Kinetic Behavior of Ordering in B2-type Alloys

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Kinetic Behavior of Ordering in B2-type Alloys

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Kinetics of ordering in B2-type FeCo alloy was investigated both experimentally and theoretically. Kinetic equation for B2-type ordering was generally derived from the two physical conditions, namely the symmetry between two sublattices in the B2-type structure and the stability of the equilibrium state. The general kinetic equation with third order term of the degree of order has an advantage over the others in that it is simpler in form and more general, and it is applicable to the analysis of the kinetic behavior on ordering in B2-type alloys. The variation of lattice constant on isothermal ordering for the equiatomic FeCo alloy was observed by X-ray diffraction, and analyzed using present kinetic equation. Isothermal change of lattice constant above 823K was reproduced well by the equation, but not satisfactorily below 773K, particularly about a two-step change of lattice constant observed at an early stage of annealing. This two-step change was interpreted very well by the extended kinetic equation containing the vacancy concentration. The values for the formation and migration energies of vacancies in the FeCo alloy were determined as 91 and 139 kJ/mol, respectively.

1. Introduction

There have been many investigations concerned with the kinetics of ordering of alloys. Since the Bragg and Williams theory, various kinds of kinetic equations were presented on the basis of various points of view, such as chemical rate theory, vacancy mechanism and discrete lattice theory. However, the disadvantage of these kinetic equations is that they are too complex to be readily compared with experimental results.

On the experimental side, it is essential to carry out kinetic studies directly in terms of the degree of long range order. As almost any physical property of alloy, particularly lattice constant, resistivity or elastic constant, is sensitive to the degree of order, each of them has been used in the study of kinetics of ordering.

In the case of FeCo alloy it is not easy to obtain directly the degree of order by X-ray diffraction, because the atomic scattering factors for Fe and Co are so similar with each other that it is difficult to detect the superlattice line quantitatively even if by making use of the anomalous dispersion effect. For this reason Yokoyama et al. used the relation between the characteristic temperature $\theta$ in dynamic equilibrium state and the actual temperature $T$, and Kuroki et al. the temperature derivative of electrical resistivity, instead of examining the degree of order directly in order to interpret the so-called “550°C anomaly”. Seehra and Sillinsky also used the temperature derivative of electrical resistivity, the thermoelectric power, and Rajkovic and Backley, Eymery et al. and Rogers et al. the antiphase domain sizes. The major difficulty is that the connection between the degree of order and the various physical properties which have been used for kinetic studies is not established clearly either theoretically or experimentally.

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In this work, the kinetic equation for B2-type ordering was derived on the basis of general consideration of B2 structure, namely the symmetry between two sublattices and the equilibrium condition and its stability. This kinetic equation is very simple in its form and more general, and can be easily applied to the practical analysis of experimental results in B2-type ordering alloys. Isothermal change in lattice constant of FeCo alloy, initially quenched from a disordered state, was observed by means of X-ray diffraction instead of examining directly in terms of the degree of order. It was found that there exists a linearity between the lattice constant and the degree of order squared in thermal equilibrium state. The change in lattice constant on high temperature annealing was reproduced well by this general kinetic equation, and the activation energy for ordering in FeCo alloy was obtained. However, at lower temperature the lattice constant exhibited a two-step change at an early stage of annealing indicating the ordering by a vacancy mechanism, first with quenched-in excess vacancies and then with equilibrium ones. The two-step change was analyzed well by the extended kinetic equation to include the change in vacancy concentration, and the formation and migration energies of vacancies in FeCo alloy were reasonably obtained.

2. Derivation of Kinetic Equation

2.1 General kinetic equation
As a rate of ordering or disordering depends on the temperature and the degree of order, the rate of change in the degree of order with time is given by

\[ \frac{dS}{dt} = G(S, T), \]  

where \( S \) is the degree of order in Bragg-Williams' sense and \( T \) the temperature. If the form of \( G(S, T) \) is known, the kinetic equation of the degree of order \( S \) is obtained. In derivation of \( G(S, T) \) we need not assume any special model for ordering, but take into account the following two physical conditions which must be satisfied generally.

(i) The symmetry of two sublattices
It is well known that the unit cell of B2-type superstructure consists of two simple cubic sublattices \( \alpha \) and \( \beta \) and the structure has a symmetry with respect to the interchange of \( \alpha \) and \( \beta \) sublattices. This operation corresponds to the inversion of ordering parameter \( S \rightarrow -S \), and requires eq. (1) to be invariable. The function \( G(S, T) \) has the following property,

\[ G(S, T) = -G(-S, T). \]  

(ii) The equilibrium condition and its stability
For the equilibrium state, the rate of change in the degree of order \( S \) is zero. Then the equation

\[ \frac{dS}{dt} = G(S, T) = 0, \]  

has the solutions of \( S = 0 \) and \( S = \pm S_e(T) \), in which the first one corresponds to the disorder state and the other two the equilibrium state, respectively. Below the critical temperature \( T_c \) of the order-disorder transformation, the solution \( S = \pm S_e(T) \) should be stable while \( S = 0 \) unstable. Therefore, \( G(S, T) \) has the following properties,

\[
\begin{align*}
|\frac{dG(S, T)}{dS}|_{S=0} & > 0, \\
|\frac{dG(S, T)}{dS}|_{S=\pm S_e} & < 0. 
\end{align*}
\]  

(4)

If the function \( G(S, T) \) which satisfies above conditions (i) and (ii) may be expressed as a polynomial expression of order parameter \( S \), the simplest function with third order term of \( S \) can be found. The kinetic equation with the product of two terms depending on the degree of order \( S \) and the temperature \( T \) can be written as

\[
\frac{dS}{dt} = \frac{1}{2} F(T) S(S^2 - S_e^2),
\]

(5)

where \( F(T) \) is a positive function depending only on \( T \), and does not depend on \( S \) and \( t \) explicitly. As any special model for the ordering process was not assumed in derivation of eq.(5), the equation is more general and very simple in its form. Eq.(5) is a general kinetic equation for B2-type ordering. In the next section we shall try to apply this general kinetic equation to the case of isothermal ordering.

2.2 Application to isothermal ordering

In the case of isothermal ordering, as \( F(T) \) is a constant, the change in the degree of order with time is obtained by integrating eq.(5). Let \( X = S^2 \) for simplicity, the expression for \( X \) is easily given as

\[
X = X_e \left[ \frac{1}{X_o + \left( X_o - X_e \right) \exp \left| -X_e F(T) t \right|} \right],
\]

(6)

where \( X_e \) is the degree of order squared in the thermal equilibrium state, and \( X_o \) the initial value of \( X \) at \( t = 0 \). It is noted that the non zero value of \( X_o \) is required in a practical analysis of experimental results, because the ordering can not start in the case of \( X_o = 0 \) owing to the property of the equation.

If the relation between \( X \) in eq.(6) and some physical quantities is found out, the experimental results can be analyzed. As the temperature dependence of lattice constant is resemble to that of the degree of order and besides the structure of B2-type order is symmetrical with respect to the interchange of two sublattices, we assumed in the present work that the lattice constant \( P \) at room temperature is a simple even function of \( S \), or

\[
P = A + B X,
\]

(7)

where \( A \) and \( B \) are constants depending on neither the temperature \( T \) nor the degree of order \( S \). The validity of this assumption will be checked in the next chapter. Substitution of eq.(6) into \( X \) in eq.(7) gives for \( P \):
Kinetic Behavior of Ordering in B2-type Alloys

\[ P = A + B X_e \left[ a + (1-a) \exp \left(-\frac{t}{\tau}\right) \right]. \]  

where

\[ a = X_e / X_o, \quad 1/\tau = X_e F(T). \]

Once the four parameters \(A, B, X_e\) and \(\tau\) in eqs. (8) and (9) are estimated from the experimental results, information about the isothermal ordering can be obtained.

3. Isothermal Ordering in Fe-Co Alloy

3.1 Specimen preparation and X-ray measurement

Alloy specimen with equiatomic Fe-Co was prepared from 99.90% electrolytic iron and 99.50% cobalt. The required amount of them was melted in vacuum in a high frequency induction furnace, cast into a pure alumina mold and then cooled in the furnace. After being hot-forged under air at 1273-1373K, the ingot was annealed in vacuum at 1473K for 72ks for homogenization and then filed into powder with a diamond instrument finer than 300 mesh for X-ray diffraction experiment. The temperature during the heat treatment was carefully controlled within ±2K. Chemical analysis showed a composition of 49.8±0.1 at%Co. The powders were sealed in evacuated silica tubes, and undergone following heat treatment. All specimens were initially held for disordering at 1073K for 3.6ks, and followed by a quench into iced brine. Each specimen thus solution-treated was annealed isothermally in the temperature range between 623 and 923K for various lengths of time, and then quenched again into iced brine. Lattice constant measurements were carried out at room temperature with a SHIMADZU-VD1A type diffractometer using CoKα radiation. Powders of \(\alpha-Al_2O_3\) (99.9%) and pure iron (99.96%) were used as a internal standard. The peak maximum position of line profile was determined by the method of least squares from ten points which were approximated by a parabola.

3.2 Analysis by general kinetic equation

Isothermal changes in lattice constant of the Fe-Co alloy at various temperatures are shown in Figs. 1 and 2. Here the results of annealing at 773 and 723K are presented in the both figures for the later analysis. A characteristic two-step change of the lattice constant is clearly seen at temperatures below 773K (Fig. 2), but not above 823K (Fig. 1).

In order to check the relation between the lattice constant \(P\) and the degree of order \(S\) assumed in eq. (7), the equilibrium value of lattice constant at each annealing temperature obtained experimentally was plotted in Fig. 3 against the degree of order squared \(X = S^2\) in the equilibrium state taken from the B-W theory.

The solid line was drawn by eq. (7) with the values of \(A = 2.84975 \times 10^{-10}\) and \(B = 0.00322 \times 10^{-10}\) m determined from a least squares analysis of the experimental data. The lattice constant of the specimen quenched from 1073K in the disordered state was adopted as the value for \(S = 0.0\). It is found from the figure that there is a linear relation between the lattice constant \(P\) and the degree of order squared \(X = S^2\), and eq. (7) is valid over a wide range of temperature. Since the parameters \(A\) and \(B\) are thus obtained, the remaining two parameters \(a\) and \(\tau\) are determined so as to reproduce the observed change in the lattice
Fig. 1  Isothermal change in lattice constant of FeCo alloy at various annealing temperatures above 723K (measured at room temperature), and also theoretical curves given by eqs. (8) and (9).

Fig. 2  Isothermal change in lattice constant at various annealing temperatures below 723K, and theoretical curves given by eqs. (7), (14) and (15) with values of the parameters in Table 1.

Fig. 3  Relation between lattice constant measured at room temperature and degree of order squared in the equilibrium state calculated from B-W theory. The marks correspond to the equilibrium values of lattice constant at various temperatures shown in Fig. 1.

Fig. 4  Initial degree of order at various temperatures (a) and determination of activation energy E (b). Solid curve and line represent $S_o = 0.5S_e$ and $- \ln F(T)$ with $E = 235$ kJ/mol obtained by the use of a least squares method, respectively.
constant at each annealing temperature by the least squares on eq. (8). Computer calculation was repeated and repeated again by varying the initial values \( S_0 \) and \( \tau \) until the theoretical curves fit the experimental data reasonably well. The initial degree of order \( S_0 \) obtained through \( \alpha = X_e / X_s \) in eq. (9) is shown in Fig. 4.

The solid curve (a) represents \( S_0 = 0.5 s(T) \). The variations of lattice constant calculated by eq. (8) using these values of parameters \( A, B, \alpha \) and \( \tau \) are also shown by the solid curves in Fig. 1. These curves agree very well with the experimental values at annealing above 823K, but do not reproduce the observed change in all respects below 773K. For example, at an early stage of annealing there is a large difference between them. This disagreement will be discussed in the next section.

The activation energy for ordering can be estimated from \( \tau \) and \( X_e \) obtained from the experiment and B-W theory, respectively. In eq. (5), \( F(T) \) is a positive function depending only on temperature \( T \) and does not include \( S \) and \( t \) explicitly. Here we assumed an Arrhenius type of function as

\[
F(T) = \nu \exp \left( -\frac{E}{RT} \right),
\]

where \( \nu \) is the atomic frequency factor, \( E \) the activation energy and \( R \) the gas constant. From eqs. (9) and (10), the activation energy for ordering and the atomic frequency factor in FeCo were obtained as 235 kJ/mol and \( 0.6 \times 10^{13} \) s\(^{-1} \), respectively, as is shown with the solid line (b) in Fig. 4. The values of activation energy \( E = 235 \) kJ/mol is somewhat different from \( E = 266 \) kJ/mol proposed by Kuroki et al.\(^{10} \) to explain the so-called “550°C anomaly”, \( E = 216 \) kJ/mol by Yokoyama et al.\(^{20} \) obtained from the change of electrical resistivity on the isothermal ordering and \( 260 - 278 \) kJ/mol by Pierron-Bohnes et al.\(^{22} \) used to explain the experimental results of neutron diffuse scattering. However our value is in good agreement with that for self-diffusion \( 230 \pm 4 \) kJ/mol obtained from the diffusion of Fe\(^{59} \) in bcc FeCo by Fishman et al.\(^{23} \). The atomic frequency factor \( \nu = 0.6 \times 10^{13} \) s\(^{-1} \) agree well with \( \nu = 1.0 \times 10^{13} \) s\(^{-1} \) proposed by Kuroki et al.\(^{10} \).

The present results show that so long as the temperature of isothermal annealing is not too low, our general kinetic theory is easy to handle to compare with experiment and works very well.

### 3.3 Effect of vacancies on ordering

As mentioned in section 3.2, the theoretical curves of lattice constant calculated from eq. (8) fit the experimental data reasonably well at the annealing above 823K, but not sufficiently below 773K, especially the two-step increase in lattice constant at the early stage of ordering. Such a characteristic kinetic behavior implies that the ordering takes place by a vacancy mechanism, first with quenched-in excess vacancies and then with equilibrium ones. The specimen quenched from a higher temperature necessarily contains some excess vacancies which are not taken into account in the present kinetic equation, and these vacancies vanish rapidly in the course of annealing at higher temperatures but remain for a long time at lower temperatures. For this reason, at the annealing above 773K, the theoretical curves agree well with the experimental ones measured after the excess vacancies had already annealed out. However, as the excess vacancies remain for a long time at the
annealing below 773K, the lattice constant changes in two stages. In the case of quenching from higher temperatures it might be thought that the general kinetic equation could be applied to the reaction after the alloy had partly ordered so as to be 50% of equilibrium degree of order, as was predicted from the initial value \( S_0 \) in Fig. 3.

In order to interpret the experimental results more exactly the kinetic equation (5) is extended into the form to include the change of vacancy concentration. We assume that the rate of ordering or disordering depends not only on the temperature and the degree of order but on the vacancy concentration. Namely, we consider that the first stage of two-step change in lattice constant is caused by excess vacancies retained in sample quenched from high temperatures and such vacancies will anneal out with time. In this case eq.(5) is extended as the following form,

\[
\frac{dS}{dt} = \frac{1}{2} C_v F(T) S(S_{e}^2 - S^2),
\]

where \( C_v \) is the vacancy concentration, of which time dependence may be given by

\[
C_v(t) = C_v(T) + |C_v(T_q) - C_v(T)| \exp(-\gamma(T)t),
\]

where \( T_q \) is a quenching temperature. The equilibrium vacancy concentration at T, or \( C_{ve}(T) \), and the decay constant at T, or \( \gamma(T) \), are assumed to be expressed approximately in the single form of Arrhenius type as

\[
C_{ve}(T) = C \exp(-E_f/RT),
\]

and

\[
\gamma(T) = D \exp(-E_m/RT),
\]

where \( C \) and \( D \) are constants, and \( E_f \) and \( E_m \) the formation and the migration energies of vacancies.

Let’s apply these equations to the case of isothermal ordering. The change in the degree of order with time is a constant during the isothermal change. The expression for the degree of order squared \( X (= S^2) \) is given as

\[
X = X_0 \left[ 1 + \left( \alpha - 1 \right) \exp\left(-\tau - \beta + \beta \exp(-\gamma(T)t)\right) \right],
\]

where

\[
\frac{1}{\tau} = X_0 F(T) C_{ve}(T),
\]

\[
\alpha = X_0/X_e = S_e^2/S_0^2,
\]

\[
\beta = X_0 F(T) |C_{ve}(T_q) - C_{ve}(T)|/\gamma(T).
\]

Isothermal changes in lattice constant below 773K are reanalyzed using eqs.(7), (14) and
Values of three parameters $\beta$, $\gamma$, and $\tau$ were determined so as to reproduce the observed change of lattice constant at each annealing temperature by the least squares method, and they are summarized in Table 1.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>873</th>
<th>823</th>
<th>773</th>
<th>723</th>
<th>673</th>
<th>623</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>1.87</td>
<td>2.82</td>
<td>3.41</td>
<td>3.56</td>
<td>3.80</td>
<td>4.03</td>
</tr>
<tr>
<td>$\gamma$ (s$^{-1}$)</td>
<td>$-1.60 \times 10^{-2}$</td>
<td>$4.64 \times 10^{-3}$</td>
<td>$1.23 \times 10^{-3}$</td>
<td>$1.57 \times 10^{-4}$</td>
<td>$2.67 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$\tau$ (s)</td>
<td>74</td>
<td>298</td>
<td>$3.25 \times 10^1$</td>
<td>$4.10 \times 10^4$</td>
<td>$8.49 \times 10^6$</td>
<td>$9.74 \times 10^6$</td>
</tr>
</tbody>
</table>

The initial degree of order squared $X_o$ was estimated to be 0.016 in this analysis. The results calculated using these values of parameters are also shown in Fig. 2 with solid lines. As can be seen in the figure, theoretical curves show quite excellent agreement with the experimental data in the whole temperature ranges. In particular, the characteristic two-step change in lattice constant observed at the early stage of annealing are reproduced satisfactorily. As is obvious from eqs. (13) and (15), the migration energy of vacancies can be determined from a plot of $\ln \gamma(T)$ versus $1/T$, and also the formation energy of vacancies from that of $\ln (1 + \beta \gamma \tau)$ versus $1/T$ since the following equation holds:

$$1 + \beta \gamma \tau = C_{ce}(T_q)/C_{ce}(T).$$

From the analysis shown in Fig. 5, the values of $E_f$ and $E_m$ were obtained as:

$$E_f = 91 \text{ kJ/mol}, \quad E_m = 139 \text{ kJ/mol}.$$  \hspace{1cm} (17)

![Fig. 5 Determination of migration energy $E_m$ (a) and formation energy $E_f$ (b) of vacancies in FeCo alloy.](image)

There are no values in literature for $E_f$ and $E_m$ of FeCo alloy, but they seem to be reasonable comparing with the values of other ordered alloys containing at least one kind of transition metals, for example, $E_f = 86.8$ and $E_m = 116 \text{ kJ/mol}$ in Fe-Co-2% V$^{18}$, $E_f = 96.5^{24}$.
and $E_m = 135 \text{ kJ/mol in NiAl}^{25}$, or $E_f = 77.2 - 86.8$ and $E_m = 144.7 - 154.4 \text{ kJ/mol in Fe-40at}\%\text{Al}^{26}$.

In this analysis we assumed that the formation and migration energies of vacancies do not depend on the degree of order, and that the equilibrium vacancy concentration at $T$, or $C_v(T)$, and the decay constant at $T$, or $\gamma(T)$, are expressed approximately in the simple form of Arrhenius type. There seems to be considerable difference in these quantities between ordered and disordered states, as was suggested from the self-diffusion studies$^{27,28}$. In order to discuss these problems in detail, further quantitative experimental and theoretical studies will be required. But this is not our present subject.

As a result, it might be concluded that the kinetic equations presented in this work are very simple and readily applicable to the actual analysis of experimental data. An application of these kinetic equations to another case, such as isochronal ordering, is actually possible and the result is already reported$^{29}$.

4. Conclusion

A simple kinetic equation for B2-type ordering was generally derived from the two physical conditions of B2-type superstructure without assuming any special model for ordering, and applied to the analysis of the change in lattice constant of FeCo alloy obtained by X-ray diffraction.

It was found that there is a linear relation between the lattice constant and the degree of order squared. Observed lattice constant on isothermal annealing exhibits a monotonous change at higher temperatures greater than about 800K, while below this temperature it shows a two-step increase at an early stage of annealing, indicative of the ordering process by a vacancy mechanism.

The theoretical change in lattice constant obtained by the general kinetic equation fitted well the experimental one except for an early stage of ordering at the lower temperature, and gave the activation energy for ordering and atomic frequency factor as 235 kJ/mol and $0.6 \times 10^{13} \text{s}^{-1}$, respectively. Furthermore, the extended kinetic equation including the vacancy concentration even reproduced the lower temperature data quite well, and gave the formation and migration energies of vacancies in FeCo alloy as 91 and 139 kJ/mol, respectively.

As a result the present general kinetic equation and its extended one are very simple in their forms and are shown to be easily applicable to the practical analysis of experimental results.

References

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Kinetic Behavior of Ordering in B2-type Alloys