Growth kinetics of antiphase domain in Ti$_3$Al intermetallic compound

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Abstract

Growth kinetics of antiphase domain (APD) which increases the yield strength of Ti$_3$Al by a factor of five, was investigated in Ti$_3$Al compounds with compositions of 22.6, 24.6 and 34.7 at.%Al by quenching from disordered state and subsequent isothermal annealing at 973–1173 K. The variation in APD size exhibited positive deviation from the conventional ‘parabolic-growth-law’ in the early stage in all the compounds, while negative deviations were observed in the late stage in all the compounds except the stoichiometric one (Ti–25 at.%Al). The variation in the APD size in the stoichiometric compound was numerically calculated by considering the variation in the long range order in the matrix $\langle S \rangle$ and that in the mobility of the APDBs which was enhanced by non-equilibrium excess vacancies which were introduced by the quenching. The calculated variations in APD size could be successfully fitted to the experimental results in the early stage, and therefore, the positive deviation was attributed to the enhancement of the mobility of APDBs by the excess vacancies. In the late stage, the segregation of excess atoms (i.e. Ti atoms in Ti-rich composition and Al atoms in Al-rich composition) was detected in the compounds of off-stoichiometric composition by energy-dispersive X-ray spectroscopy, while any heterogeneity of composition was not observed in the stoichiometric compound. Faceted APDBs were observed in this stage. The mechanism of the negative deviation was attributed to the segregation and the facet which decrease the mobility and/or the driving force of the APDB migration.

Keywords: Kinetics; APD; APDB; Ordering; Ti$_3$Al; Intermetallic compound; Excess vacancy; Diffusion; Mobility; Driving force; Parabolic-growth-law; Long range order parameter; Boundary; Migration; Calculation; Ultrafine microstructure

1. Introduction

Recently, extensive efforts have been made in trying to understand and predict the formation and the stability of ultrafine microstructures in many kinds of materials [1–3] since excellent properties of materials caused by the ultrafine microstructures were found [1–5]. Properties of some intermetallic compounds are significantly affected by antiphase domain (APD) structures, which are formed during the formation process of the ordered arrangement of different atom species. For example, the yield stress of Cu$_3$Au can be raised up to the double of that of Cu$_3$Au without APD by controlling the APD size [6]. Bend ductility of rapidly-solidified Fe-doped Ni$_3$Al, which contains fine APDs, is about ten times as large as that of B-doped Ni$_3$Al with coarse APDs [7].

Ti$_3$Al is one of the intermetallic compounds which have received much attention as advanced materials, such as high temperature structural materials for aerospace application [4,8] and functional materials for electronics devices, [9,10]. For about 30 years, Ti$_3$Al-based alloys have been developed as candidates of materials for components of aerospace turbine engine, such as compressor rotor and afterburner nozzle, because of its good oxidation resistance and strength-to-weight ratio at high temperatures up to 1000 K [8]. Some kinds of Ti–Al alloys containing Ti$_3$Al have already been applied for components of automobile engines, such as turbo-fan rotor and exhaust valve. Most of TiAl-based alloys consist mainly of $\gamma$-TiAl phase and $\alpha_2$-Ti$_3$Al phase [11]. The $\alpha_2$-Ti$_3$Al phase significantly affects the mechanical properties of Ti–Al based alloys [12,13]. Ti$_3$Al has the D0$_{19}$-type ordered structure which is based on the HCP structure [14]. Mechanical properties of Ti$_3$Al have been studied by many experiments using single crystals with various compositions focusing on the anisotropy [15–21]. Three kinds of slip systems, that is, $\{1\overline{1}00\} < 1\overline{1}20 >$
prism slip, (0001) < 1120 > basal slip and \{1121\} < 1126 > pyramidal slip, operate depending on the loading axis. The prism slip operates much more easily than the other slip systems. The critical resolved shear stress (CRSS) for the prism slip is considerably smaller than those for other slip systems at temperatures below 1000 K. The prism slips operate dominantly in the wide range of orientation, while the other slip systems operate only in limited orientations where the resolved shear stress for the prism slip is very small. This characteristic is common for fully ordered Ti3Al compounds with various concentrations of Al and alloy elements although the stress level depends on the composition.

More recently, it was found that the plastic behavior by the prism slip significantly depends on the APD size. For example, the CRSS for Ti3Al with average APD size of 35 nm was about six times higher than that of Ti3Al without APD [22]. It seems possible to improve the mechanical properties of Ti3Al by controlling the APD microstructure appropriately. Growth of APD in Ti3Al with stoichiometric composition has briefly investigated by Sastry and Lipsitt [23]. They measured the variation in APD size during isothermal annealing. They presented only small number of experimental data, although they analyzed the variation in APD size following the parabolic-growth law. They measured the APD size at only three annealing times for each annealing temperature. The measurements were performed only in Ti3Al with stoichiometric composition. Hence, the entire picture of the APD growth of Ti3Al has never been obtained. Kinetics of APD growth have been investigated experimentally and theoretically in other intermetallic compounds such as Cu3Au [24–26], Fe3Al [27], Ni3Fe [28], CuZn [29], FeCo [30] and so on. However, the experimental data and the theoretical consideration are not enough to predict and control the APD growth. The parabolic-growth-law is applicable in some cases [26,30] but not in other cases [24,28]. Dominant factors governing the mobility and the driving force of the APD boundary migration are still under discussion. Little has been understood on the relationships between APD growth rates and other thermodynamic aspects.

In the present study, the variations in APD size in Ti3Al compounds with three Al concentrations during isothermal annealings at various temperatures were investigated. The kinetics of APD growth in the stoichiometric Ti3Al is discussed by calculating the factors which govern the mobility and the driving force of the APD boundary (APDB) migration by taking the crystallographic and the thermodynamic characteristics of Ti3Al into account.

2. Experimental procedure

Three kinds of ingots of Ti3Al compound with the nominal compositions of Ti–23 at.%Al, Ti–25 at.%Al and Ti–33 at.%Al, were made by melting high-purity metals of 99.9 mass% Ti and 99.99 mass% Al more than six times with over-turning the ingots in an argon arc furnace. These compounds are hereafter denoted Ti–23Al compound, Ti–25Al compound and Ti–33Al compound, respectively. For homogenization, each ingot was crushed to fine pieces after the arc-melting, and then these fine pieces were remelted into the ingots by the repeated arc-melting more than six times with over-turning. The ingots were cut into alloy bars of about 10 × 10 × 50 mm3. The Ti3Al bars were wrapped with tantalum-foils and subsequently sealed into quartz capsules with high purity argon gas of about 20 kPa. They were annealed at 1273–1373 K for 72 ks for homogenization. The homogenization was carried out at different temperatures for each compound with different Al concentrations so that the phase separation in the α + c2 two phase region was avoided. The homogeneity of the ingots was verified by an electron probe microanalyzer (EPMA). The compositions of the Ti–23Al, Ti–25Al and Ti–33Al compounds were Ti–22.6 at.%Al, Ti–24.6 at.%Al and Ti–32.6 at.%Al, respectively.

Rods of about 3 × 3 × 5 mm3 were cut from the compound bars. The rods were loosely wrapped with tantalum foils, and then sealed into quartz capsules with high purity argon gas of about 20 kPa. The Ti–23Al, Ti–25Al and Ti–33Al compounds were respectively annealed in the α single phase region at 1373, 1393 and 1463 K for 1 h and then quenched into ice-water with the quartz capsules broken. Chips of 3 × 3 × 1 mm3 were cut from the quenched rods by spark machining. The chips were again wrapped with tantalum foil and sealed into quartz capsules with argon gas. They were isothermally annealed at five temperatures from 973 to 1173 K for 0.5–500 ks. Thin foils for transmission electron microscope (TEM) observation were made from the chips by mechanical grinding and electrolytic polish using the twin-jet method with a solution of 10 vol% perchloric acid–20 vol% glycerine–70 vol% methanol at 243 K [31].

The APDs were observed by a Hitachi H-800 TEM operated at an accelerating voltage of 200 kV. The images of APDs were obtained in dark field with superlattice reflection. The average linear intersection lengths of APDBs were measured from micrographs with more than two hundred intersections. There are three types of APDBs in D019 structure with different element displacement vectors of \( \mathbf{R}_1 = 1/6[2110], \mathbf{R}_2 = 1/6[1210], \mathbf{R}_3 = 1/6[1120] \) as shown in Fig. 1. The three types of displacement vector of APDBs are completely equivalent to each other in the manner of crystallography. Any displacement vector is identical to one of the three elemental displacement vectors since all of possible displacement vector is expressed as a sum of an element displacement vector and a fundamental vector which does not disorder the atom arrangement. For example, the \( \mathbf{R}_1 \) is expressed by \( \mathbf{R}_2 \) and a fundamental vector, \( \mathbf{A} \), as \( \mathbf{R}_1 = \mathbf{A} - \mathbf{R}_2 \). When the product of \( \mathbf{g} \) and \( \mathbf{R} \) is integer, where \( \mathbf{g} \) is reflection vector, the APDB is invisible.
Therefore, only two thirds of the APDBs are visible with any $g$. In addition, the distortions in the images of APDs are taken into account to evaluate the average APD size from the images accurately. The images of APDs are obtained by tilting the thin foils so that the superlattice reflection for observation is excited. The images of the APDs obtained are projections of the APDs in the tilted foil to the plane perpendicular to the beam direction of the TEM. When a circular APD is observed with the foil tilted from the plane perpendicular to the beam direction by an angle $u$ as shown in Fig. 2, the relationship between the average APD size, $l$, and that of the image of APD, $l'$, is given by:

$$l' = l \frac{\int_0^{2\pi} r'(\psi) d\psi}{2\pi r} = \frac{l}{2\pi} \int_0^{2\pi} \left( \frac{\cos^2 \theta \cos^2 \theta + \sin^2 \psi}{\cos^2 \psi} \right)^{1/2} d\psi$$

Therefore, the $l$ was evaluated using this relationship from the $l'$ which was obtained by multiplying the average linear intersection length measured in the micrograph by $2/3$. Local chemical compositions around APDBs were analyzed by energy-dispersive X-ray spectroscopy (EDS). The analyses were carried out using an electron probe of approximately 1 nm in diameter in a Hitachi HF-2000 TEM equipped with a field emission gun, operating at 200 kV.

3. Results

Fig. 3 shows, by way of example, the images of APDs in the Ti–25Al compounds. Fig. 3(a) shows the APDs in the compound quenched from the disordered state, while Fig. 3(b) and (c) show the APDs in the compounds annealed at 1073 K for 5 and 50 ks after the quenching, respectively. The very fine APDs were developed in the as-quenched state. The shapes of APDs were irregular but almost isotropic as is often observed in many other intermetallic compounds [23,30]. The $l$ in the as-quenched compound was 14 nm. The $l$ increased to 53 and 130 nm after annealing at 1073 K for 5 and 50 ks, respectively. Similar APDs were observed in Ti–23Al and Ti–33Al compounds, while the variation in the APD size significantly depended on the annealing temperatures and the compositions. Remarkable change in the shape of APDs was not observed except the small facets, in contrast with the case in Cu$_3$Au where the anisotropy of the shape of APDs changes dramatically [26]. Fig. 4 shows the image of APDs in the Ti–25Al compound annealed at 1073 K for 50 ks, which were observed with a foil parallel to (0001) plane. The beam direction is near the [0001] direction. Facets are observed on APDBs as indicated by arrowheads. The traces of {11\bar{2}0} planes are indicated in the image by white dashed lines. Some of the facets are parallel to the traces. It seems that the facets are on {1\bar{1}0x} planes, although the index $x$ is unknown since the traces of {1\bar{1}0x} in (0001) plane are parallel to each other.

Fig. 5(a)–(c) show the variation in $l$ as a function of annealing time at various temperatures in Ti–23Al, Ti–25Al and Ti–33Al compounds, respectively. Both vertical and horizontal axes are in logarithmic scale. The dashed lines show the calculated variations in APD size at various growth rates based on the parabolic-growth-law:

$$l^2 - l_0^2 = kt$$

where $l_0$ is the initial average APD size, $k$ is the growth rate coefficient and $t$ is the annealing time. If the APD growth...
obeys the parabolic-growth-law, the data points at each temperature fall on a curve parallel to one of the dashed lines. Some of the data points during a certain period are on a curve parallel to the dashed lines, which means that the APD growth follows the parabolic-growth-law during the periods. In the stoichiometric Ti–25Al compound (Fig. 5(b)), deviations of data points toward larger APD size are observed in the early stages at all temperatures except for 1173 K. Such deviation is hereafter termed as positive deviation. The positive deviations are observed in the Ti–23Al and the Ti–33Al compounds as well. In the Ti–23Al and Ti–33Al compounds, the data points are deviated from the dashed lines toward smaller APD size in the late stages at all of the temperatures, while such deviation is not observed in the Ti–25Al compound. Such deviation is hereafter termed as negative deviation. Similar negative deviations were observed in Au-rich Cu₃Au, while it was not observed in Cu₃Au with near-stoichiometric composition. It has been suggested that the negative deviations were caused by segregation of the excess Au atoms which are unnecessary to form completely ordered...
The structure of Cu₃Au [24]. The segregation of excess atoms may be responsible for the negative deviation observed in the present study as well. In order to examine whether the negative deviations are accompanied by the segregation of excess atoms, the local chemical composition analysis was carried out in the vicinity of APDBs in Ti₃Al compounds. Fig. 6 shows an example of the local chemical composition analysis performed in the Ti–23Al compound annealed at 1073 K for 100 ks where the negative deviation was observed. The analysis was carried out at the points indicated by crosses in Fig. 6(a). The point B is just on an APDB which is almost parallel to the beam direction, while the points A and C are about 80 nm away from the APDB. The Al concentrations measured at these points are shown in Fig. 6(b). The Al concentrations at the points A and C are close to the wide-area concentration measured by the EPMA which is shown by a dashed line. The difference between the Al concentrations measured at these points and the wide-area concentration is about 1 at.% and it is within the error range of the EDS analysis. On the other hand, the Al concentration measured at the point B is about 3 at.% lower than the wide-area concentration. The difference is larger than the usual error in the EDS analysis. In order to understand this result, the size of the electron probe and the analyzed region must be taken into account. The probe size of electron beam used in the EDS is about 1 nm in diameter. In addition, taking the beam spreads in its way through the specimen into account, the size of the analyzed region is expected to be much larger than the width of APDBs. Although the APDBs appear wider due to the inclination of the boundary from the beam direction, the width of APDBs is considered to be comparable to interatomic distance. Therefore, a significant amount of signals from the matrix is included in the composition analysis of the point B, which results in the underestimation of the Al concentration. The actual Al concentration on the APDB seems much lower than the measured one.

Fig. 7 shows the results of the local chemical composition analyses performed in the Ti₃Al compounds with different chemical compositions. The analyses were carried out with the Ti–23Al and Ti–33Al compounds annealed at 1073 K for 100 ks where the negative deviation was observed. The specimen annealed for 50 ks was used for the analysis in the stoichiometric Ti–25Al compounds since most of APDBs disappeared the annealing for 100 ks. The Al concentrations measured on APDBs are compared to those measured within APDs, that is, in the matrix. In the Ti–23Al compound, the Al concentration measured on APDB is obviously lower than that in the matrix as mentioned above. This indicates that Ti atoms segregate on the APDBs in this compound. In the Ti–25Al compound, there is no difference between the Al concentration measured in the matrix and that on the APDBs. In the Ti–33Al compound, the Al concentration measured on APD boundary is about 1 at.% higher than that in the matrix. Although the difference is only a little larger than the usual error in the EDS analysis, similar results were obtained repeatedly. It is likely that the Al atoms segregate on APDBs in this compound. Accordingly, it is concluded that the excess atoms, i.e. Ti-atoms in Ti-rich compounds and Al atoms in Al-rich compounds, tend to segregate on APDBs in Ti₃Al compound.

Rase and Mikkola [24] insisted that there exist a limit of APD size in Au-rich Cu₃Au and the similar negative deviation is the process where the APD size approaches the limit. They assumed that there is a solubility limit of excess Au within APDs and the excess atoms beyond the limit segregate to APDBs. Then, the APD growth would stop when the total area of APDBs decreased by the APD growth so that the sites on APDBs were saturated with the excess
Au atoms. However, the existence of particular solubility limit within APD is not easily accepted since the solubility limit must be lower than that presented in the equilibrium phase diagram according to their explanation. Furthermore, the limit of APD size was not observed in the APD growth in Ti$_3$Al. Therefore, the mechanism is not applicable to the negative deviation. Nevertheless, the segregation decreases the growth rate by decreasing the mobility of APDB and/or the energy of APDB, which govern the APD growth rate. Furthermore, the existence of the facets as shown in Fig. 4 may be responsible for the negative deviation observed in the off-stoichiometric compound, although the effect of the facet is not so large in the stoichiometric Ti–25Al compound. Further study is necessary to elucidate the quantitative relationship between the segregation, the facets and the growth behavior of APDs especially in the late stages.

4. Discussion

The APD growth in the Ti$_3$Al compounds could not be simply explained by the parabolic-growth-law because of the positive deviation and the negative deviation. These deviations are not negligible in controlling and predicting the APD growth. It is quite important to clarify the mechanism of the deviations for controlling the APD structures. In this section, the kinetics of APD growth is discussed by calculating the variation in APD size in the stoichiometric Ti–25Al compound focusing on the causes of the positive deviation.

The conventional parabolic-growth-law (Eq. (2)) was derived by integrating the following differential equation which is based on the assumption that the time differentiation of the $l$ is proportional to the curvature of APDBs which is proportional to the inverse of $l$ by analogy with the grain growth kinetics [32].

$$\frac{dl}{dt} = \frac{k}{2l}$$

(3)

where $k$ is the constant depending on the composition and the temperature [32]. The $k$ is given by:

$$k = \mu \gamma f$$

(4)

where $\mu$ is the mobility of APDB, $\gamma$ the APD energy and $f$ is a constant which depends on the shape of APDs. Although Eq. (2) is derived when the $\mu$, the $\gamma$ and the $f$ are constant, it cannot be derived if any of the three factors is a function of time. The deviations from the parabolic-growth-law are due to the variations in these factors. In the present study, the variations in these factors are evaluated and the variations in APD sizes were calculated in order to clarify the effect of the variation in those factors on the APD growth. In the calculation, some assumptions and some modification coefficients were introduced since some parameters and equations required for the calculation are unavailable from literatures.

The $\mu$ is closely related to the diffusivity of atoms on the APDB since the migration of APD is caused by the rearrangement of atoms on the interface. Fig. 8 shows the variation in the atom arrangement accompanying the migration of an APDB. Open and solid circles show the Ti atoms and Al atoms, respectively. It can be seen that the boundary moves by an interatomic distance, when the atoms on the APDB move along the boundary by an interatomic distance as indicated by gray arrows. This means that migration of an APDB is caused by the diffusion of atoms along the APDB. The self-diffusion on APDB is considered to occur by the vacancy mechanism as well as in the matrix since the atoms are arranged in the fundamental lattice, i.e. HCP lattice in D0$_{19}$ structure, and there is no excess free volume on APDB in contrast with the case of grain boundaries. Although the formation of anti-site atom is required for the bulk diffusion of minority atoms in A$_3$B type compounds [33], it is not required for the diffusion on APB boundary since the Al atoms on the APDB are already located at anti-sites of the adjoining domain beyond the boundary, thereby the diffusion for the migration of APDB is possible without formation of anti-site atoms. Therefore, the diffusion coefficient of the self-diffusion on APDB ($D^{\text{APDB}}$) is expressed as follows:

$$D^{\text{APDB}} = D_0^{\text{APDB}} C_V P_m$$

(5)

where $D_0^{\text{APDB}}$ is the constant, $C_V$ is the vacancy concentration on APDB and $P_m$ is the probability of vacancy migration. Although the vacancy concentration is usually considered to be constant during isothermal annealing, the $C_V$ is a function of the annealing time, $t$, since there are excess non-equilibrium vacancies which are induced in the quench process from the high temperature above the $T_c$ and the excess vacancies vanish during the annealing. When it is assumed that the concentration of excess vacancy, $\Delta C^{\text{ex}}$, decreases exponentially with $t$, the variation in vacancy concentration is given by:

$$C_V(t) = C_V^{\text{eq}} + \Delta C_V^{\text{ex}} \exp(-t/\tau_V)$$

(6)

where $C_V^{\text{eq}}$ is the equilibrium vacancy concentration for the annealing temperature, $\Delta C_V^{\text{ex}}$ is the concentration of the excess vacancy at the initial state of annealing ($t = 0$) and $\tau_V$ is the relaxation time of excess vacancy, that is, the time
required for the concentration of the excess vacancy to decrease to $1/e$. Assuming that the $\mu$ is proportional to the $D_{\text{APDB}}$, the $\mu$ is derived from Eqs. (5) and (6) as follows:

$$\mu = \mu_0 D_{\text{APDB}} = \mu_0 D_0 \text{APDB} \left[ c^\text{eq}_\text{V} + \Delta c^\text{ex}_{\text{V},0} \exp(-t/\tau_V) \right] P_m$$  \hspace{1cm} (7)

where $\mu_0$ is the constant of proportionality. The diffusion coefficients on APDB $D_{\text{APDB}}$ have never been obtained either by experimental or by calculation. The migrations of APDB require diffusions of both Ti atom and Al atom as seen in Fig. 8. The diffusion experiments have shown that the diffusion of Al atom is much slower than that of Ti atom in Ti$_3$Al [34,35]. Hence, the migration of APDBs is controlled by diffusion of Al atom on APDBs, and it seems that the mobility of APDB can be evaluated from the diffusion data of Al in Ti$_3$Al. However, the difference between the diffusion of Al on APDB and that in matrix should be taken into account.

Generally, the equilibrium vacancy concentration at a temperature $T$ is given by:

$$c^\text{eq}_\text{V} = c_0 \exp\left(-\frac{H_\text{f}}{RT}\right)$$  \hspace{1cm} (8)

where $c_0$ is the constant, $H_\text{f}$ the formation enthalpy of vacancy and $R$ is the gas constant. In order to estimate the vacancy concentration on APDB which is required to evaluate the $\mu$, the formation enthalpy of vacancy on APDB $H_{\text{f}}^{\text{APDB}}$ should be substituted for the $H_\text{f}$. While there are no data on $H_{\text{f}}^{\text{APDB}}$ unavailable in literature, the $H_\text{f}$ in the ordered matrix $H_{\text{f}}^{\text{order}}$ has been obtained by positron life time study [36]. The $H_{\text{f}}^{\text{APDB}}$ is considered to be closely related to that in the matrix. Therefore, a modification coefficient $\beta$ is introduced so that the $H_{\text{f}}^{\text{APDB}}$ is given by:

$$H_{\text{f}}^{\text{APDB}} = \beta H_{\text{f}}^{\text{order}}$$  \hspace{1cm} (9)

The vacancy formation enthalpy in the disordered state $H_{\text{f}}^{\text{disorder}}$ is also unknown, although it is needed for estimating the concentration of excess vacancy induced in the quenching from the disordered state. Therefore, another modification coefficient $\lambda$ is introduced so that the $H_{\text{f}}^{\text{disorder}}$ is given by:

$$H_{\text{f}}^{\text{disorder}} = \lambda H_{\text{f}}^{\text{order}}$$  \hspace{1cm} (10)

When the cooling rate during the quenching process is high enough, the initial vacancy concentration is equal to the equilibrium vacancy concentration at the temperature for disordering. Then, the initial excess vacancy concentration $\Delta c^\text{V}_{\text{ex},0}$ is given by:

$$\Delta c^\text{V}_{\text{ex},0} = c_0 \left\{ \exp\left(-\frac{\lambda H_{\text{f}}^{\text{order}}}{RT_\text{d}}\right) - \exp\left(-\frac{\beta H_{\text{f}}^{\text{order}}}{RT_\text{d}}\right) \right\}$$  \hspace{1cm} (11)

where $T_\text{d}$ is the temperature for the disordering process. The relaxation time of excess vacancy $\tau_\text{r}$ for a given temperature $T$ is given by:

$$\tau_\text{r} = \tau_0 \exp\left(\frac{H_m}{RT}\right)$$  \hspace{1cm} (12)

where $\tau_0$ is constant and $H_m$ is the migration enthalpy of vacancy. The probability of vacancy migration on APDB for a given temperature $T$ is expressed as:

$$P_m = \exp\left(-\frac{H_m}{RT}\right)$$  \hspace{1cm} (13)

The APDB energy $\gamma$ is proportional to the square of the long-range order parameter $S$ in the matrix, and is expressed as follows [37]:

$$\gamma = \gamma_0 S^2$$  \hspace{1cm} (14)

where $\gamma_0$ is the constant of proportionality. The $S$ should be zero if the cooling rate of the quenching is high enough. Then the $S$ approaches to the equilibrium value during the annealing. By applying the Feder and Cahn’s method [38], the variation in the $S$, i.e. the time differentiation of the $S$, is obtained as follows:

$$\frac{dS}{dt} = \frac{1}{\tau_\text{s}} (S_{\text{eq}} - S)^n$$  \hspace{1cm} (15)

where $\tau_\text{s}$ is the relaxation time for ordering, $S_{\text{eq}}$ is the equilibrium long-range order parameter for the annealing temperature, and $n$ is the order of reaction. The variation in $\gamma$ as a function of $t$ can be derived from Eqs. (14) and (15). The relaxation time of ordering for a given temperature is expressed as:

$$\tau_\text{s} = \tau_{0,\text{s}} \exp\left(\frac{H_\text{s}}{RT}\right)$$  \hspace{1cm} (16)

where $\tau_{0,\text{s}}$ is a constant and $H_\text{s}$ is the activation energy of ordering. Since the ordering in Ti$_3$Al proceeds by the rearrangement of the minor atoms, i.e. Al atoms, the $H_\text{s}$ is considered to be equal to the activation energy of the self-diffusion of Al, $Q_{\text{Al}}$. However, in practice, the $Q_{\text{Al}}$ in the ordering process is different from that of usual bulk self-diffusion since the $Q_{\text{Al}}$ is affected by the variation in the $S$ itself. Therefore, the sum of the $H_{\text{f}}^{\text{APDB}}$ and the $H_\text{m}$ was tentatively substituted for the $H_\text{s}$.

The variation in the $\gamma$ is important if the shape of APDs changed significantly. In the early stages, a significant change in the shapes of APDs was not observed as shown in Fig. 3. Therefore, the variation in $\gamma$ is small and not responsible for the positive deviation in the early stages. On the other hand, the facets were observed on APDBs in the late stage of APD growth as shown in Fig. 4. It may be responsible for the negative deviation in the late stage in the Ti–23Al and Ti–33Al compounds. However, the negative deviation was not observed in the Ti–25Al compound, and it seems that the effect of the variation in $\gamma$ due to the facet is very small in the Ti–25Al compound. Therefore, the effect of variation in the $\gamma$ can be neglected in calculating the APD growth in the Ti–25Al compound. Thus, the variation in
the APD size in the Ti–25Al compound was calculated by using Eqs. (3)–(16) and appropriate values for the parameters. The parameters used in the calculation are listed in Table 1. As shown in Table 1, the values of the parameters, \( f, D_0^{APDB}, \mu_0, \gamma_0, c_0, \beta, \lambda, T_0, V \) and \( \tau_{0,V} \) are unknown unfortunately, while other parameters are available from literatures. It is required to estimate the values by fitting these parameters so that the calculated variations in APD size approach the experimental result. In the fitting process, some restriction must be put on the relationship among the parameters. When the product of the parameters \( f, D_0^{APDB}, \mu_0, \gamma_0, c_0 \) is constant, the result of calculation does not change even if each parameter is set variously since the APD size is proportional to all of these five parameters. Therefore, the number of unknown parameter can be reduced from 9 to 5 by defining another new parameter \( \zeta \) as follows:

\[
\zeta = fD_0^{APDB} \mu_0 \gamma_0 c_0
\]  

(17)

Since those five parameters must be independent of the temperature, the values of the parameters can be inevitably determined by optimize these parameters so that the calculated variations in APD size at five temperatures approach simultaneously to the experimental results of corresponding temperatures. The parameters determined in the calculation are also listed in Table 1. The values of the fitting parameters are reasonable. Fig. 9 shows the results of calculation of APD growth in the Ti–25Al compound. Lines show the calculated variations in APD sizes. The experimental results are shown by symbols together.

The calculation results are in agreement with the experimental results. The positive deviations observed in the early stages exist in the calculation results as well as in the experimental results. The positive deviations are more remarkable at lower temperatures. According to the calculation results, the APDs rapidly grow in the very early period. After the rapid growth, there is a period where the APD size exhibits almost no change. Such period is hereafter termed the plateau. The APD sizes increase again after the plateau. The APD growth in this period follows the parabolic-growth-law. Thus, it has been clarified that the positive deviation corresponds to the transition from the plateau to the parabolic-growth. In order to clarify the dominant cause of the anomalous variation in the APD size, the calculated variation in the APD size is compared with those of the \( C_V \) and the \( S \). Fig. 10(a)–(c) shows the calculated variations in the APD size, the \( C_V \) and the \( S \) in the Ti–25Al compound at 1073 K respectively. The dashed line in Fig. 10(a) shows the variation in the APD size calculated by virtually fixing the \( S \) to the equilibrium value for the annealing temperature. On the other hand, the dotted line shows the calculation result with the \( C_V \) fixed to the equilibrium vacancy concentration. In the very early period before about 10 s, where the APD size exhibits little change, the \( S \) is quite small while the \( C_V \) is hundreds times as high as the equilibrium value. Therefore, the very small growth rate in this period is attributed to the small \( \gamma \) due to the small \( S \). This is consistent with that the APD size increases rapidly even in this period in the case that the \( S \) is fixed to the equilibrium value as shown by the dashed line in Fig. 10(a). When the APD size exhibits remarkable increase around 10 s, the \( S \) also exhibits remarkable increase while the \( C_V \) exhibits only slight decrease. Therefore, the increase in the growth rate is attributed to the increase in the \( \gamma \) due to the increase in the \( S \) in addition to the high \( C_V \). The effect of the high \( C_V \) is evident from that the APD size does not increase in

Table 1
Parameters used in the calculation of APD growth in Ti–25Al compound

| Parameter | Value | Reference/comments |
|-----------|-------|--------------------|
| \( H_{f_{\text{oxide}}} \) | 150 kJ/mol | Wurshum et al. [36] |
| \( \beta \) | 0.93 | Determined by fitting |
| \( \lambda \) | 0.86 | Determined by fitting |
| \( T_0 \) | 1393 K | Experimental value |
| \( T_C \) | 1373 K | Obtained from equilibrium phase diagram [39] |
| \( \tau_{0,V} \) | 5 \times 10^{-5} s | Determined by fitting |
| \( H_m \) | 140 kJ/mol | Wurshum et al. [36] |
| \( S_{eq} (973 K) \) | 0.91 | Estimated from \( T_c \) by Bragg–Williams theory [40] |
| \( S_{eq} (1023 K) \) | 0.88 | Estimated from \( T_c \) by Bragg–Williams theory [40] |
| \( S_{eq} (1073 K) \) | 0.86 | Estimated from \( T_c \) by Bragg–Williams theory [40] |
| \( S_{eq} (1123 K) \) | 0.83 | Estimated from \( T_c \) by Bragg–Williams theory [40] |
| \( S_{eq} (1173 K) \) | 0.79 | Estimated from \( T_c \) by Bragg–Williams theory [40] |
| \( \tau_{0,S} \) | 5 \times 10^{-11} s | Determined by fitting |
| \( n \) | 1 | Order of order–disorder transformation |
| \( \zeta \) | 4 \times 10^{13} m^2/s | Determined by fitting |

![Fig. 9. Calculated variations in the APD size in the Ti–25Al compound at various temperatures. Experimental results are also shown by symbols for comparison.](image-url)
the case that the $C_V$ is fixed to the equilibrium value as shown by the dotted line in Fig. 10(a). When the APD growth become moderate after the remarkable growth, the $C_V$ rapidly decreases while the $S$ increases almost steadily. This means that the moderation and the plateau of the APD growth are caused by the decrease in the $\mu$ due to the rapid decrease in the $C_V$. This is consistent with that similar moderation and plateau exist also in the calculation result with the fixed $S$. Finally, the closer the $C_V$ and the $S$ become the respective equilibrium values, the closer the variation in the APD size becomes to that of the parabolic-growth-law. Thus, the effects of the variation in the $C_V$ and the $S$ on the APD growth have been understood.

5. Conclusions

In the present study, the growth of APDs in three kinds of Ti$_3$Al compounds with different Al concentrations were investigated, and its kinetics was discussed by taking the variation in the vacancy concentration and the degree of order in the matrix into account. The APD growth does not follow the simple parabolic-growth-law. The positive deviations occur in the early stages of the growth in all of the Ti$_3$Al compounds investigated. The negative deviations occur in the Ti$_3$Al compounds with off-stoichiometric compositions. The positive deviations are attributed to the variations in the mobility and the driving force of the APDB migration which are caused by the excess vacancies induced in the quenching process and the ordering of the matrix, respectively. The negative deviations are attributed mainly to the segregation of the excess atoms on APDBs, although the formation of the facets on APDBs may be responsible for the negative deviation to some extent.

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