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KINETIC STUDY OF THE SOLID STATE REACTION OF ZINC AND ARSENIC AT HIGH TEMPERATURE AND HIGH PRESSURE

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The rate of the solid state reaciton between zinc and arsenic in powder form has been studied at temperatures of 150~400°C at pressures of 20~40 kbar. The reaciton product was Zn_3As_2 only. The reaction rate was followed by using the two peaks in the X-ray diffraction pattern of Zn_3As_2 and As. The reaction yield-time curves could be clearly divided into two parts which consisted of the initial and the latter process of the reaction.

It was assumed that the initial process of the reaction was phase-boundary controlled and kinetically analogous to ordinary chemical reactions. The kinetic data were analyzed by the second-order rate equation. The apparent activation energy E_a and the activation volume $\Delta V^{\ne}$ for the initial process were evaluated in the temperature range 150~300°C to be 10~12 kcal/mol and −0.3~−0.5 cm³/mol, respectively.

It was concluded that the latter process was diffusion controlled because the rate was retarded with increasing pressure. The kinetic data fitted the Dünwald-Wagner diffusion rate equation. The apparent activation energy E_a and the activation volume $\Delta V^{\ne}$ for the diffusion process were evaluated in the temperature range 150~250°C to be 9~12 kcal/mol and 0.7~1.4 cm³/mol, respectively. The diffusing species was proved to be zinc by measuring the Kirkendall effect. The reason was also successfully interpreted by the pronounced Kirkendall effect why the present activation parameters were smaller than those for the self-diffusion of zinc.

Introduction

In the binary systems of group II elements A (Zn, Cd) and group V elements B (P, As), several compounds of A_3B_2 and AB_2 have been known. In the case of zinc and arsenic, tetragonal Zn_3As_2[1] and monoclinic $ZnAs_2$[2] were reported. These compounds were synthesized by flowing arsenic vapor on molten zinc in a silica tube in the temperature range 700~1000°C[3]. However, as for the kinetic study of the solid state reaction in this system, there is no data. Until now, few papers have reported the kinetics of solid state reactions between two kinds of elements under high temperature and high pressure except for the Zn-P system[4].

One of the purposes of the kinetic researches in solid phase is to find the most probable path for the reaction and, that is, to obtain the insight into the reaction mechanism. It is usual to postulate

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[1] H. Cole, F. M. Chambers and H. M. Dunn, *Acta Cryst.*, 9, 685 (1956)

[2] M. E. Senko, H. M. Dunn, J. Weidenborner and H. Cole, *ibid.*, **12**, 76 (1959)

[3] W. Heike, *Z. anorg. allg. Chem.*, **118**, 264 (1927)

[4] Y. Tanaka, *This Journal*, **38**, 137 (1968)

the path for the reaction, to split it into a sequence of possible steps, and then to identify the rate determining step. In general, in consideration of the topochemical character, many rate equations have been derived and their functional forms depend on the mechanism controlling the reaction, the size and the shape of the reacting particles. The models which have been proposed for solid state reactions in the mixture of fine powders can be divided into three major classes according to the reaction geometry, *i. e.*, (1) diffusion of reactants through the continuous product layer, (2) nuclei formation and growth and (3) phase-boundary reactions. In many solid state reaction systems at atmospheric pressure, in which one of the processes mentioned above is the rate determining step, the reaction rate is mostly controlled by the diffusion process[5~8]. On the other hand, there is an example that in the ZnO-Al_2O_3 system the initial stage of the reaction is phase-boundary controlled and the latter stage is diffusion controlled[9].

In the present research, the kinetic treatment of the solid state reaction in the Zn-As system and the considerations concerning the reaction mechanism were attempted.

Experimentals

Materials

Extra pure zinc and arsenic were obtained from Merck Co. and Nakarai Chemicals Ltd. and mixed thoroughly with the atomic ratio of $Zn : As = 3 : 2$ in an agate mortar. The particle size of the powder mixture was 200~250 mesh. The samples were always stored in a vacuum desiccator in order to prevent from oxidation.

High pressure apparatus and procedure

A compact cubic anvil apparatus was used for compression. The details of the construction and the calibration of the apparatus were reported earlier[10]. The sample of about 150 mg was packed in a cylindrical pyrophyllite capsule. A 6 mm-diameter glassy carbon heater containing the sample capsule was inserted into the pressure transmitting pyrophyllite cube having an edge length of 13 mm. Temperature was measured by the chromel-alumel thermocouples which were taken out through the pyrophyllite gaskets between the anvils. The junction of the thermocouple was situated in contact with the outside center of the heater. The temperature differences between the inside and the outside of the heater were corrected previously and the temperature was controlled within ±3°C. Temperature was elevated up to the appointed value in a minute after pressure was generated. In each run, an almost instantaneous quench from the elevated temperature to the room temperature was achieved by cutting off the electric current, and then pressure was released in about three minutes.

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5) D. L. Fresh, *J. Phys. Chem.*, **70**, 3198 (1966)
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The quantitative analysis was carried out in the following way. The reaction of the powder mixture of Zn : As=3 : 1 at 400°C and 20 kbar took place completely for an hour. The excess zinc was removed from the sample in the 5N-NaOH solution. Thus the pure tetragonal Zn_3As_2 was obtained. The calibration curve between the weight ratio and the X-ray intensity ratio, of Zn_3As_2 to As, was made by adding the pure Zn_3As_2 to As. The peak of As, $d=2.77$Å ($2\theta=32.3°$) and the peak of Zn_3As_2, $d=3.42$Å ($2\theta=26.1°$) were utilized for the quantitative analysis, because the strongest peak of Zn_3As_2, $d=2.09$Å ($2\theta=43.3°$) was overlapped with that of Zn.

In order to determine the diffusing species, the Kirkendall effect was examined by using a Pt marker and the measurement of the Electron Microprobe X-ray Analyzer (Shimadzu EMX-SM) was also carried out.

Results and Discussions

Identification of reaction products

The X-ray diffraction pattern of the pure product is shown in Fig. 1 (a). It was confirmed that the X-ray diffraction pattern of this product was completely in accordance with that of the product synthesized at atmospheric pressure and also with that of the tetragonal Zn_3As_2 reported by Cole *et al.* except for the several weak peaks. In the range of the starting ratio of Zn/As=1/2~3, the product obtained at temperatures of 150~300°C and pressures of 20~40 kbar was only the tetragonal Zn_3As_2. No reaction took place at 100°C. Fig. 1 (b) shows the X-ray diffraction pattern in the case of the equal weight mixture of Zn_3As_2-As. According to Kennedy *et al.*[11], the melting point of zinc increases

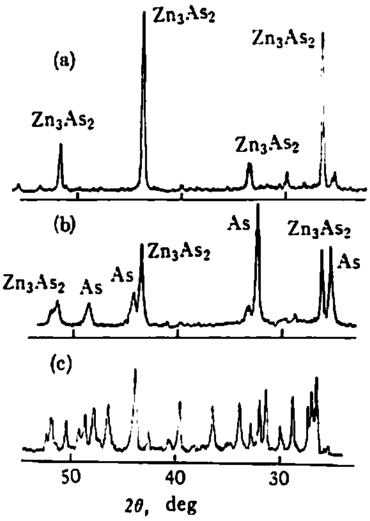

Fig. 1 X-ray diffraction patterns of (a) the pure product Zn_3As_2, (b) the Zn_3As_2-As mixture (weight ratio: As/Zn_3As_2=1) and (c) the high pressure phase (40 kbar, 400°C)

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[11] G. C. Kennedy and R. C. Newton, "Solids under Pressure", p. 163, ed. by W. Paul and D. M. Warschauer, McGraw-Hill, New York (1963)

linearly with pressure from 419°C at atmospheric pressure to about 600°C at 50kbar. According to Chaney *et al.*[12], the melting point of arsenic increases also linearly with pressure from 818°C at 36 bar to about 870°C at 15 kbar. On the other hand, the melting point of Zn_3As_2 is 1015°C as seen in the phase diagram of the Zn-As system. Consequently, both the reactants and the product are all in solid phase under the present experimental conditions. The reaction in the Zn-As system is regarded as a solid state reaction.

At 40 kbar the new product was obtained in a few minutes at 400°C and in more than an hour at 300°C. The composition of the product at high pressure was Zn_3As_2 because the unreacted zinc and arsenic were not observed at all. The crystal structure of the product is not clear. Fig. 1 (c) shows the X-ray diffraction pattern of the new product at 400°C and 40 kbar. This new product does not agree with the data of Jayaraman *et al.*[13] and Banus *et al.*[14] reported as the high pressure phases of Zn_3As_2. At above 600°C other unknown high pressure products were formed together with zinc oxide as a by-product.

Yield *vs.* time curves

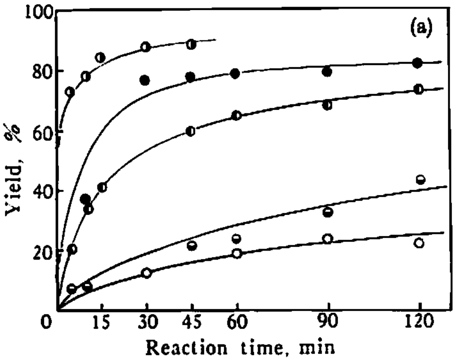

Fig. 2 (a)

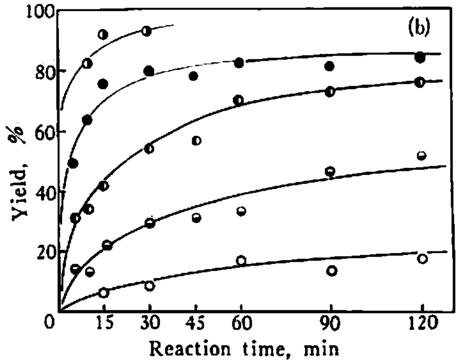

Fig. 2 (b)

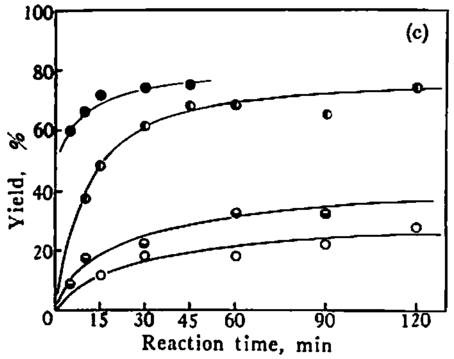

Fig. 2 (c)

Fig. 2 Relation between reaction yields and reaction time
(a) 20 kbar, (b) 30 kbar (c) 40 kbar
○ : 150°C, ◒ : 200°C, ◐ : 250°C,
● : 300°C, ◑ : 400°C

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[12] P. E. Chaney and S. E. Babb, Jr., *J. Chem. Phys.*, **43**, 1071 (1965)

[13] A. Jayaraman, T. R. Ananthararaman and W. Klement, Jr., *J. Phys. Chem. Solids*, **27**, 1605 (1966)

[14] M. D. Banus and M. C. Lavine, *High Temperatures-High Pressures*, **1**, 269 (1969)

The reaction yield can be expressed as follows;

$$\frac{\text{weight of } Zn_3As_2 \text{ formed}}{\text{total weight of the specimen}} \times 100\,(\%).$$

The reaction yield-time curves for various experimental conditions are shown in Fig. 2. The experimental errors were within ±7% under the condition of 250°C and 20 kbar. It can be considered that they are mainly due to the size distribution of the spherical particles, the surface state of the specimen and the temperature control. It was found that the size distribution of the particles had an appreciable influence on the reaction yields. Namely, the reaction yields of the 350~400 mesh mixture were higher by about 10~15% than those of the 200~250mesh mixture at 250°C and 20kbar. The yield *vs.* time curve for the 350~400mesh mixture almost falls on the curve at 300°C and 20kbar shown in Fig. 2. Fig. 2 indicates that the reaction yields become saturated abruptly after about 30 minutes. Then we consider the two stages separately, such as the initial and the latter process of the reaction.

Initial process of the reaction

Sharp *et al.*[15,16] proposed the method by which the kinetics of solid state reactions could be analyzed. We utilized their data in order to decide the rate determining process of this reaction. In consequence, it was found that the yield-time curves shown in Fig. 2 corresponds to the typical diffusion controlled process. With increasing pressure, however, the rate of the initial process was not retarded, but accelerated above 200°C. Therefore, the initial process does not seem to be diffusion controlled, but phase-boundary controlled. On the assumption that the formation rate of Zn_3As_2 is in proportion to the product between the unreacted Zn and As, we applied the following second-order rate equation[9];

$$\frac{d\alpha}{dt}=k_i(1-\alpha), \qquad (1)$$

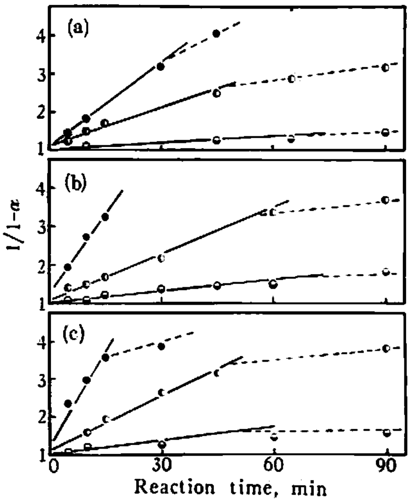

Fig. 3 Relation between $1/(1-\alpha)$ and t
(a) 20 kbar, (b) 30 kbar, (c) 40 kbar
⊖ : 200°C, ◐ : 250°C, ● : 300°C

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[15] J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, *J. Amer. Ceram. Soc.*, **49**, 379 (1966)

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Table 1 Kinetic data for the reaction; $3Zn+2As \rightarrow Zn_3As_2$

Pressure (kbar)	Temperature (°C)	Initial rate constant, $k_i \times 10^3$ (min^{-1})	Rate constant, $k_d \times 10^4$ (min^{-1})	Diffusion coefficient, $D \times 10^{12}$ ($cm^2 \cdot sec^{-1}$)
20	150	2.3	4.7	7.1
	200	6.3	15	23
	250	31	35	53
	300	80	45	69
30	150	2.5	2.5	3.8
	200	8.3	12	18
	250	37	30	46
	300	100	40	61
40	150	4.3	1.8	2.7
	200	8.6	10	15
	250	40	26	40

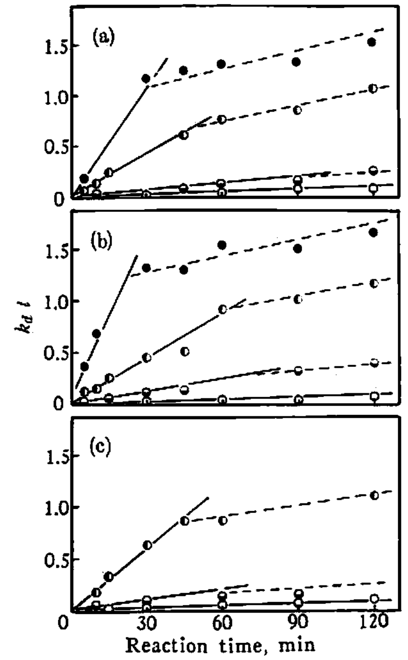

Fig. 4 Relation between $k_d t$ and t
(a) 20 kbar, (b) 30 kbar, (c) 40 kbar
○ : 150°C, ◒ : 200°C, ◐ : 250°C, ● : 300°C

where α is the yield at time t and k_i is the initial rate constant. Integrating eq. (1), we have

$$\frac{1}{1-\alpha}=k_i t+1. \qquad (2)$$

The plots of $1/(1-\alpha)$ *vs.* t are given in Fig. 3 (a), (b) and (c) for 20, 30 and 40 kbar, respectively. It is observed that the values of $1/(1-\alpha)$ increase approximately linearly with time in the initial stage of the reaction as shown by the solid lines. The values of the initial rate constant calculated by the slopes of the straight lines are listed in Table 1.

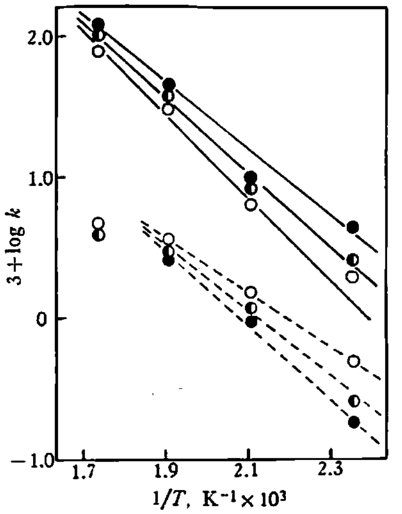

Fig. 5 Plots of log k against $1/T$
—— initial process, - - - diffusion process
○ : 20 kbar, ◐ : 30 kbar, ● : 40 kbar

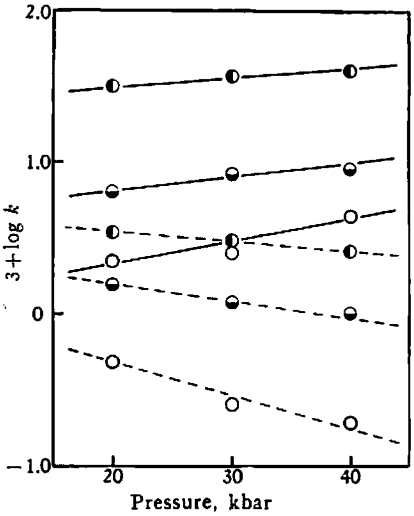

Fig. 6 Plots of log k against pressure
—— initial process, - - - diffusion process
○ : 150°C, ◒ : 200°C, ◐ : 250°C

The apparent activation energy E_a can be estimated from the plots of log k against $1/T$ by the following relation;

$$\left(\frac{\partial \ln k}{\partial T}\right)_P = \frac{E_a}{RT^2} . \tag{3}$$

The Arrhenius plots for the initial process at 20, 30 and 40 kbar are presented by the solid lines in Fig. 5. The apparent activation volume $\Delta V^{\ast}$ can be estimated by the following relation;

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\ast}}{RT} . \tag{4}$$

The solid lines in Fig. 6 show the relation between log k_i and pressure for the initial process at 150, 200 and 250°C. The values of E_a and $\Delta V^{\ast}$ calculated are given in Table 2.

As seen in Table 1, the initial process is accelerated with pressure. In the case of the Zn-P system, however, the corresponding Zn_3P_2 formation reaction was retarded with pressure over the entire range. The rate constants of the initial process are 5∼20 times larger than those of the latter process, which will be discussed below. From the above observations, it can be considered that the rate of the combination reaction with zinc and arsenic at the interface between the product layer and arsenic is not faster than that of the diffusion of zinc through the product layer, because of the existence of many vacancies in the product layer. Therefore, it is assumed that the rate-determining factor is phase-boundary in the initial process, in which at first, the disorder solid solution will be formed by zinc and arsenic at the interface between the product layer and arsenic and then the product is formed with the mechanism analogous to the ordinary chemical reactions.

Latter process of the reaction

As seen in Fig. 2, the rate of the increase of the reaction yields in the latter process is retarded with increasing pressure below 250°C. The yield *vs.* time curves are parabolic. For these reasons, the

Table 2 Apparent activation energies and activation volumes for the reaction; $3\,Zn+2As\rightarrow Zn_3As_2$

Activation energy E_a(kcal/mol)			Activation volume $\Delta V^{\ast}$(cm^3/mol)		
Pressure (kbar)	Initial process	Volume diffusion	Temperature (°C)	Initial process	Volume diffusion
20	12.3	9.1	150	−0.5	1.4
30	11.8	10.6	200	−0.4	0.8
40	10.3	11.7	250	−0.3	0.7

diffusion through the product layer can be considered to be the rate determining process. Then the Dünwald-Wagner diffusion rate equation was applied[17,18].

$$1-\alpha=\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-n^2k_dt\right), \qquad (5)$$

where the rate constant k_d is equal to π^2D/a^2 in the diffusion controlled process, a the radius of spherical particles, D the diffusion coefficient based on Fick's laws and n the integer. Giess[19] tabulated the relation of k_dt *vs.* α by calculating eq. (5). We can find in the table the values of k_dt corresponding to α measured experimentally at time t. The values of k_d can be obtained from the slopes of the lines in Fig. 4 which shows the relation of k_dt *vs.* t. The two parts in Fig. 4 will give the reasonable suggestion to divide the reaction into the initial and the latter process. The diffusion coefficient D can be calculated by the relation, $D=k_da^2/\pi^2$. The values of k_d and D are also included in Table 1. Comparing eq. (5) with other diffusion rate equations[20,21], the significant difference could not be confirmed beyond the experimental error. In Fig. 5, the Arrhenius plots for the diffusion process are presented by the dashed lines at 20, 30 and 40 kbar. In Fig. 6, the values of log k_d is plotted against pressure for the diffusion process by the dashed lines at 150, 200 and 250°C. The values of E_a and $\Delta V^{\ast}$ are included in Table 2. For the self-diffusion of single crystal of zinc, according to Liu and Drickamer[22], the activation enthalpies are 19.6~25.0 kcal/mol within the limits of 8 kbar and the activation volumes at 307°C are 2.68~3.62 cm^3/mol near 10 kbar. Similarly, the activation energies are reported to be 21.9~23.0 kcal/mol at atmospheric pressure[23] and the temperature dependence of the activation volumes is reported to be 3.97~4.28 cm^3/mol in the temperature range of 350~400°C[24]. The values of the apparent activation energies and the activation volumes for the diffusion of zinc in the Zn-As system are 9~12 kcal/mol up to 40 kbar and 0.7~1.4 cm^3/mol in the temperature range of 150~250°C. These values are very small as compared with those for the self-diffusion reported by

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17) H. Dünwald and C. Wagner, *Z. physik. Chem.*, **B 24**, 53 (1934)
18) B. Serin and R. T. Ellickson, *J. Chem. Phys.*, **9**, 742 (1941)
19) E. A. Giess, *J. Amer. Ceram. Soc.*, **52**, 74 (1969)
20) W. Jander, *Z. anorg. allg. Chem.*, **163**, 1 (1927)
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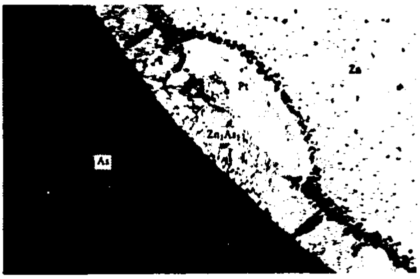

Fig. 7 Cross section of the reaction interface (Sample, ×100)

Liu and Drickamer, Peterson *et al.* and Gilder *et al.*. On the other hand, the activation parameters for the diffusion of zinc in the Zn-P system are 14.2～17.5 kcal/mol up to 27 kbar and 3.3～4.1 cm^3/mol in the temperature range of 200～250°C4), whose values are comparatively in good agreement with those of the references. The differences among Zn-As system, Zn-P system and Zn self-diffusion can be considered to be due to the differences in vacancy concentration and medium.

Diffusion coefficient and Kirkendall effect

The self-diffusion coefficient of zinc at atmospheric pressure increases from $5.9\times10^{-11}cm^2/sec$ at 240°C to $3.7\times10^{-10}cm^2/sec$ at 290°C, and at 307°C it decreases from $8.3\times10^{-10}cm^2/sec$ at atmospheric pressure to $1.9\times10^{-10}cm^2/sec$ at 10 kbar22). At 250°C the diffusion coefficient indicated in Table 1 may be in good agreement with the above values. In the present system the diffusion of zinc has smaller temperature and pressure coefficients than the self-diffusion, so that the activation parameters become smaller than those of the self-diffusion. Above 300°C, temperature in particular has little influence on the diffusion coefficient as expected in the lower temperature, which comes from the saturated phenomena in the yield-time curve.

In many diffusion controlled reactions, the diffusion of one component of the reactants generally governs the reaction rate. By using a piece of platinum foil, the inert marker studies were carried out under the condition of 20 kbar, 400°C and 10 hr in order to identify the diffusive species in the Zn-As system. The marker placed on the Zn-As boundary moved in the direction of the Zn-Zn_3As_2 interface, as shown in Fig. 7. The EMX measurement also indicates undoubtedly that the product layer exists on the side of As and that a Pt marker exists on the side of Zn. Therefore, the diffusing species is zinc and there is no counter-diffusion. Such a pronounced Kirkendall effect suggests that the diffusion of zinc originates from the vacancy mechanism. It is believed that the vacancies are produced when the crystal lattice of the product phase is formed at the interface between the product and arsenic. Presumably, such vacancy formation is not caused by the thermal process, but by the imperfect formation of the crystal lattice25,26). The activation parameters for the diffusion process can be considered as the combination of the changes associated with the vacancy formation and the migration. In the vacancy mechanism both values are positive. Only the contribution from the vacancy migration may be enough to be considered, because of the existence of relatively many vacancies.

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25) M. Onishi, Y. Wakamatsu and T. Sasaki, *Nippon Kinzoku Gakkaishi*, 37, 724 (1973)

26) M. Onishi and Y. Wakamatsu, *ibid.*, 37, 1279 (1973)

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This would be the reason why the activation parameters in the Zn-As system are smaller than those of the self-diffusion of zinc.

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