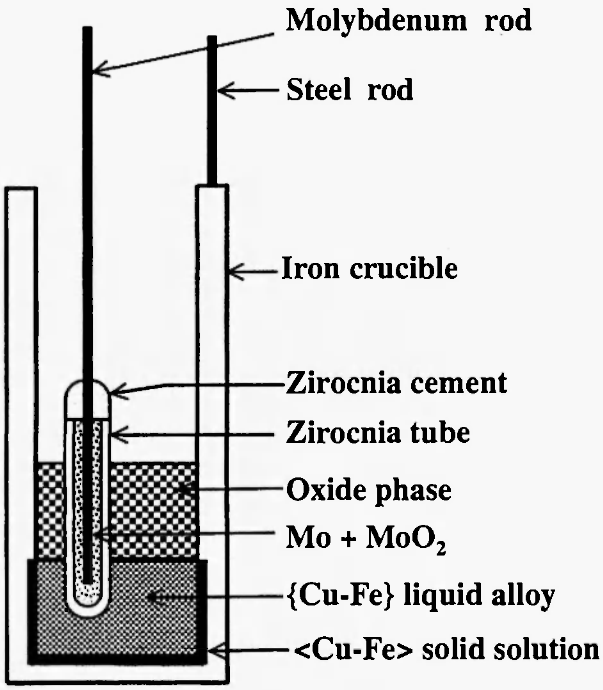

Fig. 2: A schematic diagram of experimental setup.

type temperature regulator. The overall errors in temperature measurements and control were estimated to be less than ±2 K.

An iron crucible was charged with about 5 g of oxide phase and about 70 g of pure copper, and heated to 1600 K for over 12 hours, in order to form {Cu-Fe} liquid alloys and <Cu-Fe> solid solutions at the inner wall of the iron crucible. The experimental procedure consisted of measuring the open-circuit cell potentials of the solid-state oxygen probe and sampling the {Cu-Fe} liquid alloys for chemical analysis of iron, to determine the liquidus composition at the experimental temperatures. The concentrations of iron in liquid alloys were determined with an inductively coupled plasma spectrometer. The cell potentials generated were monitored on a strip-chart recorder of 2 MΩ internal impedance with an accuracy of ±0.1 mV, and more precisely read by a digital voltmeter of 100 MΩ input resistance with an accuracy of ±0.01 mV. After the emf values remained stable for over 1 hour, samples were withdrawn from the liquid alloy by means of a silica sampling tube of 3.5mm i.d. The reproducibilities of cell potentials were confirmed by temperature cycling. After the experimental run, the iron crucible was taken out of the furnace at 1548 K, cooled and submitted to electron probe microanalysis in order to determine the solidus compositions.

EXPERIMENTAL RESULTS AND DISCUSSION

The liquidus compositions, X_{Fe}^{L}, determined in this study are given in Table 1, while the solidus composition, X_{Fe}^{S}, obtained at 1548 K was 0.915±0.027. Figure 3 compares the present data for the liquidus and solidus compositions with those given in a phase diagram compilation of the ASM Handbook /2/. The present results were in very good agreement with the literature data.

The measured cell potentials are also summarized in Table 1. The equilibrium oxygen partial pressures, P_{O_2}, were calculated via the following equation /3/:

$$E = \frac{RT}{F} \ln \frac{(ref.)^{1/4} + P_e^{1/4}}{P_{O_2}^{1/4} + P_e^{1/4}} + E_t, \qquad (1)$$

where T is temperature, E_t is thermo-emf between

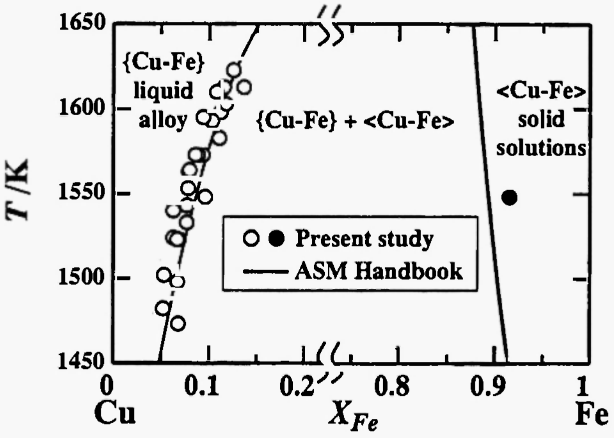

Fig. 3: Liquidus and solidus compositions of the system Cu + Fe.

Mo(positive) and Fe(negative), R is the gas constant, F is the Faraday constant, and P_e is the oxygen partial pressure at which the ionic and the n-type electronic conductivities are equal /7/. Values for this parameter for the magnesia-stabilized zirconia tubes used in this study have been reported elsewhere[4]:

$$\log(P_e/\text{atm}) = +20.40 - 6.45 \times 10^4/(T/\text{K}). \qquad (2)$$

The thermo-emf, E_t, is given as[5];

$$E_t/\text{mV} = -14.69 + 0.0227(T/\text{K}). \qquad (3)$$

The oxygen partial pressures at the reference electrode, Mo + MoO_2, $P_{O_2}(ref.)$, were calculated by using the authors' previous results /6/;

$$\log(P_{O_2}(ref.)/\text{atm}) = +8.84 - 3.01 \times 10^4/(T/\text{K}). \qquad (4)$$

The logarithm of the equilibrium oxygen potentials obtained with cells (I) through (V) are plotted against reciprocal temperature in Figure 4. By using the least-squares method, the following expressions were obtainable for cells (I), (II), (III), (IV) and (V), respectively;

$$\log\{P_{O_2}(\text{I})/\text{atm}\} = +7.40 - 2.84 \times 10^4/(T/\text{K}) \pm 0.01 \qquad (5)$$
$$\log\{P_{O_2}(\text{II})/\text{atm}\} = +4.87 - 2.50 \times 10^4/(T/\text{K}) \pm 0.03 \qquad (6)$$
$$\log\{P_{O_2}(\text{III})/\text{atm}\} = +5.11 - 2.52 \times 10^4/(T/\text{K}) \pm 0.01 \qquad (7)$$
$$\log\{P_{O_2}(\text{IV})/\text{atm}\} = +0.85 - 1.91 \times 10^4/(T/\text{K}) \pm 0.01 \qquad (8)$$
$$\log\{P_{O_2}(\text{V})/\text{atm}\} = -1.50 - 1.56 \times 10^4/(T/\text{K}) \pm 0.01 \qquad (9)$$

Table 1

Experimental results with cells (I), (II), (III), (IV) and (V)

Cell	T/K	E/mV			$log(PO_2/\text{atm})$			a_{Fe}			X_{Fe}^{L}	X_{Fe}^{S}
(I)	1473	42.25	±	0.14	-11.92	±	0.02	1.01	±	0.02	n.d.	n.d.
(I)	1538	48.91	±	0.10	-11.11	±	0.01	0.99	±	0.02	n.d.	n.d.
(I)	1495	42.31	±	0.02	-11.61	±	0.01	0.97	±	0.02	n.d.	n.d.
(I)	1571	49.97	±	0.03	-10.69	±	0.01	0.94	±	0.01	n.d.	n.d.
(I)	1512	43.80	±	0.01	-11.39	±	0.01	0.96	±	0.02	n.d.	n.d.
(I)	1553	48.14	±	0.02	-10.90	±	0.01	0.95	±	0.01	n.d.	n.d.
(I)	1613	54.59	±	0.07	-10.23	±	0.01	0.93	±	0.01	n.d.	n.d.
(I)	1593	52.97	±	0.08	-10.46	±	0.01	0.94	±	0.01	n.d.	n.d.
(I)	1523	45.43	±	0.02	-11.26	±	0.01	0.96	±	0.02	n.d.	n.d.
(I)	1582	51.66	±	0.06	-10.58	±	0.01	0.94	±	0.01	n.d.	n.d.
(I)	1482	40.92	±	0.10	-11.77	±	0.02	0.97	±	0.02	0.052	n.d.
(I)	1573	48.03	±	0.01	-10.64	±	0.01	0.91	±	0.01	0.086	n.d.
(I)	1524	46.67	±	0.04	-11.27	±	0.01	0.98	±	0.02	0.063	n.d.
(I)	1610	54.65	±	0.04	-10.27	±	0.01	0.94	±	0.01	0.108	n.d.
(I)	1540	46.95	±	0.02	-11.06	±	0.01	0.95	±	0.01	0.063	n.d.
(I)	1595	51.11	±	0.03	-10.41	±	0.01	0.91	±	0.01	0.094	n.d.
(I)	1502	44.38	±	0.03	-11.54	±	0.01	0.99	±	0.02	0.053	n.d.
(I)	1564	51.02	±	0.01	-10.80	±	0.01	0.97	±	0.01	0.080	n.d.
(II)	1613	85.86	±	0.01	-10.62	±	0.01	0.94	±	0.02	0.116	n.d.
(II)	1573	80.81	±	0.03	-11.06	±	0.01	1.02	±	0.02	n.d.	n.d.
(II)	1533	69.03	±	0.03	-11.44	±	0.01	1.01	±	0.02	0.077	n.d.
(II)	1593	83.62	±	0.26	-10.84	±	0.02	0.98	±	0.03	n.d.	n.d.
(II)	1553	67.75	±	0.04	-11.16	±	0.01	0.91	±	0.02	n.d.	n.d.
(II)	1623	84.74	±	0.40	-10.49	±	0.02	0.89	±	0.03	0.126	n.d.
(II)	1543	67.82	±	0.04	-11.29	±	0.01	0.95	±	0.02	n.d.	n.d.
(II)	1563	78.71	±	0.11	-11.17	±	0.01	1.03	±	0.02	0.079	n.d.
(III)	1543	64.58	±	0.12	-11.25	±	0.01	0.96	±	0.02	0.077	n.d.
(III)	1563	66.88	±	0.27	-11.01	±	0.02	0.91	±	0.02	n.d.	n.d.
(III)	1583	71.42	±	0.05	-10.82	±	0.01	0.90	±	0.02	0.111	n.d.
(III)	1533	62.86	±	0.09	-11.36	±	0.01	0.98	±	0.02	n.d.	n.d.
(III)	1593	75.90	±	0.06	-10.75	±	0.01	0.92	±	0.02	0.103	n.d.
(III)	1613	78.88	±	0.07	-10.54	±	0.01	0.89	±	0.02	0.137	n.d.
(III)	1553	65.43	±	0.06	-11.13	±	0.01	0.93	±	0.02	n.d.	n.d.
(III)	1603	75.94	±	0.12	-10.62	±	0.01	0.89	±	0.02	0.118	n.d.
(IV)	1573	97.91	±	0.11	-11.28	±	0.01	0.93	±	0.03	n.d.	n.d.
(IV)	1613	116.04	±	0.55	-11.00	±	0.02	0.91	±	0.05	n.d.	n.d.
(IV)	1533	82.28	±	0.21	-11.61	±	0.02	1.00	±	0.03	n.d.	n.d.
(IV)	1553	91.16	±	0.10	-11.46	±	0.01	0.98	±	0.03	n.d.	n.d.
(IV)	1513	74.31	±	0.09	-11.78	±	0.02	1.03	±	0.03	n.d.	n.d.
(IV)	1593	104.94	±	0.13	-11.12	±	0.01	0.89	±	0.03	n.d.	n.d.

Table 1 (continued)
Experimental results with cells (I), (II), (III), (IV) and (V)

Cell	T/K	E/mV	$log(PO_2/atm)$	a_{Fe}	X_{Fe}^L	X_{Fe}^S
(IV)	1563	94.22 ± 0.07	-11.37 ± 0.01	0.95 ± 0.03	n.d.	n.d.
(IV)	1503	67.82 ± 0.03	-11.84 ± 0.01	1.01 ± 0.02	n.d.	n.d.
(IV)	1603	110.34 ± 0.03	-11.06 ± 0.01	0.90 ± 0.03	n.d.	n.d.
(V)	1573	110.28 ± 0.12	-11.44 ± 0.01	0.95 ± 0.04	n.d.	n.d.
(V)	1513	77.20 ± 0.01	-11.82 ± 0.01	1.01 ± 0.03	n.d.	n.d.
(V)	1613	131.64 ± 0.05	-11.20 ± 0.01	0.91 ± 0.04	n.d.	n.d.
(V)	1533	89.59 ± 0.05	-11.71 ± 0.01	1.01 ± 0.03	n.d.	n.d.
(V)	1593	119.96 ± 0.07	-11.31 ± 0.01	0.92 ± 0.04	n.d.	n.d.
(V)	1553	100.24 ± 0.03	-11.58 ± 0.01	0.99 ± 0.03	n.d.	n.d.
(V)	1523	82.80 ± 0.09	-11.76 ± 0.02	1.00 ± 0.03	n.d.	n.d.
(V)	1603	126.93 ± 0.02	-11.27 ± 0.01	0.93 ± 0.04	n.d.	n.d.
(V)	1563	103.71 ± 0.01	-11.49 ± 0.01	0.95 ± 0.03	n.d.	n.d.
(V)	1503	73.44 ± 0.04	-11.91 ± 0.01	1.05 ± 0.03	n.d.	n.d.
(V)	1583	112.37 ± 0.05	-11.34 ± 0.01	0.90 ± 0.04	n.d.	n.d.
*	1598	n.d.	n.d.	n.d.	0.112	n.d.
*	1573	n.d.	n.d.	n.d.	0.094	n.d.
*	1548	n.d.	n.d.	n.d.	0.096	n.d.
*	1498	n.d.	n.d.	n.d.	0.067	n.d.
*	1523	n.d.	n.d.	n.d.	0.069	n.d.
*	1473	n.d.	n.d.	n.d.	0.068	n.d.
*	1553	n.d.	n.d.	n.d.	0.078	n.d.
*	1573	n.d.	n.d.	n.d.	0.089	n.d.
*	1548	n.d.	n.d.	n.d.	0.067	0.915

* Emf measurements were not conducted for these runs.

The correlation factor, r^2, for equations (5) through (9) were better than 0.99. The equilibrium oxygen partial pressures for mixtures (i)° through (V)°, respectively, have been reported as given by equations (10) /7/) through (14) /8,9/.

(i) "pure" FeO + pure <Fe>
(ii) $C + C3S + L$ + pure <Fe>
(iii) $C3S + C2S + L$ + pure <Fe>
(iv) $C2S + C3S2 + L$ + pure <Fe>
(v) $C3S2 + CS + L$ + pure <Fe>

$$\log \{P_{O_2}(\mathrm{i})^\circ/\mathrm{atm}\} = 6.71 - 2.74 \times 10^4/(T/\mathrm{K}) \quad (10)$$

$$\log \{P_{O_2}(\mathrm{ii})^\circ/\mathrm{atm}\} = +3.64 - 2.31 \times 10^4/(T/\mathrm{K}) \quad (11)$$

$$\log \{P_{O_2}(\mathrm{iii})^\circ/\mathrm{atm}\} = +3.56 - 2.29 \times 10^4/(T/\mathrm{K}) \quad (12)$$

$$\log \{P_{O_2}(\mathrm{iv})^\circ/\mathrm{atm}\} = -0.92 - 1.64 \times 10^4/(T/\mathrm{K}) \quad (13)$$

$$\log \{P_{O_2}(\mathrm{v})^\circ/\mathrm{atm}\} = -3.22 - 1.30 \times 10^4/(T/\mathrm{K}) \quad (14)$$

The activities of Fe in {Cu-Fe} liquid alloys in equilibrium with <Cu-Fe> solid solutions can now be calculated by combining equations (5), (6), (7), (8) and (9), respectively, with (10), (11), (12), (13), and (14), respectively. The a_{Fe} values thus obtained are shown in Figure 5, while the least squares method yielded the following;

$$\log a_{Fe} = -(0.58 \pm 0.07) + (0.083 \pm 0.011) \times 10^4/(T/\mathrm{K}) \quad (15)$$

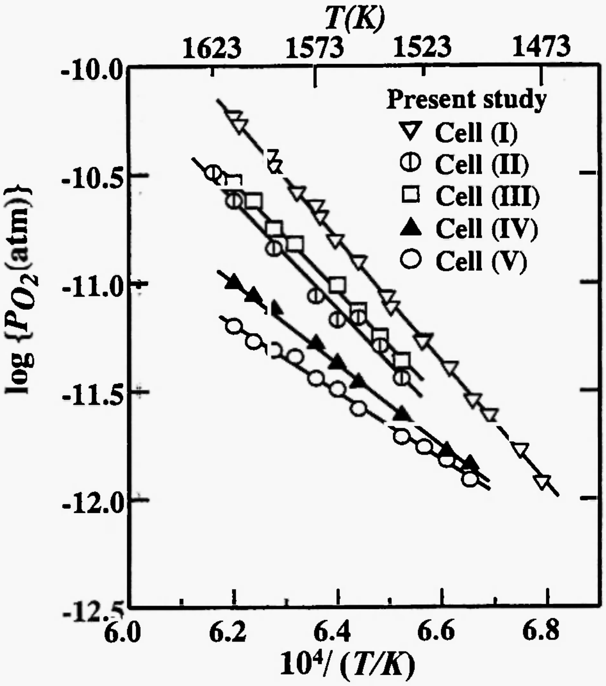

Fig. 4: Equilibrium oxygen partial pressures determined in this study.

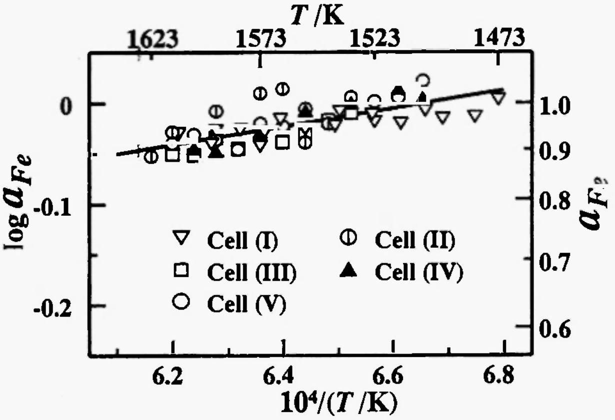

Fig. 5: Logarithmic plot for iron activity in {Cu-Fe} liquid alloy in equilibrium with <Fe-Cu> solid solution as a function of reciprocal temperature.

Equation (15) is based upon all the experimental data obtained with cells (I) through (V).

In Figure 6, the iron activity data are compared with the literature data /11-14/; the present values for a_{Fe} at 1473 K and 1573 K would be consistent with those reported by Kulkarni /12/ (1473 K) and Park and Gaskell /13/ (1573 K).

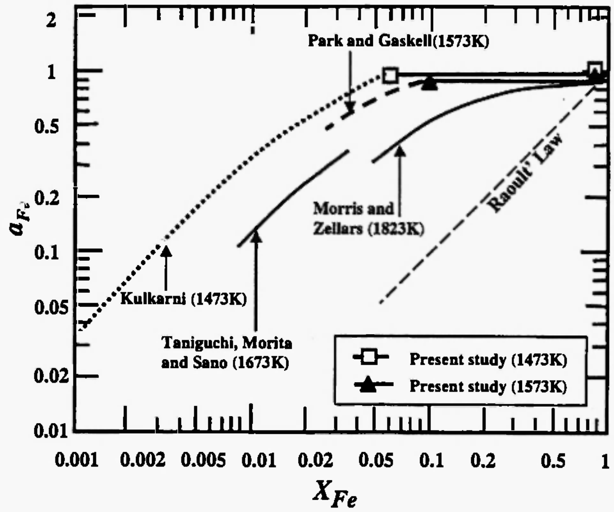

Fig. 6: Activity of iron in {Cu-Fe} liquid alloys saturated with <Cu-Fe> solid solutions, in comparison with the literature data.

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