NEWLY DEVELOPED EMF CELL WITH ZIRCONIA SOLID ELECTROLYTE FOR MEASUREMENT OF LOW OXYGEN POTENTIALS IN LIQUID Cu-Cr AND Cu-Zr ALLOYS

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Abstract

In order to measure the very low oxygen potential by use of stabilized zirconia solid electrolyte emf method, a new cell construction was devised. The idea was based on Janke but a zirconia rod was used instead of the zirconia crucible which contacts liquid alloy electrode.
The cell was used for determination of the oxygen potentials in liquid dilute Cu-Cr and Cu-Zr alloys. The reference electrode was Cr,Cr_2O_3 . Emf measurements were performed in the temperature range of 1400-1580 K and composition range of 0.198-3.10at%Cr-Cu alloys, and 1380-1465K, 0.085-0.761at%Zr-Cu alloys. The composition of liquid alloys were determined by picking up from the liquid alloys and ICP analysis. By use of the newly devised cell construction in this study, stable emf values were obtained at each temperature and alloy composition. Emf values were corrected by using the parameter for electronic contribution of the YSZ.
Activity of Cr obeys Henry's law and activity coefficient at infinitely dilute alloys of Cr in Cu-Cr alloys are:
$ln\gamma^o_{Cr}$ =(3.80 at 1423K), (3.57 at 1473K), (3.38 at 1523K) and (3.20 at 1573K).
At 1423 K activity coefficient of Zr at infinitely diluted alloy is $ln\gamma^o_{Zr}$ = −4.0.

Keywords: Oxygen sensor development; Zirconia solid electrolyte; Cu-Cr liquid alloys; Cu-Zr liquid alloys; Thermodynamic activity

1. Introduction

Thermodynamic properties of alloys have been measured by choosing suitable methods for the corresponding alloy systems, and database have been constructed combining the experimental data and model calculations. Since the original work by Rapp and Maak [1], emf method with stabilized zirconia solid electrolyte have been used for determination of the activity of component elements in alloys under the condition of ionic transference number (t_{ion}) of the electrolyte is unity. Outside of the regions of temperature and oxygen potential where t_{ion} becomes smaller than unity, emf values obtained from the cell must be corrected by use of the parameters of $P_\ominus$ and/or $P_\oplus$ of the solid electrolyte [2]. The method of correction is useful at higher temperatures and lower oxygen potential of alloy systems, but it is necessary that the regions in the electrodes are not far from

electrolytic domain of the electrolytes. For alloys including very active elements, for example Mg, Al, rare earth metals etc. emf method with CaF_2 is suitable [3], but at higher temperatures the utility of the method is limited because of the high reactivity of CaF_2 with alloy or reference electrode.

Experimentally Janke et al. [4] devised a new cell construction to measure the oxygen potential in liquid silicon. Copper based alloys containing active elements (Zr, Cr, Mg and so on) become attractive because of their remarkable properties. In the producing process of precipitated alloys and/or amorphous alloys some problems i.e. atmosphere control, and solidification control must be solved. Oxygen potential of these copper based alloys becomes lower than the electrolytic domain (t_{ion}<1) in the solid electrolyte, and some kind of device is necessary to get reliable emf values.

In this study cell construction is newly developed

Dedicated to the memory of Professor Zbigniew Moser

for measuring the lower oxygen potential and activity measurement of dilute Cu-Cr and Cu-Zr alloys. Original idea by Janke et al. [4] is used in this study but important difference from theirs is that a zirconia rod is used instead of their zirconia crucible. A mixture of (YSZ powder +5 wt% alumina) was used also to good performance of emf measurement under the reference electrode and a zirconia rod was stuck into the mixture.

2. Experimental

2.1 Principles

Yttria-stabilized zirconia (YSZ) can be used under the condition of solid electrolyte region i.e. ionic transference number t_{ion} is nearly unity. The ionic conductivity decreases outside of this region and the effect of electronic and/or hole conductivity becomes bigger.

In the oxygen concentration cell:

Po_2(I) | YSZ | Po_2(II)   (cell I)

we can get emf (electromotive force) at high temperatures by the eq.1

$$E = (1/F) \int_{Po_{2(I)}}^{Po_{2(II)}} t_{ion} d ln\mu_{O_2} = (RT/4F) ln\{Po_2(II)/Po_2(I)\} \quad (1)$$

where E is cell voltage, F is the Faraday constant, R is gas constant, T is temperature, Po_2 is the oxygen pressure and μ_{O_2} is the chemical potential. This equation can be used in the region $t_{ion} = 1$.

In the low oxygen potential, electronic contribution must be considered for the values of E by eq.2

$$E = (RT/F) ln\left\{ \left[P_e^{1/4} + Po_2(II)^{1/4} \right] / \left[P_e^{1/4} + Po_2(I)^{1/4} \right] \right\} \quad (2)$$

where P_e is the parameters where ionic conductivity and electronic conductivity become the same values. In this study as the parameter for $ZrO_2(+0.25Y_2O_3)$ [5] was used.

$$logP_e / bar = 14.18 - 58319 / T / K \quad (3)$$

At the oxygen pressure lower than the solid electrolyte region, (eq.2) for the correction becomes important.

From measured value of E, we can derive the value of Po_2(I) or Po_2(II) by use of the reference electrode where Po_2(I) or Po_2(II) is well known.

2.2 Cell construction and experimental procedure

Some types of the oxygen sensors were constructed to find out for good performance of emf measurements at low oxygen potential: i.e. conventional type (1), improved type (2) by Janke [4], and newly developed type in this work (3 and 4), which are shown in Fig.1 schematically. From the preliminary experiments in this study, a conventional type of sensor did not give stable emf values nor clear relationship between temperature and cell emf for Cu-0.375at% Cr alloys. The cell type (2) could be used only for short time measurements. Type (4) is presented in detail. Type(3) was similar to type(4), but alumina powder was not added to YSZ powder.

The main part of the experimental apparatus is shown in Fig.2. Into an alumina tube a stabilized zirconia rod ($5 \times 1^\square \times 40^{length}$, Nikkato Co.Ltd.) is stuck
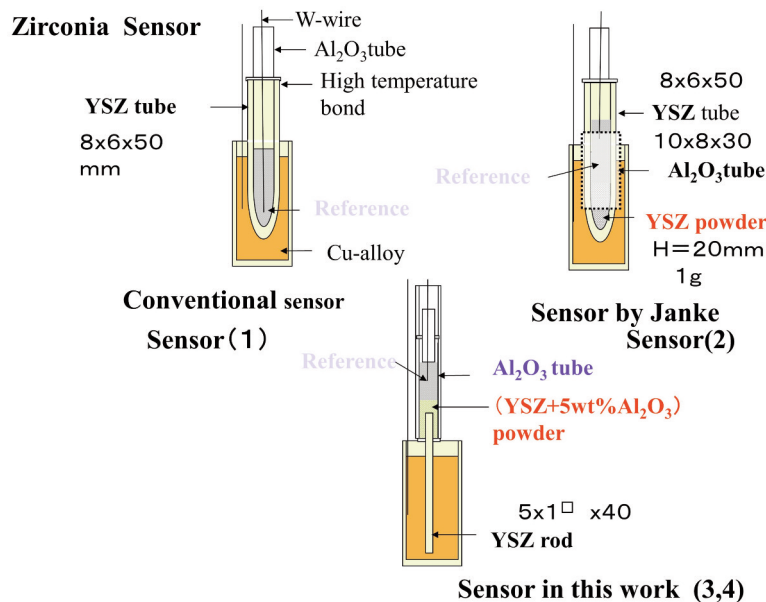

Figure 1. Schematic diagram of cell construction.

and above which fine powder of stabilized zirconia (grain size<100 µm, Nikkato Co.Ltd.) mixed with 5 wt% alumina powder(totally more than about 0.2 g) is tapped. The very small space between the alumina tube and zirconia rod is filled with zirconia cement. A tungsten lead wire (0.5 mmϕ) contacts the mixture of the zirconia and alumina powders. A lead wire for liquid alloy is a $LaCrO_3$ rod connected with tungsten wire. Cr powder (0.3 g, 99.9% purity, Yamanaka Chem.Co.Ltd.) and Cr_2O_3 powder (0.1g, reagent grade, Wako Chem.Co.Ltd) are mixed as the reference electrode, and the mixture of them is put on the mixture of YSZ +Al_2O_3 powders. The cell is shown:

$Cr,Cr_2O_3 \mid \{(ZrO_2)_{0.92}\,(Y_2O_3)_{0.08} + 5\ wt\%\ Al_2O_3\}$ powder $\mid\{(ZrO_2)_{0.92}(Y_2O_3)_{0.08}\}$ rod $\mid$ Cu- alloy cell (4).

The cell apparatus and experimental method are quite similar to those used for Ni-O and Cu-O systems [6] except cell structure.

The cell was settled up in an even temperature region of the reaction tube (alumina), and in an alumina crucible weighed amount of oxygen free copper (oxygen free Cu(O <5 ppm, about 80 g, Mitsubishi Materials Co.Ltd.)) was put. The zirconia sensor was settled above the crucible. The reaction tube was evacuated and back-filled with purified argon gas. The operation was repeated several times and cell was heated to melt the copper under argon gas atmosphere. At high temperatures known amount of Cr or Zr chips were added to the liquid copper and the melt was stirred. During the stirring the sensor was immerged into the melt and emf measurement started. The temperature of the cell was measured by a calibrated Pt-13RhPt thermocouple. Emf values were measured with a digital volt-meter with high impedance. At a constant temperature emf

measurement was performed to get stable emf and after that the small amount of copper alloy was sampled and rapidly cooled into the ice water for ICP analysis to determine the alloy composition, and then the cell temperature was settled to the next one.

3. Experimental results

In order to confirm the cell performance, the following cell was used.

Mn, MnO $\mid$ YSZ rod $\mid$ YSZ+5 wt% Al_2O_3 $\mid$ Cr,Cr_2O_3

Corrected oxygen partial pressure was obtained by using the eq.2 and parameter shown by eq.3. They are shown in Fig.3. Even at higher temperature (1573K), stable value of logPo_2/atm = -17.9 was kept for more than 300 min which is in good agreement with the value –17.8 derived from the databook by Barin [7].

3.1 EMF measurement for Cu-Cr alloys

In Table 1 experimental results by cell (4) are shown for dilute Cu-Cr liquid alloys with Cr,Cr_2O_3 reference electrode.

The solubility of Cr in Cu is small and it takes a longer time to get homogeneous Cu-Cr alloy. It was found that Cr content in Cu-Cr alloys was lower than that of nominal concentration. So in this work the Cr content was determined by ICP analysis. Temperature of the furnace was heated to 1573K and after that Cr chip was added to the liquid Cu. During the emf measurement the liquid was always stirred, because without the handling emf became bigger with the time. When emf–value held within ±0.5 mV drift for 3 min we decided it the equilibrium value. After the stable value was obtained, the temperature was
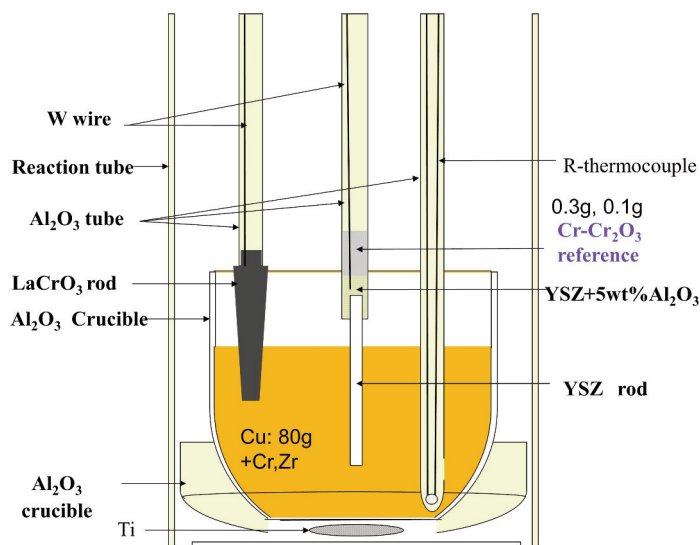

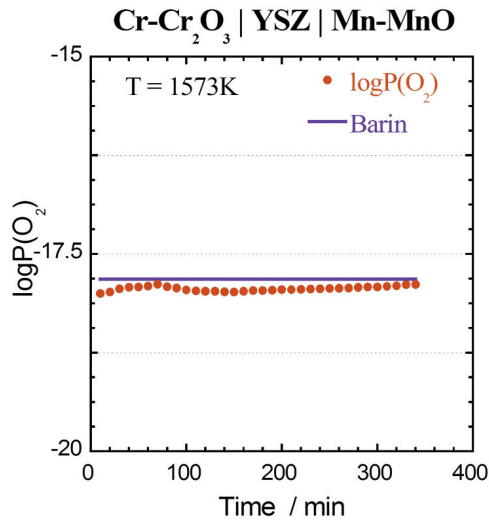*Figure 2. Main part of experimental apparatus.*

Figure 3. *Preliminary study by the cell:*
Cr,Cr$_2$O$_3$|YSZ powder|YSZ-rod|Mn,MnO

changed to the next one. After the temperature dependence of emf was obtained, the sampling of the liquid alloy was performed for ICP analysis, i.e.pulling up the sample by a syringe and silica tube and quickly quenched in to ice+water. For all compositions linear relations between *E* and *T* hold as shown in Fig.4. By use of the parameter P_e in (eq.2) and eq.(3), corrected values of Cr activity can be calculated.

The results are shown in Table 2. Activity was calculated from 1423 to 1573 K for 50 degree intervals. At each temperature Henry's law holds in low concentration region of Cr. Corrected activities are a little smaller than the experimental ones. They are shown in Fig. 5 with the data by some investigators. Ono et al. [9] used Knudsen cell-mass spectrometry method (1573K), and Inoue et al. [10] used galvanic cell technique

$$Mo / Mo + MoO_2 / ZrO_2 (MgO) / (Cu\text{-}Cr)_{alloy} + \\ + Cr_2O_3 + \{Cr_2O_3 + CaCl_2\}_{slag} / Mo$$
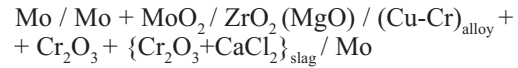
The results in this study are in agreement with
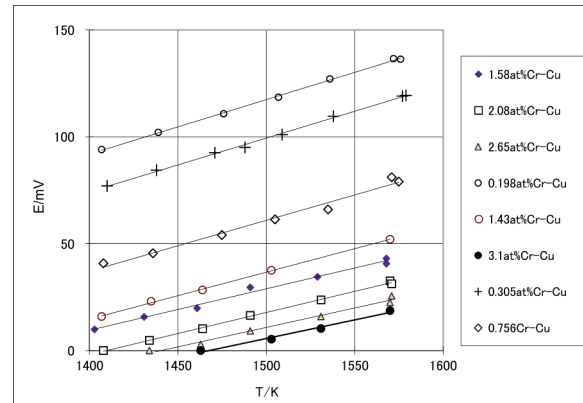
Figure 4. *Temerature dependence of emf of cell:*
Cr,Cr$_2$O$_3$|YSZ+Al$_2$O$_3$|YSZ-rod|Cu-Cr liq. alloy

Table 1. *Emf data by cell (4) for Cu-Cr alloys (reference Cr,Cr$_2$O$_3$)*

0.198at%Cr		0.305at%Cr		0.756at%Cr		1.58at%Cr	
T/K	*E*/mV	*T*/K	*E*/mV	*T*/K	*E*/mV	*T*/K	*E*/mV
1576	136.2	1579	119.3	1575	79.0	1568	43.0
1507	118.5	1509	101.0	1505	61.3	1491	29.5
1536	127.0	1538	109.5	1436	45.5	1529	34.4
1439	102.0	1438	84.3	1475	54.0	1431	15.7
1476	110.7	1471	92.5	1408	40.8	1461	19.8
1407	94.0	1410	77.0	1535	66.0	1403	9.9
1572	136.5	1488	95.0	1571	81.0	1568	40.6
		1577	119.0				
E=-264.8+0.2548*T*		*E*=-277.2+0.2511*T*		*E*=-296.0+0.2379*T*		*E*=-262.1+0.1940*T*	
1.43at%Cr		2.08at%Cr		2.65at%Cr		3.1at%Cr	
T/K	*E*/mV	*T*/K	*E*/mV	*T*/K	*E*/mV	*T*/K	*E*/mV
1570	52.0	1570	32.6	1571	25.5	1570	18.7
1503	37.5	1491	16.4	1491	9.2	1503	5.3
1435	23.0	1531	23.7	1531	15.9	1531	10.3
1464	28.3	1434	4.75	1463	2.9	1463	0
1407	15.9	1464	10.25	1570	22.5		
		1571	31.2	1434	0		
		1408	0				
E=-293.2+0.2199*T*		*E*=-281.3+0.1994*T*		*E*=-279.7+0.1934*T*		*E*=-297.0+0.201*T*	

Table 2. *Emf and activity of Cr in Cu-Cr alloys*

T/K	Experimental		Corrected values	
	E/mV	a_{Cr}	Ecorr/mV	a_{Cr}
0.198Cr	E=−264.8+0.2548*T			
1423	97.8	0.091	98.6	0.090
1473	110.5	0.073	111.4	0.072
1523	123.3	0.060	124.6	0.058
1573	136	0.049	131.7	0.054
0.305Cr	E=−277.2+0.2511*T			
1423	80.1	0.141	81.3	0.137
1473	92.7	0.112	93.4	0.110
1523	105.2	0.090	106.4	0.088
1573	117.8	0.074	118.1	0.073
0.756Cr	E=−296.0+0.2379*T			
1423	42.5	0.354	42.7	0.352
1473	54.4	0.276	54.8	0.274
1523	66.3	0.220	67.2	0.215
1573	78.2	0.177	77.0	0.181
1.43Cr	E=−293.2+0.2199*T			
1423	19.7	0.618	20.0	0.613
1473	30.7	0.484	31.0	0.481
1523	41.7	0.386	42.4	0.379
1573	52.7	0.311	53.7	0.305
1.58Cr	E=−262.1+0.1940*T			
1423	14	0.710	13.9	0.712
1473	23.7	0.571	23.8	0.570
1523	33.4	0.466	34.1	0.459
1573	43.1	0.385	43.2	0.385
2.08Cr	E=−281.3+0.1994*T			
1423	2.45	0.942	2.5	0.940
1473	12.4	0.746	12.4	0.746
1523	22.4	0.599	22.7	0.595
1573	32.4	0.488	32.7	0.485
2.65Cr	E=−279.7+0.1934*T			
1423	0	1.000	0	1.000
1473	5.18	0.885	5.2	0.885
1523	14.85	0.712	15.1	0.708
1573	24.52	0.581	25.1	0.574
3.1Cr	E=−297.0+0.2010*T			
1423	0	1.000	0	1.000
1473	0	1.000	0	1.000
1523	9.12	0.812	9.4	0.807
1573	19.2	0.654	19.6	0.648

Figure 5. *Activity of Cr in Cu-Cr alloys*

those reported by the two groups within experimental uncertainty limits. Timberg and Toguri [11] studied Cu-Cr alloys by a high temperature mass spectrometric technique but their temperature range and also concentration range are too high for the comparison.
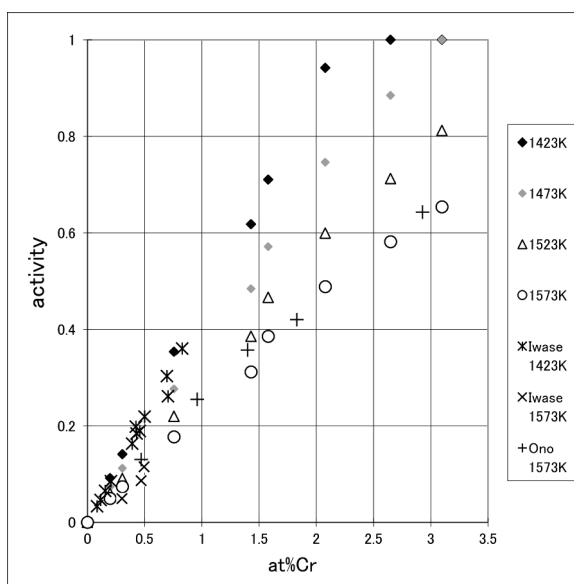
Activity coefficients of Cr at infinitely diluted region are:

ln γ^0 = 3.80 (T = 1423K), 3.57(T = 1473K),

3.38 (T =1523K9 and 3.20 (T = 1573K).

3.2 EMF measurement for Cu-Zr alloys

In Fig.6, time dependence of Po_2 in Cu-Zr alloy

derived from our cell with Cr,Cr_2O_3 reference electrode. By addition of Zr, Po_2 shaply dropped and showed stable value, in agreement with Sommer's result by vapor pressure measurment at 1423K. A conventional cell and an improved cell by Janke showed sharp drop immediately after Zr addition, but with time Po_2 increased gradually because of the effect of atmosphere.

Experimental data are shown in Fig.7 and Table 3. For all compositions linear relations between E and T hold with some scattered values. In order to calculate the corrected activity and oxygen pressure at 1423K, we used the following values:

P_e/atm =1.54×10⁻⁶, Po_2/atm(in Cr_2O_3) = 1.42×10⁻¹⁹ and Po_2/atm(in ZrO_2) = 3.16×10⁻³¹ [5, 7]

The calculated results are shown in Table 4. We can derive the activity and activity coefficient of Zr in dilute Cu-Zr alloys. Activity coefficient at infinitely diluted alloy is $\ln\gamma^o_{Zr}$ = -4.0 in agreement with Sommer's results (-4.1). Zeitsev et al. [12] studied by Knudsen-cell mass spectrometry over 701-1823K, but concentration of Zr was too high for the comparison. And Na Wang et al. [13] made re-assesment for this alloy system using the data of Zeitsev et al.

4. Discussion

When a zirconia sensor is used to measure the very low oxygen potentials, we must consider the electronic contribution to the measured values of emf. In the conventional cell structure the reference electrode should be chosen in order to become smaller value of emf.
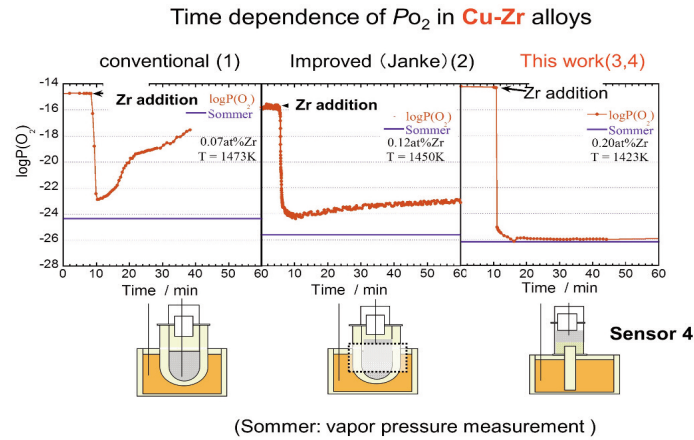
Time dependence of Po_2 in **Cu-Zr** alloys

(Sommer: vapor pressure measurement)

Figure 6. *Time dependence of Po_2 in Cu-Zr alloys*

Table 3. *Emf data for Cu-Zr alloy by cell (4) (reference Cr,Cr$_2$O$_3$)*

0.085at%Zr		0.093at%Zr		0.176at%Zr		0.232at%Zr	
T/K	E/mV	T/K	E/mV	T/K	E/mV	T/K	E/mV
		1418	417	1399	456	1418	455
1448	401.2	1448	402.2	1414	448	1388	473
1388	419.5	1388	431	1444	433	1448	441
1408	411	1408	424	1408	449	1428	450.2
1438	400	1438	409.2	1425	439	1398	461.5
1398	412	1398	427.8			1438	439
1428	403	1428	414.5				
		1418	418.2				
E=847.9-0.3104*T*		*E*=1092.0-0.4754*T*		*E*=1170.5-0.5116*T*		*E*=1215.6-0.5370*T*	
0.375at%Zr		0.484at%Zr		0.570at%Zr		0.761at%Zr	
T/K	E/mV	T/K	E/mV	T/K	E/mV	T/K	E/mV
1432	458	1411	469	1428	466	1453	462
1411	465	1429	463	1408	474	1463	459
1438	452	1450	455	1436.5	463	1433	472
1456	440.5			1456	456	1403	483
1448	446			1447	459	1421	475
1419	460			1418	469.5	1413	478
1400	466.5			1400	476	1443	465
1428	455.5			1426	465		
E=1124.1-0.4679*T*		*E*=976.5-0.3596*T*		*E*=985.8-0.3641*T*		*E*=1049.4-0.4040*T*	

Table 4. *Calculation of Zr in Cu-Zr alloys at 1423K (corrected values)*

at%Zr	E_1(mV)	E_0(mV)	E_2(mV)	a_{Zr}	Po_2(corrc)	a_{Zr}(correc)
0.085	406	822	416	$1.27*10^{-6}$	$7.05*10^{-26}$	$4.48*10^{-6}$
0.093	416	822	407	$1.72*10^{-6}$	$4.60*10^{-26}$	$6.86*10^{-6}$
0.173	443	822	380	$4.15*10^{-6}$	$1.22*10^{-26}$	$2.58*10^{-5}$
0.232	451	822	371	$5.56*10^{-6}$	$7.59*10^{-27}$	$4.16*10^{-5}$
0.375	458	822	364	$6.95*10^{-6}$	$5.19*10^{-27}$	$6.08*10^{-5}$
0.484	465	822	357	$8.60*10^{-6}$	$3.56*10^{-27}$	$8.87*10^{-5}$
0.570	468	822	355	$9.45*10^{-6}$	$3.00*10^{-27}$	$1.05*10^{-4}$
0.761	475	822	348	$1.18*10^{-6}$	$1.97*10^{-27}$	$1.61*10^{-4}$
P$_e$/atm=$1.54*10^{-27}$		E_1:Emf in this work		E_0: Emf between Zr,ZrO$_2$ and Cr,Cr$_2$O$_3$			
E_2: Emf between Zr,ZrO$_2$and Cu-Zr,ZrO$_2$				Po_2(in Cr$_2$O$_3$)/atm=$1.422*10^{-19}$			
Po_2(in ZrO$_2$)/atm=$3.156*10^{-31}$							
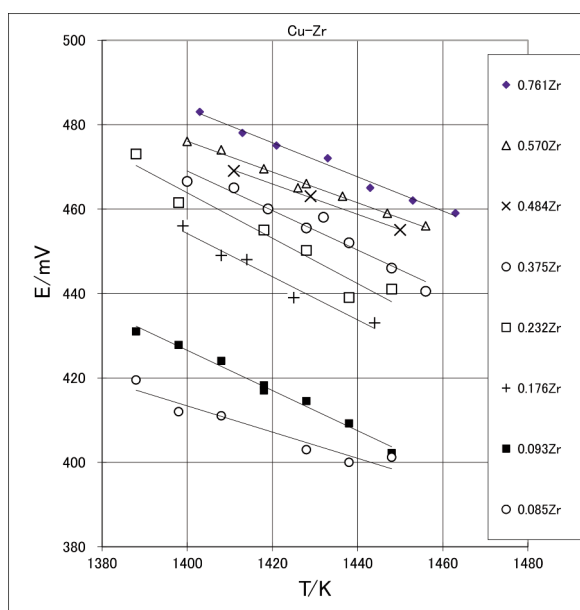
Figure 7. *Temperature dependence of emf of cell:*
$Cr,Cr_2O_3|YSZ+Al_2O_3|YSZ$-rod$|Cu$-$Zr$ liq. alloy

Janke devised a cell structure i.e. between the zirconia crucible and reference electrode fine powder of the solid electrolyte was placed. This powder addition made the small electronic contribution to the emf value negligibly small. It is known that small amount of alumina powder to the zirconia solid electrolyte makes ionic conductivity larger. In our preliminary experiment up to 10 wt% alumina addition was usefel. In this study 5 wt% alumina powder was added to the zirconia powder. By the conventional cell the electronic conductivity could not be neglected especially after the Cr or Zr was added to the liquid Cu.

In our cell, the length of the sensor became a little longer and it deviated from the even temperature region, but the response time was very short and the utility of the cell was not bad.

5. Conclusion

By a newly developed zirconia oxygen sensor very stable values of oxygen potential out side of the electrolytic domain of the solid electrolyte can be derived.

Activity coefficientsof Cr at infinitely diluted region in Cu-Cr alloys are:

ln γ^0 = 3.80 (*T*/K = 1423), 3.57 (*T*/K = 1473), 3.38 (*T*/K = 1523) and 3.20 (*T*/K = 1573).

Activity of zirconium in dilute Cu-Zr liquid alloys were measured in the temperature range of 1390-1460 K. At 1423 K activity coefficient of Zr at infinitely diluted alloy is $\ln\gamma^o_{Zr}$ = -4.0 .

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