Journal of Mining and Metallurgy, 39 (3‡4) B (2003 453-464)

THERMODYNAMIC STUDY OF SEMICONDUCTING RELATED MATERIALS BY USE OF EMF METHOD WITH SOLID ELECTROLYTE

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(Received 3. October 2002; accepted 5 May 2003)

Abstract

Electromotive force method with solid electrolyte is briefly explained, and a thermodynamic study of semiconducting compound solid solution ZnTe-CdTe is picked up to show the way how thermodynamic functions of this system are obtained by several experimental methods based on our published papers and recently published data are added for comparison.

Keywords: Thermodynamics, semiconductors, solid electrolyte

1. Introduction

Solids materials whose ionic conductivities approach those of molten salts and electrolyte solutions, and whose electronic and hole contribution to the electric conductivities are negligibly small can be used as solid electrolytes for thermodynamic study of inorganic materials at high

temperature. They are used for emf measurement and for titration method: The former is to measure the chemical potential difference in both electrodes between which solid electrolyte is insertedm as electromotive force produced from the concentration cell. The latter is to control the chemical potential in one side of the electrodes by applying the voltage to the cell .In both cases reference electrode whose chemical potential is well established and known becomes important.

The chemical potential of the electrodes corresponds to the kind of the ion which moves predominantly in the solid electrolytes; In the thermodynamic study of inorganic materials at high temperature, stabilized zirconia(O^{2-}), oxide doped thoria(O^{2-}), β -alumina(Na⁺) and CaF₂(F⁻)have been used often, and recently perovskite type oxides are used as the proton conductor to measure the hydrogen or H₂O in liquid alloys.

The principle of the experimental method or properties of the solid electrolytes were already shown in the classic text books[1] in detail.

In this paper emf method with stabilized zirconia is treated and materials studied are semiconducting alloys and compounds.

Since the original work by Kiukkola and Wagner[2] in 1957 to show that the thermodynamic properties of the inorganic materials could be obtained by emf method with solid electrolyte, so many data have been accumulated. Rapp and MaakŠiĆshowed originally that the activity of the component of alloys could be derived from the oxygen potential measurements. After that so many alloy systems have been studied under the conditions that:

- 1) ionic transference number of oxygen ion in the solid electrolyte is nearly unity, that limits the utility of the solid electrolyte and electrode under suitable oxygen potential and temperature range,
- 2) phase relationship in the alloy system containing oxygen(or oxide) is clear,
- the difference in the Gibbs energy of formation of the related oxide (which is added to keep or produce the oxygen potential at the electrode to be studied at constant values) is large enough not to cause the displacement reaction,
- 4) the oxygen solubility in the alloys is negligibly small. In a similar way, CaF₂ solid electrolyte which is the F-ion conductor has been used for the thermodynamic study of active metal-containing materials.

In this paper, the examples of the study on Zn-Te-Cd ternary system is

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picked up and:

- 1) activity measurements of related binary system,
- 2) determination of the phase relation between the ZnTe-CdTe compound solid solutions and liquid metal or alloys,
- 3) activity measurement of the ZnTe-CdTe compounds are explained mainly based on our experimental study[4], and they are compared to the calculated values obtained from the model calculation based on the data of the related 3 binary alloys(Kaufman's treatment).

2. Experimental

The ternary aloys used in this study were prepared from high purity materials (ZnTe and CdTe: 99.9999 mass% purity, polycrystal, Furukawa Co.Ltd). They were ground to fine powder, weighed to give mixtures with desired compositions, mixed, pressed into a pellet and heat-treated in a sealed evacuated quartz ampoule at 913k over 1.7 10⁶ s. After the heat-treatment the formation of the solid solution was confirmed with an X-ray diffractometer, and lattice parameter was measured. In order to make a constant oxygen potential of the alloy electrode, ZnO powder was mixed with the solid solution. And a very small amount of Te was added to the mixture to hold the alloy electrode is composed from 3 phases including ZnO. On the other hand for the Te-poor side electrode, Zn or Cd was added to the mixture, pressed into a pellet and heat-treated at 843K for 1.2 10⁶ s in a sealed evacuated quartz ampoule before emf measurement. The composition of the solid solution was determined from its lattice parameter.

The electrolyte tube , closed at one end, $(0.92\text{ZrO}_2+0.08\text{Y}_2\text{O}_3, \text{ OD 8mm}, \text{ID 5mm}, \text{ and length 300mm})$ was obtained from Nikkato Co.Ltd.

In this study, air,Pt was used as a reference electrode. Re wires $(0.254\text{mm}\phi, 5\text{mm})$ were spot-welded to kanthal wires for the alloy electrode as electric lead materilas to avoid the reaction between the Ga-containing electrode and lead wire. The electrode was charged in the bottom of the zirconia tube with the lead wire. At the start of each experimental run the inside of the zirconia tube was evacuated and flushed with purified argon gas repeatedly, and the

cell was heated in a kanthal-resistant furnace. The emf of the cell was measured with a digital voltmeter with a printer.

To determine the tie lines between the solid solutions of ZnTe-CdTe and liquid alloys in the Te-rich and Te-poor regions, the binary compound or solid solution was sealed in a small evacuated quartz ampoule with a appropriate amount of pure metal. The ampoule was held at 873K for more than 1.6 10^6 s for equilibration, and quenched into ice-water. The specimen showed two phases(compound solid solution + alloy).The composition of the solid solution was determined from the lattice parameter and that of the alloy by EPMA analysis.

3. Results and Discussion

3.1. Lattice parameter measurement

The lattice parameters are $(x_{ZnTe}:d/nm)=(0:0.6482)(0.05:0.6456)$ (0.10:0.6642)(0.20:0.6408)(0.40:0.6326)(0.60:0.6257)(0.80:0.6186) (1: 0.6101). and they obey Vegard's law and are excellent agreement with the published values.

They were used to check the composition change of the solid solution before and after emf measurements and to determine the composition of the solid solutions in the quenched specimen for the study of the phase relation.

3.2. Phase relation between the liquid alloy and the ZnTe-CdTe solid solutions

The compositions of the liquidus line of Zn-Te and Cd-Te binary alloys at 873K were:

(sample; liquid phase)= $(x_{ZnTe}:x_{Zn}=1:1; x_{Zn}>0.99)$ ($x_{ZnTe}:x_{Te}=1:1; Zn_{0.0435}Te_{0.9565}$),($x_{CdTe}:x_{Cd}=1:1;Cd_{0.030}Te_{0.970}$) ($x_{CdTe}:x_{Te}=1:1; Cd_{0.031}Te_{0.969}$).

The compositions of the ternary phase diagram at 873K were : (starting sample; composition of solid phase; composition of liquid phase) = $(x_{ZnTe}/x_{Cd}=1/1;x_{ZnTe}=0.797; x_{Te}=0.033),$ $(x_{ZnTe}/x_{Cd}=1/3;x_{ZnTe}=0.673; x_{Te}=0.021)$

 $(x_{CdTe}/x_{Zn}=1/1;x_{ZnTe}=0.819;x_{Te}=0.028),$ $(x_{CdTe}/x_{Zn}=1/3;x_{ZnTe}=0.951;x_{Te}=0.009),$ $(x_{0.4Zn0.6CdTe}/x_{Cd}=1/1;x_{ZnTe}=0.341;x_{Te}=0.026)$ $(x_{0.4Zn0.6CdTe}/x_{Te}=1/1;x_{ZnTe}=0.412;x_{Te}=0.968)$ $(x_{0.8Zn0.2CdTe}/x_{Cd}=1/1;x_{ZnTe}=0.810;x_{Te}=0.974)$

3.3. Emf measurement of the pseudobinary system of ZnTe-CdTe

From the emf value E of the following cell(I), activity of zinc in the ZnTe-CdTe solid solution can be calculated by eq.(1)

(-) $Zn,ZnO | ZrO_2 (+Y_2O_3) | ZnTe-CdTe,\underline{M},ZnO (+)$ (I) -2EF=RTln a_{Zn} (1)

where F is the Faraday constant, R is the gas constant. <u>M</u> in cell(I) is Te or Zn or Cd dissolved in the alloy phase which coexists with the solid solution of ZnTe-CdTe, and very important because of holding the composition of the solid solution on the Te-rich or Te-poor side in the two phase region.

In this study the following cell was used:

(-) kanthal $|\text{Re}| (\text{ZnTe})_x (\text{CdTe})_{1-x}, \text{Te or } Cd, \text{ZnO} | \text{ZrO}_2 (+Y_2O_3) | \text{air,Pt} (+) (II)$ (-) Zn, ZnO $| \text{ZrO}_2 (+Y_2O_3) | \text{air,Pt} (+)$ (III)

Experimental data are arranged as follows:

Emf of cell (III)

 $E_{\rm III}/\rm{mV}\pm0.9 = 1832.3-0.5874T/K$ (767-1007K), and

thermo-emf of (-)Pt/kanthal(+) is:

 $E_{\rm th}/{\rm mV}\pm 0.08 = -6.34 + 0.0137 T/{\rm K}$ (800-1000K).

From these data, temperature dependence of the emf of cell(I) is arranged to be:

Te-rich side(M=Te),

 $(x_{\text{ZnTe}}:E/\text{mV}) = (1:739.3 - 0.2387T/\text{K}) (0.8:741.0 - 0.2330T/\text{K})$

(0.6: 787.3-0.2760*T*/K)(0.4: 794.2-0.2683*T*/K) (0.2: 813.9-0.2763*T*/K) (0.1: 773.4-0.2056*T*/K)(0.05:788.0-0.1904*T*/K);

Te-poor side(M=Zn),

 $(x_{ZnTe}:E/mV) = (1:-0.933+1.215 \times 10^{3}T/K), (0.913:59.1-0.0657T/K),$

(0.779:160.9-0.1342*T*/K),(0.574:127.3-0.0594*T*/K),

(0.189: 155.8-0.0343*T*/K).

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Activities of Zn in ZnTe-CdTe solid solution coexisting with Te-rich and Te-poor liquid alloys at 873K and 923K are: Te-rich side; $(x_{ZnTe}:a_{Zn}/10^{-7} \text{ at } 873\text{K}:a_{Zn}/10^{-7} \text{ at } 923\text{K})=$ (1:7.38±0.36:21.4±1.0)(0.8:6.17±0.38:18.0±1.0) (0.6:4.88±0.23:15.2±0.9) (0.4:3.40±0.23:10.7±0.6) (0.2:2.43±0.12:7.84±0.38)(0.1:1.38±0.09:4.21±0.25) (0.05:0.658±0.041:2.05±0.12). Te-poor side; $(x_{ZnTe}: a_{Zn} \text{ at } 823\text{K}: a_{Zn} \text{ at } 873\text{K})=$ (1:0.998±0.001:0.997±0.025)(0.912:0.868±0.032:0.955±0.033) (0.779:0.241±0.013:0.313±0.016)(0.574:0.110±0.006:0.135±0.007) (0.189:0.0273±0.00351±0.0027)

The calculation method proposed by Kaufman and Bernstein[5] is applied to this system, using the following binary data from the literatures:

$\Delta G_{Zn}^{o \ FCC \to L} = 4480,35 - 9,16739 \cdot T - 4,7051$	$10^{26} \cdot T^{-9}$ [A.T.Dinsdale:Calphad,15(1991),317],
$\Delta G_{Zn}^{o \text{ FCC} \rightarrow L} = 4268 - 8,368 \cdot T$	[L.Kaufman: Calphad, 5(1981),185],
$\Delta G_{Zn}^{\circ FCC \rightarrow L} = -8,368 \cdot T$	[L.Kaufman: Calphad, 5(1981),185],
$\Delta G_{\rm CdTe} = -61191 + 13.075 \cdot {\rm T}$	[L.Kaufman: Calphad, 5(1981),185]
$\Delta G_{\text{ZnTe}} = -69851.41 + 15.178 \cdot \text{T}$	[O.Kubaschewski,C.B.Alcock,"Metallurgical
	Thermochemistry 5thed.Pergamon Press(1979)]
Te-poor side:	

F,	
<i>E</i> _{CdTe} =112968-159 <i>T</i>	[L.Kaufman: Calphad, 5(1981),185],
$E_{\rm CdZn} = 9200$	[S.Ban-ya, N.Maruyama: J.Jpn.Inst.Met, 42(1978),80],
$E_{\rm ZnTe}$ =15256-24.905T	[R.C.Sharma,Y.A.Chang:J.Cryst.Growth,88(1988),193],
Te-rich side;	
$E_{\rm CdTe} = -75312 - 20.92T$	[L.Kaufman: Calphad, 5(1981),185],
$E_{\rm ZnTe} = -70621$ at 873K; -69886 at 9	923K [R.C.Sharma, Y.A.Chang: J.Cryst .Growth, 88(1988), 193]

In Fig.1a,b activities of Zn are shown with the calculated values. Although no fitting parameters are used between experimental values and calculated ones, both of the concentration dependence and temperature dependence of the activity are in good agreement in both Te-rich and Te-poor regions.





3.4. Derivation of the activity of ZnTe in ZnTe-CdTe compound solid solution coexisting with Te

When the following cell is constructed, emf gives the activity of ZnTe in the solid solutions by eq.(2):

$$ZnTe, \underline{Te}, ZnO | ZrO_{2}(+Y_{2}O_{3})|ZnTe-CdTe, \underline{Te}, ZnO$$
(IV)
$$-2E_{IV}F=RT \ln a_{ZnTe}$$
(2)

From the emf values in Te-rich region in this study, we can derive the activity of ZnTe indirecly. The activity of ZnTe shows small positive deviations from Raoults law. The results are shown in Fig.2 with those by another researchers. Zabdyr[6]obtained the activity to obey Raoul's law at 900K by fused salt emf method. Goncharuk et al.[7] and Gupta et al.[8] report positive deviation in the whole composition range from fused salt emf method. Alikhanian et al.[9] determined the vapor pressure above ZnTe-CdTe at 900 K by Knudsen cell mass spectrometry, and obtained larger positive deviation from ideality than the values by any other researchers. It seems very difficult to determine the accurate values without control the alloy composition within the line compound by the technique.

3.5. Binary system(Zn-Te)

To obtain the Zn activity of binary Zn-Te alloys, fused salt emf method at low temperature range and zirconia electrolyte emf method (cell(I)) at higher temperature range were used. Obtained results are as follows:

For the cellcell (+) $Zn_{0.1}Te_{0.9}|LiCl-KCl+ZnCl_2|Zn(-)$:

(T/K, E/mV) = (731: 564.0) (778:553.8) (759:557.4) (808:548.5) and (745:560.3) (761:557.8) (749:559.6) (767:556.5).

For cell(I), $Zn,ZnO|ZrO_2(+Y_2O_3)|Zn_{0.25}Te_{0.75},ZnO$, (Te-rich alloy)

T/K, E/mV) =(876:538.5),(905:531.6),(839:545.2),(867:539.8)

(914:529.9),(888:535.3),(963:518.7),(949:520.0),(988:513.3).

Both data are combined and can be presented as a linear line by least regression analysis to be: $E/mV = 735.8 - 0.2345T/K\pm 1.8$.

In a similar way, emf of cell(I) for Zn-rich alloy $(Zn_{0.8}Te_{0.2})$ was measured to be:

 $E/mV = -0.933 + 0.0012T/K \pm 0.018.$

From these results, we obtain the following two equation for the activity of Zn:

ZnTe-Te side: $\log a_{Zn} = 2.365 - 7419.4/T/K$ (850-1000K),

ZnTe-Zn side: log a_{Zn} = - 0.012+9.408/*T*/K. (850-1000K).

The results show that how drastically activity changes within the line compounds.



Figure 2. Activity of ZnTe in ZnTe-CdTe alloys

3.6. Binary system Zn-Cd(l)

The emfs of cell (IV) were measured.

(-) W Zn,ZnO|ZrO₂(+Y₂O₃)|Zn-Cd(l),ZnO|W (+) (V)

The emf data are shown in Fig.3, and temperature dependence of emf is shown in Table 1. Derived activity values at 800 and 900K are listed in Table 2. Fig.4 shows the activity data obtained by several experimental

method. Only present work is from the emf method with solid electrolyte. As a whole there seems very small scatter in the experimental results. This activity curve and phase relationship described above explain the composition dependence of activity of Zn in the Te-poor region of the ZnTe-CdTe solid solution, i.e. a_{Zn} keep small value up to $x_{ZnTe} = 0.7$, but increase sharply in the region $x_{ZnTe} = 0.7$ to 1.

$X_{ m Zn}$	E/mV
0.10	$-21.4 \pm 0.0831 T/K \pm 0.1$
0.20	$-36.4 \pm 0.0808 T/K \pm 0.2$
0.30	$-23.4 \pm 0.0529 T/K \pm 0.2$
0.40	$-14.4 \pm 0.0364 T/K \pm 0.2$
0.50	$-15.8 \pm 0.0353 T/K \pm 0.3$
0.60	$-8.63 \pm 0.0222 T/K \pm 0.16$
0.70	$-1.51 \pm 0.0111 T/K \pm 0.06$
0.80	$-1.77 \pm 0.0092 T/K \pm 0.11$
0.90	$0.57 \pm 0.0028 T/K \pm 0.03$

Table 1 Temperature dependence of emf of cell(V)

Table.2 Activities of zinc and cadmium in liquid Zn-Cd alloys

X _{Zn} 800 K	azn		$a_{ m Cd}$	
	800 K	900 K	800 K	900 K
0.10	0.270 ± 0.001	0.252 ± 0.001	0.911	0.914
0.20	0.441 ± 0.003	0.392 ± 0.002	0.839	0.849
0.30	0.578 ± 0.004	0.536 ± 0.003	0.768	0.767
0.40	0.653 ± 0.004	0.622 ± 0.003	0.720	0.709
0.50	0.698 ± 0.006	0.662 ± 0.005	0.682	0.673
0.60	0.767 ± 0.004	0.745 ± 0.003	0.608	0.583
0.70	0.807 ± 0.002	0.804 ± 0.002	0.553	0.506
0.80	0.850 ± 0.003	0.845 ± 0.003	0.470	0.434
0.90	0.922 ± 0.001	0.923 ± 0.001	0.294	0.261



Figure 3. E/mV:T/K plot of cell V



Figure 4. Activity of Zn in liquid Zn-Cd alloys

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