Observation on Isothermal Reactive Diffusion between Solid Fe and Liquid Sn

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The kinetics of the reactive diffusion between solid Fe and liquid Sn was experimentally examined using Fe/Sn diffusion couples. The diffusion couples were prepared by an isothermal bonding technique and then immediately annealed in the temperature range of $T = 703$–$773$ K for various times up to $t = 90$ ks (25 h). During annealing, a compound layer of FeSn$_3$ is formed at the initial Fe/Sn interface in the diffusion couple and grows mainly into the liquid Sn specimen. At $T = 703$ K, the compound layer indicates a needle-like microstructure in the early stages but a columnar microstructure in the late stages. On the other hand, at $T = 723$–$773$ K, only the columnar microstructure is realized in the compound layer within the experimental annealing times. The mean thickness of the compound layer is proportional to a power function of the annealing time. The exponent $n$ of the power function is mostly close to 0.6. In the early stages at $T = 703$ K, however, $n$ is equal to unity within experimental uncertainty. If growth of a compound layer with a uniform thickness is controlled by volume diffusion, $n$ is equivalent to 0.5. In contrast, $n$ is equal to unity for longitudinal growth of a needle-like grain, even though volume diffusion is the rate-controlling process. This is the case for the layer growth in the early stages at $T = 703$ K. Since independent longitudinal growth of each columnar grain contributes to the growth governed by volume diffusion, $n$ is slightly greater than 0.5 for the compound layer with the columnar microstructure. Consequently, the discontinuous variation of $n$ corresponds to the transition from the needle-like microstructure to the columnar microstructure. 

Keywords: reactive diffusion, intermetallic compounds, soldering, bulk diffusion, iron–tin system

1. Introduction

The reactive diffusion between solid Cu and liquid Al was experimentally observed in a previous study. In this experiment, Cu/Al diffusion couples were prepared by an isothermal bonding (IB) technique and then annealed at temperatures of $T = 973$–$1073$ K. In the IB technique, the solid Cu and liquid Al specimens are separately preheated at the same temperature as the annealing temperature in a vacuum. After sufficient preheating, the Cu and the Al are bonded with each other and then annealed immediately. Hence, in the IB technique, the temperatures of the Cu and the Al are equivalent and remain constant during preheating, bonding, and annealing. In the Cu/Al diffusion couple, layers of the $\beta$, $\gamma_1$, and $\gamma_2$ phases are formed at the initial Cu/Al interface owing to annealing. According to a recent phase diagram in the binary Cu–Al system, the $\beta$, $\gamma_1$, and $\gamma_2$ phases are the only stable compounds at $T = 973$–$1073$ K. The mean thickness of each compound layer is proportional to a power function of the annealing time for the $\beta$ layer, the exponent of the power function is close to 0.5 at $T = 1023$–$1073$ K but nearly equal to 0.25 at $T = 973$ K. On the other hand, for the $\gamma_1$ layer, the exponent takes values between 0.25 and 0.5 at $T = 1023$–$1073$ K but that smaller than 0.25 at $T = 973$ K. The exponent smaller than 0.5 indicates that boundary diffusion contributes to the growth of the compound layer. Thus, the rate-controlling process of the layer growth varies depending on the annealing temperature in a different manner for each compound.

The IB technique was also used to observe experimentally the reactive diffusion between solid Fe and liquid Al in previous studies. In these experiments, Fe/Al diffusion couples were isothermally annealed at $T = 973$–$1073$ K and $T = 1053$–$1093$ K. A phase diagram in the binary Fe–Al system shows that FeAl$_3$, Fe$_2$Al$_5$, and FeAl$_2$ are the stable compounds at $T = 973$–$1093$ K. After annealing, however, Fe$_2$Al$_5$ and FeAl$_3$ were observed, but FeAl$_2$ was not recognized clearly. Similar experiments were conducted by Bouché et al. and Bouayad et al. In their experiments, Fe/Al diffusion couples were prepared by a melt bath (MB) technique and then isothermally annealed at $T = 973$–$1173$ K. According to their observations, only Fe$_2$Al$_5$ and FeAl$_3$ are produced as visible layers during annealing. The thickness is much smaller for FeAl$_3$ than for Fe$_2$Al$_5$, and irregular tongue-like morphology is realized for Fe$_2$Al$_5$. Owing to the irregular morphology, the growth rate of Fe$_2$Al$_5$ could not be reliably determined in their experiments. Also in a previous study, the Fe$_2$Al$_5$ layer indicates the irregular tongue-like morphology at $T = 973$–$1023$ K. At $T = 1053$–$1093$ K, however, Fe$_2$Al$_5$ is formed as a rather uniform layer. Thus, the morphology of Fe$_2$Al$_5$ varies depending on the annealing temperature. Such temperature dependence of the morphology could be detected by the IB technique but not by the MB technique.

As previously mentioned, all the stable compounds are formed in the reactive diffusion between solid Cu and liquid Al. On the other hand, all the stable compounds are not necessarily produced as visible layers in the reactive diffusion between solid Fe and liquid Al. Hence, the growth behavior of compounds during reactive diffusion varies depending on the combination of solid and liquid metals. To obtain information for the dependence of the growth behavior on the combination, the reactive diffusion between solid Fe and liquid Sn was experimentally examined in the present study. Diffusion couples consisting of pure Fe and Sn were prepared by the IB technique and then isothermally annealed in the temperature range of $T = 703$–$773$ K. The microstructure of the annealed diffusion couple was observed in a metallographical manner. The rate-controlling process for compound growth was discussed on the basis of the observation.

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2. Experimental

Polycrystalline columnar specimens with a length of 5 mm were cut from a commercial rod of pure Fe with a diameter of 8 mm and a purity of 99.7\% in a manner similar to a previous study. The Fe rod contains a trace of C, 0.01 mass\% of Si, 0.25 mass\% of Mn, 0.004 mass\% of P, 0.004 mass\% of S, 0.01 mass\% of Cu, 0.01 mass\% of Ni and 0.01 mass\% of Cr as impurities. The columnar specimens were separately annealed in evacuated silica capsules at a temperature of 1173 K for a time of 2 h, followed by air cooling without breaking the capsules. The top and bottom flat-surfaces of each annealed columnar specimen were mechanically polished on # 800–4000 emery papers.

A commercial rod of pure Sn with a diameter of 6 mm and a purity of 99.9\% was cut into columnar specimens with a length of 30 mm. Each polished Fe specimen was encapsulated together with a columnar Sn specimen in an evacuated silica capsule with an inner diameter of 8.5 mm. The silica capsule was isothermally preheated for a time of 1.8 ks (0.5 h) in the temperature range between 703 and 773 K. During preheating, the solid Fe specimen was separated from the Sn melt in the silica capsule. After preheating, a flat surface of the solid Fe specimen was immediately contacted with that of the Sn melt with a diameter of 8.5 mm and a length of 15 mm to prepare a columnar Fe/Sn diffusion couple. The diffusion couple was isothermally annealed for various times up to 90 ks (25 h) at the same temperature as preheating, followed by water quenching with breaking the capsule. The annealing temperature and time are denoted by \( T \) and \( t \), respectively.

Cross-sections of the annealed diffusion couple were mechanically polished on # 800–4000 emery papers and then finished using diamond with a diameter of 1 \( \mu \)m. The microstructure of the cross-section was observed with a differential interference contrast optical microscope (DICOM) and with a back-scattered electron image (BEI) by scanning electron microscopy (SEM). Concentrations of Fe and Sn in each phase on the cross-section were measured by electron probe microanalysis (EPMA) using pure Fe and Sn with a purity of 99.99\% as standard specimens under the following conditions: the accelerating voltage was 20 kV; the probe current was 5 nA; the analyzing crystals for Fe-K\(_\alpha\) and Sn-L\(_\alpha\) were lithium fluoride (LiF) and polyethylene terephthalate (PET), respectively; and the chemical composition was evaluated by a standard ZAF correction technique.

3. Results and Discussion

3.1 Microstructure

A typical DICOM photograph of the cross-section for a diffusion couple annealed at \( T = 773 \) K for \( t = 14.4 \) ks (4 h) is shown in Fig. 1. In this figure, the lower and upper regions are the Fe and Sn specimens, respectively. As can be seen, a compound layer with a columnar microstructure is observed between the Fe and the Sn, and the longitudinal direction of each columnar grain is almost normal to the initial Fe/Sn interface in the diffusion couple. Concentration profiles of Fe and Sn across the compound layer along the direction normal to the Fe/Sn interface were measured by EPMA. A result for the diffusion couple in Fig. 1 is indicated in Fig. 2. In this figure, the ordinate and the abscissa show the mol fraction \( y_i \) of component \( i \) and the distance \( x \), respectively, and open circles and squares indicate the mol fractions \( y_{Fe} \) and \( y_{Sn} \), respectively. As can be seen, the compound layer is FeSn\(_2\). According to a recent phase diagram in the binary Fe–Sn system, FeSn and FeSn\(_2\) are the stable compounds at \( T = 703–773 \) K. Nevertheless, only FeSn\(_2\) was observed in all the annealed diffusion couples. Here, FeSn\(_2\) is an intermetallic compound with the tetragonal CuAl\(_2\) type crystal structure. The FeSn\(_2\) layer grows mainly towards the Sn in the diffusion couple.

Various BEI photographs of the cross-section for different diffusion couples are shown in Fig. 3. The annealing temperature is \( T = 703 \) K in Fig. 3(a)–3(b) and \( T = 773 \) K in Fig. 3(c), and the annealing time is \( t = 3.6 \) ks (1 h) in Fig. 3(a) and 3(c) and \( t = 60 \) ks (16.7 h) in Fig. 3(b). In this figure, the brightest region on the upper side is the Sn,
the darkest region on the lower side is the Fe, and the intermediate region between the Fe and the Sn is the FeSn$_2$ layer. At $T = 703$ K, the FeSn$_2$ layer consists of fine needle-like grains for $t = 3.6$ ks (1 h) but coarse columnar grains for $t = 60$ ks (16.7 h). However, at $T = 773$ K, the FeSn$_2$ layer is composed of coarse columnar grains even for $t = 3.6$ ks (1 h). Although the longitudinal direction of the columnar grain is almost normal to the Fe/Sn interface in Fig. 3(b) and 3(c), that of the needle-like grain is randomly distributed in Fig. 3(a). The needle-like morphology as well as the columnar morphology indicates the anisotropy of growth behavior for FeSn$_2$ due to the tetragonal crystal structure.

The reactive diffusion between solid Fe and liquid Sn was experimentally observed also by van Beek et al.\textsuperscript{10} In this experiment, diffusion couples consisting of pure Fe and the Sn-rich liquid solution phase saturated with Fe were prepared by heating at $T = 543$ K for $t = 30$ s and then isothermally annealed at $T = 573$–753 K for various times. Thus, the initial and boundary conditions are dissimilar between the diffusion couple in the present study and that by van Beek et al. Nevertheless, the FeSn$_2$ layer with a columnar microstructure was observed in the diffusion couple also by van Beek et al.\textsuperscript{10} Furthermore, they reported that the longitudinal direction of the columnar grain was parallel to the $c$ axis of FeSn$_2$. This means that the growth of FeSn$_2$ occurs faster along the $c$ axis than along the $a$ axis. For reactive diffusion in binary alloy systems, the growth rate of a compound layer is predominantly determined by the interdiffusion coefficient of the growing compound.\textsuperscript{11–18} Consequently, the interdiffusion coefficient of FeSn$_2$ should be much greater along the $c$ axis than along the $a$ axis. At $T = 703$ K, fine needle-like grains of FeSn$_2$ are randomly distributed in the early stages as shown in Fig. 3(a). Among these, the grains with the $c$ axis almost normal to the Fe/Sn interface predominantly contribute to faster growth of the FeSn$_2$ layer. As a result, the columnar microstructure composed of such predominant FeSn$_2$ grains is realized in the late stages as indicated in Fig. 3(b). Thus, the transition from the needle-like microstructure to the columnar microstructure occurs at a certain critical annealing time. The higher the annealing temperature is, the shorter the critical annealing time becomes. Hence, at $T = 773$ K, the columnar microstructure is actualized even for $t = 3.6$ ks (1 h) as shown in Fig. 3(c).

### 3.2 Growth behavior of intermetallic layer

In OM photographs of the cross-section like Fig. 1, the FeSn$_2$ layer is clearly distinguishable from the Fe and the Sn. Hereafter, the FeSn$_2$ layer is called the intermetallic layer. A schematic microstructure of the intermetallic layer on cross-section $i$ is shown in Fig. 4. From the OM photograph, the area $A_i$ of the intermetallic layer corresponding to the partial length $w_i$ of the initial Fe/Sn interface in Fig. 4 was

![Fig. 3 BEI photographs of cross-section for the diffusion couples annealed under the following conditions: (a) $T = 703$ K, $t = 3.6$ ks (1 h); (b) $T = 703$ K, $t = 60$ ks (16.7 h); and (c) $T = 773$ K, $t = 3.6$ ks (1 h).](image)

![Fig. 4 Schematic microstructure of intermetallic layer on cross-section $i$.](image)
measured on each cross-section, and then the sums $A$ and $w$ were obtained as
\[ A = \sum_{i=1}^{m} A_i \] (1a)
and
\[ w = \sum_{i=1}^{m} w_i \] (1b)
from $A_i$ and $w_i$, respectively, where $m \geq 5$. Using the values of $A$ and $w$, the mean thickness $l$ of the intermetallic layer was evaluated at each annealing time $t$ by the following equation:\[ l = \frac{A}{w}, \] (2)
The results for $T = 723, 743, 763$ and $773 \text{ K}$ are plotted as open rhombuses, squares, inverse-triangles and circles, respectively, in Fig. 5. On the other hand, for $T = 703 \text{ K}$, the results at shorter and longer annealing times are indicated as open double-circles and triangles, respectively. In each stage, $l$ is expressed as a power function of $t$ by the following equation:\[ l = k (\frac{t}{t_0})^n, \] (3)
Here, $t_0$ is unit time, 1 s. It is adopted to make the argument $t/t_0$ of the power function dimensionless. The proportionality coefficient $k$ has the same dimension as the thickness $l$, but the exponent $n$ is dimensionless. The dimensionless argument of the power function is essentially important; otherwise the dimension of $k$ varies depending on the value of $n$. From the points plotted for $T = 723\text{--}773 \text{ K}$ in Fig. 5, $k$ and $n$ were estimated by the least-squares method as shown with various straight lines. The estimated values are indicated in Fig. 5. On the other hand, for $T = 703 \text{ K}$, the open double-circles and triangles lie well on straight lines with larger and smaller gradients at the shorter and longer annealing times, respectively. Hereafter, the stages at the shorter and longer annealing times are called stages I and II, respectively. In each stage, $l$ is expressed as a power function of $t$ by eq. (3). Thus, $k$ and $n$ were estimated by the least-squares method in each stage at $T = 703 \text{ K}$. The estimation gives $k = 1.73 \times 10^{-7} \text{ m}$ and $n = 0.516$ for stage II. On the other hand, for stage I, $n$ is evaluated to be $0.993 \pm 0.068$ and thus equal to unity within experimental uncertainty.
As a consequence, considering exactly $n = 1$, we obtain $k = 1.82 \times 10^{-8} \text{ m}$ for stage I. The values of $k$ and $n$ in stages I and II yield the two solid lines intersected at $t = t_c = 12.2 \text{ ks (3.38 h)}$ in Fig. 5. Here, $t_c$ is the critical annealing time for the transition from stage I to stage II. The exponent $n$ is equal to unity at $t < t_c$ but rather close to 0.5 at $t > t_c$. For the growth of the intermetallic layer during reactive diffusion, $n$ varies depending on the rate-controlling process.\(^3\)(4) Hence, we may anticipate that the discontinuous variation of $n$ at $t = t_c$ corresponds to the transition of the rate-controlling process.

### 3.3 Rate-controlling process
The exponent $n$ is plotted against the annealing temperature $T$ as open circles with error bars in Fig. 6. At $T = 703 \text{ K}$, however, $n$ is shown only for stage II. As can be seen, $n$ is typically greater than 0.5, though the plotted points are slightly scattered. When the layer growth is controlled by the interface reaction at the migrating interface, $n$ is equal to unity. On the other hand, $n$ is equivalent to 0.5, if the volume diffusion in the constituent phases of the diffusion couple is the rate-controlling process. Hereafter, the relationships with $n = 0.5$ and 1 are called the parabolic and linear relationships, respectively. Therefore, we expect that the
interface reaction is the rate-controlling process for stage I but the volume diffusion is that for stage II. Such a discontinuous transition of the rate-controlling process was actually observed in a previous study. For precipitation of a second phase into an untransformed matrix in binary alloy systems, the growth of the second phase controlled by volume diffusion usually obeys the parabolic relationship. If the shape of the second phase is a paraboloid of revolution or a parabolic cylinder, however, the longitudinal growth of the second phase occurs according to the linear relationship even for the diffusion rate-controlling process. As previously mentioned, the intermetallic layer grows mainly towards the Sn. Thus, the growth rate of the intermetallic layer is predominantly determined by the migration rate of the FeSn2/Sn interface. According to the BEI photographs for \( T = 703 \) K like Fig. 3(a) and 3(b), the intermetallic layer possesses the needle-like microstructure at \( t < t_c \) but the columnar microstructure at \( t > t_c \). At \( t < t_c \), each needle-like grain grows predominantly along the longitudinal direction. If the morphology of the growing cusp of the grain is considered to be a paraboloid of revolution or a parabolic cylinder, the longitudinal growth obeys the linear relationship. On the other hand, at \( t > t_c \), the parabolic relationship may hold for the layer growth with the columnar microstructure. As shown in Fig. 3(b), however, the FeSn2/Sn interface is slightly gathered due to independent longitudinal growth of each columnar grain. As a result, the linear relationship partially contributes to the layer growth, and hence \( n \) becomes slightly greater than 0.5. Consequently, the transition from stage I to stage II in Fig. 5 corresponds to that from the needle-like microstructure to the columnar microstructure. This transition should appear also at \( T = 723 \)–773 K. In this temperature range, however, only the columnar microstructure was observed for all the diffusion couples. Thus, \( t_c \) is much shorter than the experimental annealing times at \( T = 723 \)–773 K.

As mentioned earlier, the reactive diffusion between pure Fe and the Sn-rich liquid solution phase saturated with Fe was experimentally studied at \( T = 573 \)–753 K by van Beek et al. Thus, the initial and boundary conditions in their study are different from those in the present study. Only a FeSn2 layer was observed in the annealed diffusion couple in the present study, but a very thin FeSn layer as well as a FeSn layer was recognized in that by van Beek et al. Since there is no diffusional flux in the Sn-rich phase saturated with Fe, the formation of FeSn may be attributed to such initial and boundary conditions. Nevertheless, the thickness is much smaller for the FeSn layer than for the FeSn2 layer, and hence the growth of the intermetallic layer is predominated by that of the FeSn2 layer. Their result for the growth of the intermetallic layer is represented in Fig. 7. In this figure, the ordinate and the abscissa show the logarithms of \( l \) and \( t \), respectively, and open triangles, rhombuses, squares and circles indicate the results for \( T = 663, 693, 723 \) and 753 K, respectively. For \( T = 573 \) and 623 K, however, only two experimental points were obtained at each annealing temperature. Thus, the results for \( T = 573 \) and 623 K are omitted in Fig. 7. As can be seen, the plotted points are located well on a straight line at each annealing temperature. Hence, also in Fig. 7, \( l \) is expressed as a power function of \( t \) by eq. (3). From the plotted points in Fig. 7, \( k \) and \( n \) were estimated by the least-squares method as shown with various straight lines. The estimated values are shown in Fig. 7. Among these values, \( n \) is plotted against \( T \) as open squares with error bars in Fig. 6. For the open squares, \( n \) is close to 0.5 independent of \( T \). Since no diffusional flux exists in the Sn-rich phase, the gathered morphology of the migrating FeSn2/Sn surface does not influence the migration behavior. In such a case, the parabolic relationship holds for the layer growth controlled by volume diffusion. In Fig. 6, the annealing temperature range is higher for the open circles than for the open squares. Consequently, the open squares guarantee that volume diffusion is the rate-controlling process also for the open circles.

The results for \( T = 723 \) K in Figs. 5 and 7 are shown again as open circles and squares, respectively, in Fig. 8. Within the experimental annealing times in Fig. 8, \( l \) is slightly greater for the open squares than for the open circles. Since the intermetallic layer grows mainly into the Sn phase, the growth rate of the intermetallic layer is governed by the migration rate of the FeSn2/Sn interface as previously mentioned. Furthermore, the migration rate is determined by the diffusional flux balance at the FeSn2/Sn interface. For the open squares, however, there exits no diffusional flux in the Sn phase, and hence the migration rate is decided only by the diffusional flux in FeSn2. In contrast, for the open circles, the diffusional flux in the Sn works as a drag force against the interface migration. Consequently, \( l \) becomes slightly smaller for the open circles than for the open squares as indicated in Fig. 8.

As shown with the open circles in Fig. 6, \( n \) is rather insensitive to \( T \) at \( T = 703 \)–773 K. Considering an equivalent value of \( n \) at all the annealing temperatures, \( k \) and \( n \) were simultaneously evaluated from the open triangles, rhombuses, squares, inverse-triangles and circles for \( T = 703, 723, 743, 763 \) and 773 K, respectively, by the least-squares
method. The evaluated value of $n$ is shown in Fig. 6, and those of $k$ are plotted against $T$ as open circles with error bars in Fig. 9. In Fig. 9, the ordinate indicates the logarithm of $k$, and the abscissa shows the reciprocal of $T$. As can be seen, the open circles lie well on a straight line within experimental uncertainty. Therefore, the dependence of $k$ on $T$ is expressed by the following equation.

$$k = k_0 \exp\left(-\frac{Q_k}{RT}\right)$$

The pre-exponential factor $k_0$ and the activation enthalpy $Q_k$ in eq. (4) were evaluated from the open circles by the least-squares method as shown with a solid line in Fig. 9. The evaluation provides $Q_k = 100$ kJ/mol. If the parabolic relationship holds for the growth of the intermetallic layer, the dependence of $k$ on $T$ is estimated from the interdiffusion coefficients and the solubility ranges of the constituent phases in the diffusion couple by an appropriate analytical technique.\(^\text{11-18}\) As a result, $Q_k$ is compared with the activation enthalpy of the interdiffusion coefficient for each phase. Unfortunately, however, $n = 0.596$ for the open circles in Fig. 9, and hence the analytical technique\(^\text{11-18}\) cannot be used to estimate the value of $Q_k$ in a straightforward manner.

On the other hand, as shown in Figs. 6 and 7, the parabolic relationship almost holds for the result by van Beek\(^\text{10}\). Instead of eq. (3) with $n = 0.5$, they used the following equation to describe the parabolic relationship.\(^\text{10}\)

$$l^2 = Kt$$

Here, $K$ is the parabolic coefficient with a dimension of m²/s. Inserting $n = 0.5$ into eq. (3) and combining eq. (5) with eq. (3), we obtain the relationship $K = K_0 t^n$ between $K$ and $k$. Although merely two values of $l$ were measured at each temperature of $T = 573$ and 623 K as mentioned earlier, $K$ was evaluated by the least-squares method at $T = 573$–753 K and then expressed as a function of $T$ by the following equation of the same formula as eq. (4).\(^\text{10}\)

$$K = K_0 \exp\left(-\frac{Q_k}{RT}\right)$$

The pre-exponential factor $K_0$ and the activation enthalpy $Q_k$ in eq. (6) were estimated by van Beek et al."\(^\text{10}\) as follows: $K_0 = 2.00 \times 10^{-7}$ m²/s and $Q_k = 83$ kJ/mol. A dashed line in Fig. 10 shows their estimation. As previously mentioned, however, the parabolic relationship does not hold in the present study. Nevertheless, for semi-quantitative comparison of $Q_k$, the values of $K$ for $T = 703, 723, 743, 763$ and 773 K were estimated from the open triangles, rhombuses, squares, inverse-triangles and circles, respectively, in Fig. 5 by the least-squares method. The estimated values of $K$ are plotted.
against $T$ as open circles with error bars in Fig. 10. In this figure, like Fig. 9, the ordinate and the abscissa show the logarithm of $K$ and the reciprocal of $T$, respectively. Although the open circles are rather scattered in Fig. 10, $K_0 = 2.18 \times 10^{-1} \, \text{m}^2/\text{s}$ and $Q_K = 170 \, \text{kJ/mol}$ are evaluated by the least-squares method as indicated with a solid line. As can be seen, $Q_K = 170 \, \text{kJ/mol}$ is almost twice greater than $Q_K = 83 \, \text{kJ/mol}$. As mentioned earlier, the volume diffusion in the Sn phase occurs for the diffusion couple used in the present study but not for that utilized by van Beek et al. Thus, information on the temperature dependence of the Sn-phase diffusion is included in $Q_K = 170 \, \text{kJ/mol}$ but not in $Q_K = 83 \, \text{kJ/mol}$. This may be the reason why $Q_K$ is mostly twice larger for the solid line than for the dashed line in Fig. 10.

4. Conclusions

To examine the kinetics of the reactive diffusion in the solid-Fe/liquid-Sn system, the Fe/Sn diffusion couples were prepared by the isothermal bonding technique and then immediately annealed at temperatures of $T = 703\,$–$\,$773 K. At these temperatures, FeSn$_2$ and FeSn are the stable intermetallic compounds in the binary Fe-Sn system. During annealing, however, only FeSn$_2$ is formed as a visible compound layer at the initial Fe/Sn interface in the diffusion couple and grows mainly towards the liquid-Sn.

The compound layer possesses the needle-like and columnar microstructures in the early and late stages, respectively, at $T = 703 \,$K. At $T = 723\,$–$\,$773 K, however, only the columnar microstructure is actualized at the experimental annealing times. The mean thickness of the compound layer increases in proportion to a power function of the annealing time. The exponent of the power function is typically close to 0.6. In the early stages at $T = 703 \,$K, however, the exponent is equal to unity within experimental accuracy. The discontinuous variation of the exponent is attributed to the transition from the needle-like microstructure to the columnar microstructure. In spite of such a transition, the compound growth is controlled by volume diffusion under the present annealing conditions.

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REFERENCES