Ion Intensity Thermal Analysis of Ag-Mn Alloy

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Ion intensity thermal analysis by means of a Knudsen cell-mass spectrometer combination was applied to the study of invariant reactions in the Ag-Mn alloy system. In this study, the ion intensity of a component of the sample was measured as an index of temperature of the sample. Sensitivity and features of the ion intensity thermal analysis were discussed in comparison with the conventional thermal analysis with thermocouples. Temperature and type of the invariant reactions in Ag-Mn alloys were reported. Comparison of several published phase diagrams for this system was made in the light of the present study.

1. Introduction

A new method, which is referred to as ion intensity thermal analysis in this paper, was carried out for Ag-Mn alloys by the use of a Knudsen cell-mass spectrometer combination.

A method of thermal analysis by means of a Knudsen cell-mass spectrometer combination has been employed by the authors to study high temperature phase diagrams of iron based alloys^{1,2)}. This method is different from the so called mass spectrometric thermal analysis (MTA). In this method, instead of the electromotive force of a thermocouple placed close to the sample, as in the conventional thermal analysis, ion intensity of a

component of the sample is recorded during heating or cooling the sample. The ion intensity serves as an index of the temperature of the sample. This method of thermal analysis is based on the fact that vapor pressure of a substance changes exponentially with inverse temperature. Since the vapor pressure is sensitive to the change in the temperature, the vapor pressure itself may be taken as the sensitive measure of the temperature of the sample.

In this method, the sample is contained in a Knudsen cell and heated in a cell furnace. The cell furnace is coupled in vacuum with the ion source of a mass spectrometer so that the molecular beam effused from the cell orifice can enter the ionization zone of

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the ion source. The ion intensity of the vapor is continuously monitored while the sample is heated or cooled. When the sample undergoes an invariant reaction, increase or decrease of the temperature of the sample stops because of absorption or evolution of the heat of reaction. This brings about the suspension of the ion intensity. It is known that the ion intensity I_i is related to the vapor pressure p_i of substance i in the Knudsen cell heated at temperature T by the following equation³⁾.

$$I_i = \frac{Ap_i c_i}{4kT} g \sigma_i (E - E_i^0) j \frac{1}{c_i} \eta_i S_i \quad (1)$$

where, A : effective area of the orifice,
 c_i : average velocity of vapor atoms,
 g : geometric apparatus constant,
 σ_i : ionization cross section,
 E_i^0 : ionization potential,
 l : length of the path of atoms in the ionizing electron beam,
 j : intensity of ionizing electron current,
 η_i : isotopic abundance,
 S_i : sensitivity of secondary electron multiplier.

On the other hand, the temperature dependency of vapor pressure p_i is given by

$$RT \ln p_i = -H_i^v + TS_i^v \quad (2)$$

where, H_i^v and S_i^v are the enthalpy and entropy of vaporization of i .

Substituting Eq.(2) in Eq.(1), we have

$$\ln(I_i T) = -\frac{H_i^v}{RT} + C \quad (3)$$

where C is a constant.

Differentiating Eq.(3), we have Eq.(4)

which gives a relation between relative change in the ion intensity and that in the temperature.

$$\frac{dI_i}{I_i} = \left(\frac{H_i^v}{RT} - 1 \right) \frac{dT}{T} \quad (4)$$

The value of the parentheses of the right hand side of the Eq.(4) depends on the heat of vaporization of the material and the temperature at which the sample is heated. For instance, the heat of vaporization of iron is about 90kcal and when the temperature is around 2000K, the extent of relative change in the ion intensity of iron is 25 times as large as the relative change in the temperature. Thus the ion intensity turned out to be a very sensitive measure of the temperature of the sample. Ion intensity may, therefore, be employed instead of the electromotive force of a thermocouple in a thermal analysis.

In the thermal analysis, under the constant heating rate, on an invariant reaction, the length of time during which the temperature of the sample holds constant depends on the amount of heat absorbed during the invariant reaction. The amount of the heat absorbed is proportional to the amount of the substance reacted. Hence, from the composition dependence of the length of the time interval, the composition of the decomposing phase may be estimated.

A number of equilibrium phase diagrams were published for Ag-Mn alloy⁴⁻⁷⁾. In these phase diagrams, several invariant reactions were reported in the temperature range from 1260K to 1500K. However, as to the type and temperature of these reactions, there are apparent discrepancies among these phase diagrams. Temperature and

Ion Intensity Thermal Analysis of Ag-Mn Alloy

type of these invariant reactions were examined in the present study by means of the ion intensity thermal analysis.

2. Experimental

2.1. Apparatus⁸⁾

A combination of an ion source and a Knudsen cell furnace is illustrated in Fig.1. A mass spectrometer of magnetic field deflection type was used. The Knudsen cell furnace was installed directly below the ion source. A Knudsen cell was heated by electron bombardment in the cell furnace. Both ion source- and Knudsen cell-chamber were

Fig. 1. Combined ion source and Knudsen cell furnace.

1. Ion source, 2. Lens and accelerating poles,
3. Slit, 4. Analyzer tube, 5. Pump system, 6. Molecular beam shutter, 7. Radiation shields, 8. Ring filaments for electron bombardment, 9. Cell holder, 10. Knudsen cell, 11. Filament support, 12. Thermocouples.

connected with a hole through which atomic beam of the vapor effused from the Knudsen cell orifice could enter the ion source. A beam shutter which can be manipulated from the outside of the chamber was equipped over the hole and both chambers were differentially pumped to about 10^{-6} to 10^{-7} torr.

A crucible, 10mm in diameter and 11mm in height and a lid, 1mm in thickness with an orifice, 0.5mm in diameter, both made of sintered alumina were used as a Knudsen cell. About 0.5 to 1.5g of alloy sample was charged in the cell and the cell was contained in a Ta cell holder which was heated by electron bombardment. Temperature T_b of the cell holder was measured at the outside bottom of the crucible by a thermocouple.

The ionizing voltage of the ion source was set at 37volt, since it was apparent in Fig.2 that the ion intensities of Ag and Mn were stable with the ionizing voltage around this value. The ion intensity of Mn was measured in the thermal analysis because of the relatively high vapor pressure of Mn.

2.2. Experimental procedure

Fig. 2. Ionization efficiency curve of Ag and Mn. I_{Ag} and I_{Mn} in arbitrary unit.

2.2.1. Types of ion intensity measurement

Ion intensity of a component of the alloy was measured in two different ways, one is isothermal and another is dynamic.

In the isothermal ion intensity measurement, the ion intensity was measured when it stayed at a constant value for at least five minutes after the cell temperature was fixed. In the dynamic ion intensity measurement, the cell heating power was increased or decreased at a constant rate so that the temperature of the cell changed at a constant rate of about 5 to 15 degree per minute. Examples of both types of ion intensity measurement are shown schematically in Fig.3.

2.2.2. Temperature correction

The melting point of Ag (1234.9K) and A4 point of Fe (1667K) were selected as the references for the temperature correction. Isothermal measurements with these pure metals were carried out at several temperatures. Temperature T_b was measured at the bottom of the cell. The relation of the ion intensity and T_b was delineated. Successfully, the dynamic measurements were carried out over temperature ranges including the melting point of Ag or A4 point of Fe. The suspension on the ion intensity curve was observed when the metal underwent transformation. The value of ion intensity at this point was that shown by the metal when it was at its transformation point. By substituting this value in the above obtained ion intensity vs. T_b relation, one can find the value of T_b when inside the cell is at the

Fig. 3. Ion intensity curve on isothermal measurements and dynamic measurements of reaction A, B and C on heating. Sample: AgMn(6). I_{Mn} and T , electromotive force of a Pt/Rh thermocouple, are in arbitrary unit.

Ion Intensity Thermal Analysis of Ag-Mn Alloy

transformation point of the metal. Thus a correction value to be applied to T_b to give the true temperature inside the cell, was obtained. The results are shown in Table I.

2.2.3. Determination of temperature of invariant reactions

The procedure of the determination of an invariant reaction temperature is, in principle, the reverse of the above stated procedure for the temperature correction. Since the temperature correction has already been made, the true temperature inside the cell is possible to obtain from the T_b value. Both isothermal and dynamic measurements have to be carried out.

The isothermal measurements were carried out at intervals of 10 to 20 K, and at least, three or four measurements best be done in between two adjacent invariant temperatures. Knowing the correction value, true temperature T inside the cell at which the isothermal measurement was carried out now could be obtained from T_b . From the isothermal measurements a linear relation of $\ln IT$ vs. $1/T$ may be obtained within the temperature range between two adjacent invariants.

Heating and cooling dynamic measurements were then carried out over the invar-

iant temperatures. The value of ion intensity at the invariant was substituted into above obtained $\ln IT$ vs. $1/T$ relation to give the temperature at which the invariant reaction took place.

2.2.4. Determination of the amount of heat absorbed during a reaction

The length of duration of the suspension on the ion intensity curve was also measured to give the quantity q which is proportional to the amount of heat absorbed during the reaction and in turn, proportional to the amount of the phase decomposed. The value q is defined as follows. Assuming that the temperature of the cell holder increases at a constant rate and that the heat flux from the cell holder to the sample in the cell is proportional to the difference in the temperatures of the sample T and the cell holder T_b , we have the following expression of q . See appendix.

$$q = \frac{rt^2}{n} \quad (5)$$

where, r : the rate of increase of temperature T_b , (K/min),

t : the duration of the suspension on the ion intensity curve, (min).

n : number of moles of the sample.

Table I. Values for Temperature Correction.

Ag $T_m = 1234.9$ K	$T_m - T_b$	Mean value	Standard deviation
	77.9, 79.0, 80.4, 81.0, 81.6, 82.4, 82.8, 83.0, 83.5, 84.0		
Fe $T_A = 1667$ K	$T_A - T_b$	84.0	1.6
	81.1, 82.2, 82.7, 83.0, 84.4, 85.4, 85.8, 86.3		

3. Experimental results

Typical courses of the ion intensity measurement are shown in Fig.3 to 5. It is clear in Fig.3 that when the alloy undergoes the invariant reaction, although the heating power increases steadily, the ion intensity holds its value constant until the reaction finishes, indicating that the temperature of the sample does not change. When the liquid

alloy is cooled, the alloy usually undergoes supercooling, which effect appears on the ion intensity curve very clearly although the effect can not be observed on the T_b curve as shown in Fig.4. When an alloy undergoes monovariant reaction, the ion intensity does not stop during the reaction is taking place. Shown in Fig.5 is a case when temperature increases over the solid liquid two-phase region, the compositions of both phases

Fig. 4. Ion intensity curve on cooling. Sample: AgMn(6).

I_{Mn} and T , electromotive force of a Pt/Rh thermocouple, are in arbitrary unit.

Ion Intensity Thermal Analysis of Ag-Mn Alloy

change along the solidus and liquidus lines and hence the increment in the ion intensity is caused not only by the temperature increase but also by the composition change. In these charts, it is shown that the relative change in the ion intensity is much clearer than that in the temperature.

The relation between $\ln T$ and $1/T$ is shown in Fig.6. Linear behaviors are observed in every single-phase or two-phase region. The breaks on the relation corre-

spond to the invariant reactions.

The results of the ion intensity thermal analysis are given in Table II in which the detected invariants are named tentatively A, B, C and D in the order of temperature. The values for q are given in Table III. The values of q are plotted against the composition in Fig.7. This value is expected to attain maximum value at the composition of the decomposing phase. The reaction A takes place at a composition near 50at%-Mn and

Fig. 5. Ion intensity curve on monovariant reaction. Sample: AgMn(8). I_{Mn} and T_b , electromotive force of a Pt/Rh thermocouple, are in arbitrary unit.

Fig. 6. Relation between $\ln(I_{Mn}T)$ vs. $1/T$. Sample: AgMn(6).

Ion Intensity Thermal Analysis of Ag-Mn Alloy

Table II. Temperature of Detected Reactions (K).

Heat No. at%Mn	AM(8) 26.0	AM(7) 53.4	AM(5) 59.2	AM(3) 61.9	AM(2) 66.2	AM(4) 76.7	AM(6) 92.8	Mean
Solidus	1241	=	=	=	=	=	=	
Liquidus	1244	=	=	=	=	=	=	
Reaction A	=	1264	1261 1261	1259 1261	1262	1258 1259	1263	1261
Reaction B	—	=	1359 1356	(1309) (1311)	*	1356	1360 1358	1358
Reaction C	—	—	—	1415	*	1413	1416	1415
Reaction D	—	—	—	1491	*	—	1492	1491

—: Not measured, =: Not detected, *: Detected but uncertain.

Table III. Amount of Heat Absorbed During Invariant Reactions According to Eq.(5).

Heat No. at%Mn $n \times 10^2$	AM(7) 53.4 1.63	AM(5) 59.2 1.7	AM(3) 61.9 1.25	AM(2) 66.2 0.65	AM(6) 92.8 2.21
A: $dT_b/dt(K/min)$	3.1	3.6 3.1	14.8 7.4	5.3	2.4
t (min)	5.0	5.6 5.3	1.6 2.8	1.3	3.1
$q \times 10^{-2}$	48	66 51	30.3 46.4	13.8	10.4
B: $dT_b/dt(K/min)$	=	2.3	11.4 4.9	3.5	2.3
t(min)		0.6	0.5 0.8	0.7	2.0
$q \times 10^{-2}$		0.5	2.3 2.5	2.6	4.2
C: $dT_b/dt(K/min)$	—	—	4.4	3.8	2.8
t(min)			1.1	0.8	3.2
$q \times 10^{-2}$			7.0	3.7	13.0

no reaction on this temperature in the Mn-rich side is detected. Reaction B and C take place in the Mn-rich side.

The solidus and liquidus temperatures of 15.6at%·Mn alloy are respectively estimated to 1241K and 1244K.

4. Discussion

4.1. Features of the ion intensity thermal analysis

The temperature of a sample is measured usually with thermocouples. The relative change in the electromotive force with temperature of some thermocouples are shown in Table IV. Relative change in the ion intensity is also shown for some pure metals. It is clear from this table, that the ion intensity is a measure of the temperature of which sensitivity is much higher than that of the electromotive force of thermocouples.

Because of the low pressure in the cell, the possibility of collision of atoms in the

vapor phase inside the cell should be negligibly small and because of long distance between the cell and the ion source relative to the size of the orifice, the part which can be viewed from the ion source through the orifice is restricted to a small area of the sample surface. Hence the atom beam entering the ion source consists of atoms which come directly from the small part of the sample surface and is not affected by collision with gas phase particles or with any parts of the cell wall. Hence the ion intensity reflects directly the state of the sample itself.

On the other hand, temperature measurement by the use of thermocouples is affected by heat flow to and from the hot junction through cell wall, thermocouple sheath and adjacent parts which may be at different temperatures. When temperature measurement is made under nearly equilibrium condition, effects of these heat conductions will not make problems but in a dynamic temperature measurement as in the thermal analysis, the effects will become appreciable and may cause errors in the temperature measurements. Ion intensity thermal analysis is more advantageous when liquid phase appears during thermal analysis where the hot junction of thermocouple is inevitably separated from the sample by the crucible wall and/or couple sheath. Thus ion intensity offers a very sensitive and non-contactive means of temperature measurement.

4.2. Equilibrium phase diagram of Ag-Mn alloy

Several equilibrium phase diagrams have been published of Ag-Mn alloy system.

Fig. 7. Relation between heat of reaction absorbed and composition. q in arbitrary unit.

Ion Intensity Thermal Analysis of Ag-Mn Alloy

Type and temperature of invariant reactions reported in these phase diagrams and obtained in the present study are summarized in Table V. An eutectoid reaction $\gamma\text{-Mn} = (\text{Ag}) + \beta\text{-Mn}$ and a peritectic reaction $L_1 + \gamma\text{-Mn} = (\text{Ag})$ occur at temperatures very close to 1260K in Hansen's phase diagram, while four phases L_1 , (Ag), $\gamma\text{-Mn}$ and $\beta\text{-Mn}$ coexist at a temperature 1344K in the phase diagram listed in Metals Handbook. In Hansen's diagram, $\gamma\text{-Mn}$ region extends down to the eutectoid temperature. On the other hand, $\gamma\text{-Mn}$ region extends down only to 1343K in Elliott's and Hultgren's diagrams, and in the latter diagram, no reaction is shown in the Mn-rich side near the peritectic temperature, 1260K. The present results support the Hultgren's diagram. That is, an invariant reaction at 1261K occurs at composition below 50at%-Mn corresponding to the peritectic reaction and no invariant reaction is observed in the Mn-rich side, an invariant reaction at 1358K occurs in the Mn-rich side which corresponds to a remelting reaction $\gamma\text{-Mn} = L_1 + \beta\text{-Mn}$, an invariant reaction at 1415K occurs in the Mn-rich side which corresponds to $\delta\text{-}\gamma$ transformation and an invariant reaction at 1492K corresponds to a monotectic reaction $L_2 = L_1 +$

$\delta\text{-Mn}$.

5. Conclusion

Ion intensity thermal analysis of Ag-Mn alloys by means of a combination of Knudsen cell and mass spectrometer was carried out. Ion intensity of Mn of Ag-Mn alloy sample was used as a measure of the temperature of the sample. Temperature and type of invariant reactions in Ag-Mn alloys were studied. Several published phase diagrams for this system were examined in the light of the present results and the phase diagram edited by Hultgren *et al.* turned out to be most reliable.

The sensitivity of the ion intensity thermal analysis is much higher than the conventional thermal analysis in which the electromotive force of a thermocouple is used to measure the sample temperature. Though the ion intensity thermal analysis has distinct advantages, it is a method of low cost efficiency when it is used solely for thermal analysis as is the case in the present study. The ion intensity thermal analysis should be combined with Knudsen cell mass spectrometric thermodynamic studies such as activity measurements, enthalpy determination, *etc.* By doing so, one can check the

Table IV. Comparison of Sensitivity of Temperature Measurement(at 1800K).

Type (dE/E)/(dT/T)	W-Re(0/26)	Thermocouple	
		Pt-Rh(6/30)	Pt-Rh(0/13)
	1.4	1.8	1.4
Ion intensity			
Pure metal (dI/I)/(dT/T)	Ag	Mn	Fe
	17	15	25

self consistency of the informations obtained from both sides and make the informations more reliable.

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Appendix

The rate of heat transfer $dQ/d\theta$ to the sample from the cell holder is proportional to the temperature difference between the cell holder and the sample.

$$\frac{dQ}{d\theta} = h(T_h - T_s)$$

where θ is the time, h is the heat transfer coefficient and T_h and T_s are the temperature of the holder and the sample, respectively.

The temperature of the holder is elevated at a constant rate $r(=dT_h/d\theta)$. When an invariant reaction occurs, T_s keeps con-

Table V. Comparison with Previous Studies on Invariant Reactions.

	Hansen (1958)	Elliott (1965)	Metals Handbook (1973)	Selected Values (1973)	Present study
Reaction	Temperature (K)				
P; $L_2 + \delta = \gamma$	1485				
M; $L_2 = L_1 + \delta$		1481	1483	1481	1492
M; $L_2 = L_1 + \gamma$	1458				
$\delta = \gamma$		1404		1404	1415
R; $\delta = L_1 + \gamma$			1405		
?: $L_1 + \gamma = (Ag) + \beta$			1344		
R; $\gamma = L_1 + \beta$		1343		1343	1358
P; $L_1 + \beta = (Ag)$				1260	1261
P; $L_1 + \gamma = (Ag)$	1260				
E; $\gamma = (Ag) + \beta$	~1260				

Types of reaction; P: Peritectic, M: Monotectic, R: Remelting, E: Eutectoid

Ion Intensity Thermal Analysis of Ag-Mn Alloy

stant value until the reaction finishes. The temperature difference increases with the time.

$$T_h - T_s = r\theta$$

If the length of the temperature suspension is t , then the quantity of heat absorbed during the invariant reaction is given by

$$Q = \int_0^t hr \theta d\theta = \frac{hr}{2} t^2.$$

Thus the molar heat absorbed during the invariant reaction is proportional to the value q defined in the text.

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keywords

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