

Activity Measurement of Titanium-Tin Alloys by Knudsen Effusion Method

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The activity of tin in Ti-Sn alloy has been determined at 1400 K by Knudsen effusion method with electrobalance. The activity of titanium was calculated by applying the Gibbs-Duhem relation to the Ti-Sn binary system. The standard Gibbs energy of the formation of intermetallic compound such as Ti₃Sn, Ti₂Sn, Ti₅Sn₃ and Ti₆Sn₅ was calculated at 1400 K by using the activities of components. X-ray diffraction studies were additionally conducted for some samples after the activity measurement. The identified phases were consistent with the phase diagram reported in the literature. [doi:10.2320/matertrans.M-M2011801]

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1. Introduction

Titanium base alloys are used widely in various fields such as chemical plants, thermal and nuclear power plants, sporting goods, building materials, medical supplies, accessories and aircraft, and so on, because those solid solutions and intermetallic compounds are stable. Thermodynamic properties of alloys are important databases in order to know phase stabilities and the bonding force of components, and also to construct phase diagrams. However, there has not been so much report on titanium base alloys as given below. This may be due to some experimental difficulties. For instance, it takes quite long time to establish equilibrium at a high temperature, because titanium has high melting temperature. Moreover, in the experiment high vacuum condition or inert atmosphere is required, because titanium is strongly reactive with oxygen and nitrogen.

With respect to the activities of liquid titanium alloys, Predel *et al.*¹⁾ conducted the activity measurement of Ti-Cu system by Knudsen effusion method. Wagner and St. Pierre,²⁾ Furukawa and Kato³⁾ individually measured the activities of Ti-Fe system using Knudsen mass spectrometer. Maeda *et al.*⁴⁾ investigated Ti-Al system by free evaporation method. Anderson and Selvaduray⁵⁾ measured the activity of titanium in the Sn-rich side of Ti-Sn system by the aid of nitrogen-nitride equilibrium.

As for solid alloys, St. Pierre *et al.* investigated the activity of Ti-Cr system⁶⁾ by Knudsen effusion method. Hoch *et al.*, Choudary *et al.*, and Pelino *et al.* measured the activities using Knudsen mass spectrometer in the following systems: Ti-Mo system,⁷⁾ Ti-Al system (Ti-rich side β phase),⁸⁾ Ti-V system,⁹⁾ Ti-Cu system (Ti-rich side β phase),¹⁰⁾ Ti-Ir system (Ir-rich side),¹¹⁾ Ti-Ir system (Ti-rich side).¹²⁾ Moreover, Arita *et al.* measured the activities of Ti-Cu¹³⁾ and Ti-Ni¹⁴⁾ systems by the aid of hydrogen-hydride equilibrium. For the other thermodynamic property, Meschter and Worrell¹⁵⁾ measured the Gibbs energy of TiPt₈ and TiPt₃ formation in Ti-Pt system by E.M.F. method using solid electrolytes.

The objective of the present work is to determine the activity of Ti-Sn system. The system constitutes the practical titanium base alloys as with the Ti-Al system. However, there has been no report so far concerning the activities of the component in the Ti-Sn system over the whole concentration range, though the phase diagram calculation¹⁶⁾ of the system was carried out by means of CALPHAD technique. Since the vapor pressure of tin is approximately four orders of magnitude larger than that of titanium at a temperature of 1400 K, Knudsen effusion method is well suited for the activity measurement of the Ti-Sn system.

2. Principle of Knudsen Effusion Method

In the Knudsen effusion method, the vapor pressure can be calculated from the effusion rate of vapor in equilibrium with alloy in a Knudsen effusion cell through an orifice into a vacuum by eq. (1).¹⁷⁾

$$P_i = \frac{G_i}{kA} \sqrt{\frac{2\pi RT}{M_i}} \left(1 + \frac{kA}{\alpha_i B}\right) \quad (1)$$

where P_i is vapor pressure (Pa), G_i is effusion rate of vapor ($\text{kg}\cdot\text{s}^{-1}$), T is temperature (K), R is gas constant ($8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), M_i is molecular mass ($\text{kg}\cdot\text{mol}^{-1}$), and k is the Clausing factor which is a function of the ratio of the orifice thickness to radius. α_i is the accommodation coefficient which depends on a material and is taken to be unity for most metals. A and B are orifice area and effective surface area of the sample in a Knudsen effusion cell, respectively (m^2). When B is much larger than A , the value in parenthesis in the right-hand-side of eq. (1) is approximated by unity, and then eq. (2) can be derived.

$$P_i = \frac{G_i}{kA} \sqrt{\frac{2\pi RT}{M_i}} \quad (2)$$

In the present work, the effusion rate was measured from the mass loss of the sample using a Cahn's electrobalance as a function of time. When the linear relation between the mass loss and time is observed over a long time, in other words, in the case that the effusion rate is considered to be constant, the vapor pressure can be determined directly from eq. (2). However, it is difficult to determine the value of k in eq. (2)

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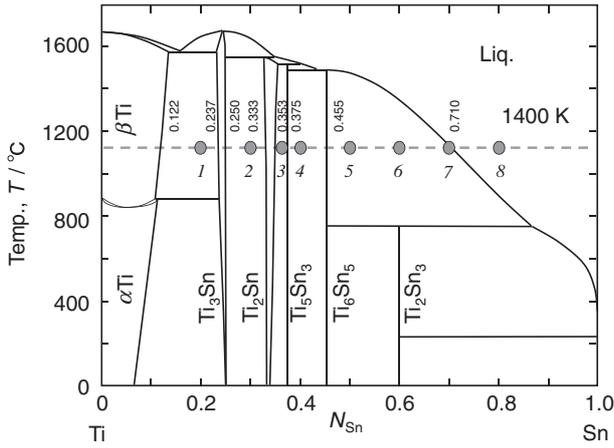


Fig. 1 Sample compositions in phase diagram of Ti-Sn system, where numerals correspond to the phase boundaries in mole fraction of tin seen in the phase diagram calculated by Yin *et al.*

properly.¹⁷⁾ The kA was then obtained as the apparatus constant. The activity of a substance is defined as the ratio of the vapor pressure of the substance to that of pure substance.¹⁸⁾ Thus, if the effusion rate is measured under the same condition for both alloy and pure substance, the activity can be determined directly from the ratio of the effusion rate by eq. (3).

$$a_i = \frac{P_i}{P_i^0} = \frac{\frac{G_i}{kA} \sqrt{\frac{2\pi RT}{M_i}}}{\frac{G_i^0}{kA} \sqrt{\frac{2\pi RT}{M_i}}} = \frac{G_i}{G_i^0} \quad (3)$$

where P_i^0 is vapor pressure of pure substance (Pa). G_i^0 is effusion rate of pure substance ($\text{kg}\cdot\text{s}^{-1}$). The vapor pressures of pure titanium and tin are $7.8 \times 10^{-6} \text{ Pa}$ ¹⁹⁾ and $2.1 \times 10^{-1} \text{ Pa}$ ²⁰⁾ at the experimental temperature 1400 K, respectively. The difference between the vapor pressures of titanium and tin is more than four orders of magnitude. Thus, the effusion rate of alloy G_i can be considered due to the effusion of tin vapor in the alloy.

3. Experimental

The samples used in the present work are metallic titanium powder (99.9 mass% purity) and two-kinds of metallic tin: one is shot-like tin (99.999 mass% purity); the other is tin powder (99.99 mass% purity). The shot-like tin was used in the experiment for pure tin. The Ti-Sn alloy sample was preliminarily prepared from titanium and tin powders. The powders were mixed at the desired compositions which were represented by solid circles in Fig. 1. This phase diagram was constructed by Yin *et al.*¹⁶⁾ by means of CALPHAD technique. In the figure numerals are the phase boundaries in mole fraction of tin seen in the phase diagram.¹⁶⁾ The mixed sample was put in an alumina crucible of 5 mm inner diameter, 7 mm outer diameter, 60 mm length. Then the crucible containing the sample was put in a quartz tube of 8 mm inner diameter. The quartz tube was evacuated to about 10^{-3} Pa and sealed for the sample numbers 1–6, while for the tin-rich alloy of the sample numbers 7 and 8, argon gas with

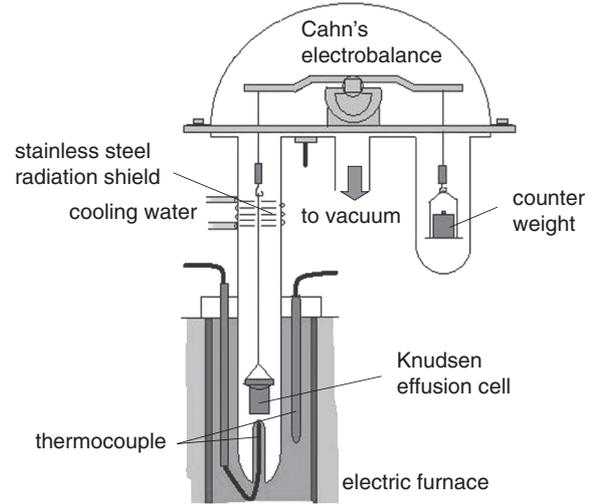


Fig. 2 Experimental setup.

13 kPa was injected into the quartz tube and sealed so as to inhibit a composition change. The quartz capsule was heated at the experimental temperature 1400 K for 5 h for a liquid alloy, while for a solid alloy the heating time was prolonged to 120 h (5 days), and then quenched in water. Figure 2 shows the experimental setup used in this study. The Knudsen effusion cell is made of molybdenum, in which an alumina crucible of 11 mm inner diameter, 13 mm outer diameter, 16 mm height was put for the sample container. An orifice was made at the center of molybdenum circular plate of $\phi 17 \text{ mm}$, 0.05 mm thickness. The diameter of the orifice was measured using an optical microscope to be $\phi 1.6 \text{ mm}$ before and after the experiments. The effusion cell was suspended from the Cahn's electrobalance into a quartz reaction tube of 36 mm inner diameter by a piece of $\phi 0.5 \text{ mm}$ molybdenum wire to measure the mass loss. While the sample was being heated to the experimental temperature, the reaction tube was filled with argon gas. When the temperature of the sample had reached the desired temperature, the reaction tube was evacuated to about 10^{-3} Pa by using an oil diffusion pump and the measurement of the mass loss was started. The temperatures in the experiment were 1350, 1375, 1400 K for pure tin, and 1400 K for Ti-Sn alloy, respectively. The temperature of 1400 K is maximum temperature due to the limitations on the use of quartz reaction tube.

4. Results and Discussion

4.1 Effusion rate and vapor pressure of pure tin

The effusion rate was measured three times at every temperature of 1350, 1375 and 1400 K for pure tin. The measured effusion rates and the calculated vapor pressures are shown in Table 1. It took 5–6 h in total to measure the effusion rate for each measurement and 1–2 h to obtain a linear relation between the mass loss and time. Figure 3 shows an example of the relation between the relative sample mass and time for pure tin at 1375 K. The vapor pressure of pure tin was expressed by the method of least squares as eq. (4) and shown in Fig. 4.

$$\log(P_{\text{Sn}}^0/\text{Pa}) = -13990/(T/\text{K}) + 9.306 \quad (4)$$

Table 1 Measured effusion rates and calculated vapor pressures of pure tin.

T/K	effusion rate/ 10^{-10} kg·s $^{-1}$	vapor pressure/Pa
1350	2.261 ± 0.040	0.08728 ± 0.00155
1375	3.485 ± 0.013	0.1358 ± 0.0005
1400	5.206 ± 0.080	0.2046 ± 0.0031

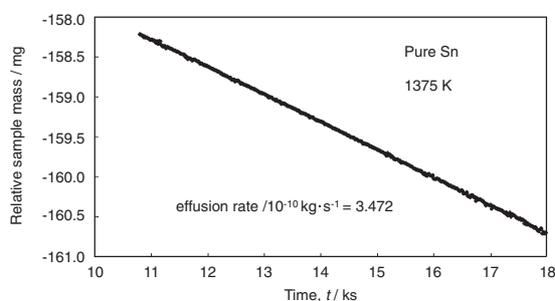


Fig. 3 Example of the relation between the relative sample mass and time for pure tin at 1375 K.

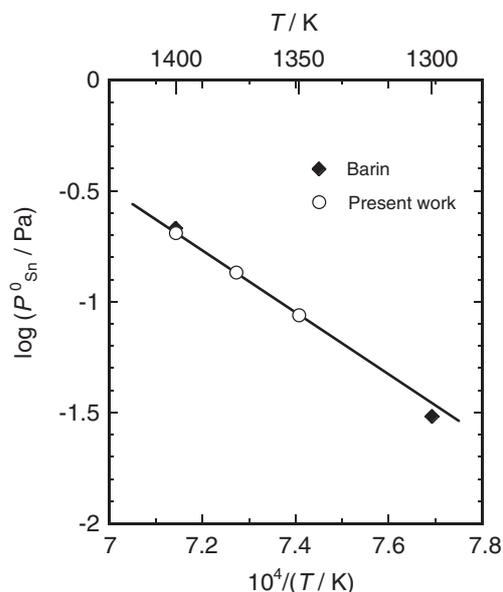


Fig. 4 Vapor pressure of pure tin.

Here, the apparatus constant kA was determined to be 1.997×10^{-6} m 2 as the mean value of the calibrated values kA for all the measurements by using the vapor pressure of tin after Barin.²⁰⁾ The Clausius factor k was then estimated at 0.993. Moreover, the standard enthalpy of vaporization of tin was calculated by the 2nd- and 3rd-law methods,¹⁷⁾ as with the previous work.²¹⁾ The calculated values shown in Table 2 agree well with the literature data²⁰⁾ within the experimental errors. The procedure for calculating the standard enthalpy of vaporization of tin was described in detail in the previous work.²¹⁾ In the present work, the standard enthalpy of vaporization of tin calculated by the 3rd-law method is the mean value of the obtained values at each temperature of 1350, 1375 and 1400 K. In the calculation, $(G_T^0 - H_{298.15}^0)/T$ and $H_T^0 - H_{298.15}^0$ was used by interpolating the thermochemical data of pure substances by Barin.²⁰⁾ This indicates that the experiment has been conducted appropriately.

Table 2 Standard enthalpy of vaporization of tin.

reaction	method	$\Delta H_{298.15}^0/\text{kJ}\cdot\text{mol}^{-1}$	
		Present work	Barin
Sn (s)=Sn (g)	2nd law	273.6	301.2
	3rd law	301.5	

Table 3 Measured effusion rates and calculated activities for Ti-Sn alloy at 1400 K.

Exp. No.	N_{Sn}	effusion rate/ 10^{-10} kg·s $^{-1}$	a_{Sn}
1-1	0.2001	0.2215	0.04255
1-2	0.2001	0.2619	0.05031
2	0.3002	0.4324	0.08306
3	0.3639	0.6013	0.1155
4	0.3999	1.161	0.2230
5-1	0.4961	3.585	0.6886
5-2	0.4988	3.555	0.6829
6-1	0.5986	3.647	0.7005
6-2	0.5995	3.592	0.6900
7	0.6992	3.749	0.7201
8-1	0.7970	3.897	0.7486
8-2	0.7993	3.915	0.7520

4.2 Activities of titanium-tin alloy

The measurement was carried out for eight compositions for Ti-Sn alloy at 1400 K. The measured effusion rates and the calculated activities are summarized in Table 3. It took 6–9 h in total to measure the effusion rate for each experiment and 1–3 h to obtain a linear relation between the mass loss and time. The amount of the sample alloy is desired to be much as far as the cell capacity permits in order to control the composition change as small as possible during the experiment. On the other hand, small amount is preferable in terms of the sensitivity of the Cahn's electrobalance. In the experiment, 3 g alloy was thus used for the sample, and then the mass loss was controlled within 50 mg. However, the composition change was observed up to 0.0041 in mole fraction. Then the composition after the experiment was adopted as the alloy composition, since the activity was held to be constant in a two-condensed-phase field.

The activities of tin and titanium in the Ti-Sn alloy at 1400 K is presented in Fig. 5. In the figure, the activity of tin was depicted as the open circle \circ and the activity line was drawn by reference to the boundaries shown in Fig. 1. The activity of titanium was calculated by applying the Gibbs-Duhem relation to the Ti-Sn binary system by the aid of the function α ²²⁾ and shown by the dashed-dotted line. The activity of tin exhibits positive deviation from Raoult's law in the two-condensed-phase field of Ti_6Sn_5 +Sn-rich liquid alloy, tending the separation between Ti_6Sn_5 and Sn-rich liquid alloy, while in the Ti-rich side composition from Ti_6Sn_5 the activity of tin shows negative deviation from Raoult's law, corresponding to the existence of some intermetallic compounds. On the other hand, the activity of titanium exhibits positive deviation from Raoult's law in the Ti-rich side composition from Ti_2Sn , while negative deviation from Raoult's law in the Sn-rich side composition from

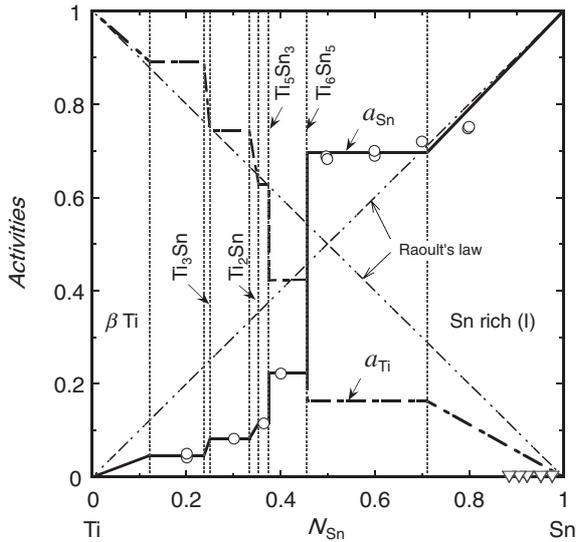


Fig. 5 Activities of tin and titanium in the Ti-Sn alloy, where open circle \circ and triangle ∇ denote the present work at 1400 K and the reported value by Anderson *et al.* at 1673 K, respectively.

Ti_6Sn_5 . In the Fig. 5 the triangle ∇ is the only reported activity of tin by Anderson and Selvadurai⁵⁾ at 1673 K. In comparison with the present work at 1400 K, the activity of titanium at 1673 K shows much negative deviation from Raoult's law and is too small value with the order of 10^{-4} even at the higher temperature. They measured the activity of titanium in the only Sn-rich side by the aid of nitrogen-nitride equilibrium.⁵⁾ Therefore, if the nitride formed in their experiment had nonstoichiometry, the reported activity would have a large experimental error. Additionally, X-ray diffraction studies were conducted for some samples after the activity measurement to identify the phase present. Figure 6 shows the X-ray diffraction patterns of the samples. The identified phases are consistent with the phase diagram in the literature.¹⁶⁾ Moreover, it was found that the reaction of alloy with the alumina crucible was not observed.

4.3 Standard gibbs energy of formation of intermetallic compound in Ti-Sn system

The standard Gibbs energy of the formation of intermetallic compound such as Ti_3Sn , Ti_2Sn , Ti_5Sn_3 and Ti_6Sn_5 was calculated at 1400 K by using the activities of components obtained in the present work. The formation reaction of the intermetallic compounds in Ti-Sn system is expressed by eq. (5)



where x and y are 2, 3, 5, 6 and 1, 3, 5, respectively. By assigning unity to the activity of Ti_xSn_y , the standard Gibbs energy of Ti_xSn_y formation is given by eq. (6).

$$\Delta G_{f,Ti_xSn_y}^0 / J \cdot mol^{-1} = RT \ln a_{Ti}^x a_{Sn}^y \quad (6)$$

The calculated values are summarized in Table 4, together with the activities of components. The difference of the calculated values between the left- and right-hand-sides of the compound is observed according to the coexistent phase in the nonstoichiometric compound such as Ti_3Sn and Ti_2Sn .

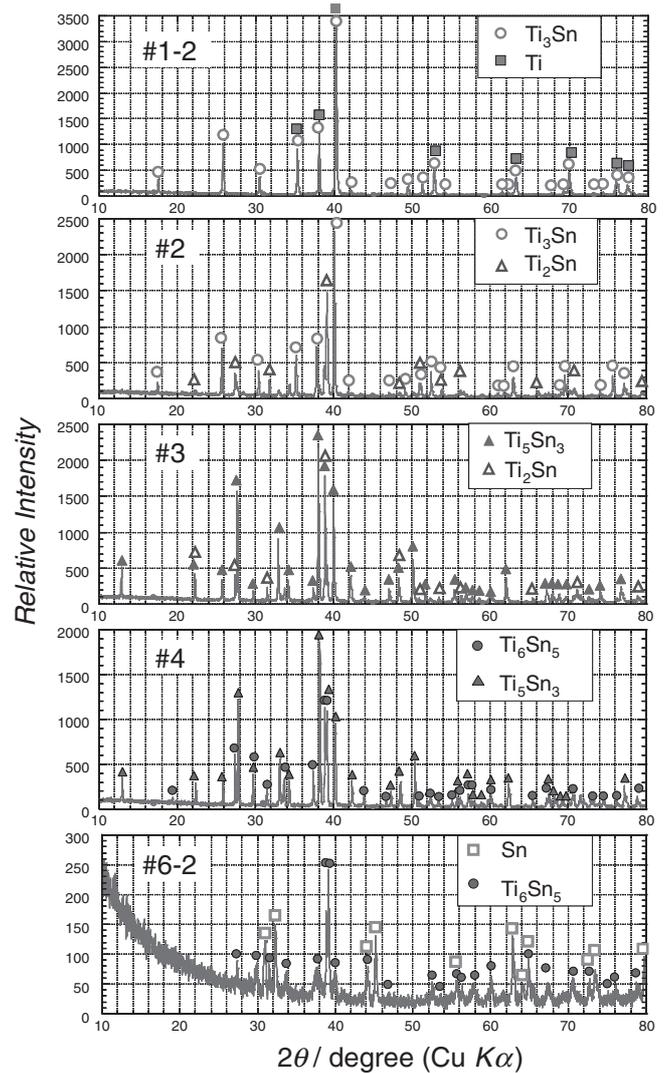


Fig. 6 X-ray diffraction patterns of the alloy samples after the activity measurement.

Table 4 Standard Gibbs energy of formation of intermetallic compound in Ti-Sn system at 1400 K.

compound	coexistent phase	a_{Sn}	a_{Ti}	$\Delta G_f^0 / kJ \cdot mol^{-1}$	$\Delta G_f^0 / kJ \cdot mol^{-1}$ (mean value)
Ti_3Sn	βTi	0.04643	0.8918	-39.73	-39.54
	Ti_2Sn	0.08306	0.7427	-39.35	
Ti_2Sn	Ti_3Sn	0.08306	0.7427	-35.89	-35.94
	Ti_5Sn_3	0.1155	0.6268	-36.00	
Ti_5Sn_3	Ti_2Sn	0.1155	0.6268	-102.6	-102.6
	Ti_6Sn_5	0.2230	0.4224	-102.6	
Ti_6Sn_5	Ti_5Sn_3	0.2230	0.4224	-147.5	-147.6
	Sn rich (l)	0.6964	0.1633	-147.6	

However, in the stoichiometric compound such as Ti_5Sn_3 and Ti_6Sn_5 , the calculated value for both side of the compound is good agreement with each other. Among the intermetallic compounds, the Gibbs energy of Ti_6Sn_5 exhibits most negative, indicating that Ti_6Sn_5 is the most stable compound in the Ti-Sn system.

5. Conclusions

The activity measurement of titanium-tin alloys has been conducted by Knudsen effusion method with the Cahn's electrobalance at 1400 K using the four orders of magnitude difference of vapor pressure between titanium and tin. The activity of titanium was calculated by integration of the Gibbs-Duhem equation for a binary alloy based on the activity of tin. By using the obtained activities of components, the standard Gibbs energy of the formation of intermetallic compound such as Ti_3Sn , Ti_2Sn , Ti_5Sn_3 and Ti_6Sn_5 was calculated at 1400 K. Additionally, X-ray diffraction studies were carried out for some samples after the activity measurement. The phases identified agree with the phase diagram calculated in the literature.

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