The general structure of the kinetic equation describing the short range ordering in binary substitutional alloys is discussed, by assuming that the ordering takes place by the migration of vacancies, which are created or annihilated at dislocations and grain boundaries. The basic equation is applied for an analysis of the observed variation in electrical resistivity of α-Cu–Al in the course of annealing at the same temperature, after the specimen is quenched from various temperatures. It is shown that by a suitable choice of the value for vacancy formation energy those data fit on a single master curve, if an appropriate transformation of the time scale is performed. The basic equation is not strictly linear, but can be linearized under certain limited circumstances. The approximate rate equation can account for the change of resistivity, specific heat and lattice constant of α-Cu–Al under various heat treatments.

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I. Introduction

In some binary substitutional alloys, such as the α-phase of the Cu–Al system\(^{(1)(2)}\), constituent atoms are arranged with a certain degree of short range order. The direct determination of the short range order parameter, for example, from the intensity of diffuse X-ray scattering\(^{(1)(3)}\), involves some technical difficulties, and we are usually obliged to obtain indirect information on the short range order from some physical quantities, which depend upon the degree of order. The purpose of the present work is to investigate the mechanism of short range ordering in binary substitutional alloys through an analysis of the changes of their physical properties under various heat treatments.

II. General Kinetic Equation

The state of short range order changes due to migration of vacancies by the exchange of sites with neighboring atoms. Consider a parameter \(x\) which describes the state of order. The change of the parameter \(x\) at a temperature \(T\) is regarded as being caused by a reaction between the state of atomic order \(x\) and the vacancy concentration \(C_v\), and the rate equation may be approximately represented as follows:

\[
\frac{dx}{dt} = C_v G(x, T),
\]

where \(G(x, T)\) is a certain function of the degree of order and temperature. Because vacancies are created or annihilated at dislocations and grain boundaries, \(C_v\) generally depends upon time \(t\).

The parameter \(x\) may stand for the short range order parameter defined by Warren and Cowley\(^{(4)}\), but may instead stand for any physical quantity which depends uniquely upon the state of order. As a typical example, we consider here the relative change of electrical resistivity in α-Cu–Al during an isothermal annealing at a temperature \(T_a\) after the...
Fig. 1 Changes of electrical resistivity of Cu-14.0 at% Al as a function of time during annealing at 121.4°C after quenching from various temperatures. $R_s$ and $R_d$ are the resistances of the specimen and dummy. $R_s/R_d$ corresponds to the physical parameter $x$ in basic eq. (1).

specimen is quenched from an equilibrium state at $T_q$. Figure 1 shows the change of the ratio of the resistance in the specimen of Cu-14.0 at% Al to that of a dummy with constant resistance, for $T_a=121.4°C$ and $T_q=360.8$, 371.4, 377.0, 389.5, 400.0, 411.4 or 418.1°C. The measurement was carried out continuously with an accuracy of $10^{-5}$ by the use of an alternative current method(5).

For an analysis of these experimental results we assume the time dependence of $C_v$ as given by

$$C_v = C_v(T_q) \exp \left(-\gamma(T_a)t\right),$$

where the equilibrium vacancy concentration at $T_q$, or $C_v(T_q)$, and the decay constant at $T_a$, or $\gamma(T_a)$, are given by

$$C_v(T_q) = A \exp \left(-E_f/kT_q\right),$$

and

$$\gamma(T_a) = B \exp \left(-E_m/kT_a\right),$$

where $A$ and $B$ are certain constants, $E_f$ and $E_m$ being the formation and migration energies of vacancies. Comparing the value of the integral $\int dx/G(x, T_a)$ for each curve in Fig. 1 over a common range of $x$, we obtain the values for the vacancy formation energy and the decay constant as $E_f = 1.031 \pm 0.008$ eV and $\gamma(T_a) = 121.4°C = 0.276 \times 10^{-2}/s$.

The reliability of these values is confirmed by the following method. Consider a transformation of $t$ into $\tau$ by

$$\tau = \frac{C_v(T_q)}{\gamma(T_a)} \left\{ \beta(T_q) - \exp \left(-\gamma(T_a)t\right) \right\},$$

and determine $\beta(T_q)$ such that $\tau=0$ for $x=x_0$, then the original rate eq. (1) is transformed into

$$\frac{dx}{d\tau} = G(x, T), \quad \text{with} \quad x=x_0 \quad \text{at} \quad \tau=0.$$ 

Thus the curves for various quenching temperatures should fall on a single master curve, as is demonstrated in Fig. 2, when the transformation (4) is performed for each curve in Fig. 1.

Figure 3 shows the curve of $G(x, T_a)$ versus $x$ at $T_a=121.4°C$ as obtained from Fig. 2. $G(x, T_a)$ approaches zero with decreasing $x$.
with a small but nonvanishing curvature, tending to the equilibrium value for \( x \), or \( x_e = 0.950 \), obtained from another experiment. As is seen from the figure the reaction in this case is not strictly linear, but may be regarded as linear when the experiment is carried out within a limited range of \( x \), and then \( G(x, T) \) is approximated by \(-\text{const} \ (x - x_e^*(T_a))\), where the effective equilibrium value for \( x \) is slightly different from \( x_e \), or \( x_e^* = 0.957 \) at \( T_a = 121.4^\circ C \).

### III. Linear Kinetic Equations as applied for Various Heat Treatments

In the following we shall adopt a linear approximation for the rate equation for Warren-Cowley's short range order parameter \( \alpha \) as:

\[
\frac{d\alpha}{dt} = -A_0(\alpha - \alpha_e(T))C_v \exp \left( -\frac{E_m}{kT} \right),
\]

where \( A_0 \exp (-E_m/kT) \) is the reaction constant at the temperature \( T \) \( (6) \). Equation (6) should be solved simultaneously with an equation which gives the time variation in the vacancy concentration \( C_v \):

\[
\frac{dC_v}{dt} = -N_d a^2 v(C_v - C_e(T)) \exp \left( -\frac{E_m}{kT} \right),
\]

where \( N_d \), \( a \) and \( v \) are the dislocation density, the lattice constant and the atomic frequency factor. Equations (6) and (7) describe the process of short range ordering caused by the migration of vacancies, which are created or annihilated at dislocations and grain boundaries expressed by a uniform distribution. The equilibrium values for the short range order parameter \( \alpha_e(T) \) and the vacancy concentration \( C_e(T) \) are given by the thermodynamical relations, with the ordering energy 0.0763 eV and the vacancy formation energy \( E_f = 1.0 \) eV for the \( \alpha \)Cu–Al system \( (9) \).

Equations (6) and (7) are used for analyses of the changes of electrical resistivity, specific heat and lattice constant in \( \alpha \)Cu–Al due to the changes in short range order by various heat treatments. In the case of an isothermal annealing the equations are solved with \( T = \text{const} \), but otherwise the time variation of the temperature is given to represent the experimental heat treatment as faithful as possible. In the process of cooling from \( T_i \) to \( T_f \), for example, the temperature is expressed by

\[
T = T_f + (T_i - T_f) \exp \left( -t/t_0 \right),
\]

where \( t_0 \) is between 0.05 and 0.5 s for water-quench, or 5000 s for furnace-cooling.

Figure 4 shows the observed dependence of electrical resistivity in Cu–15.3 at\%Al upon the quenching temperature, as compared with the calculated result (dashed curve) of the short range order parameter under the same heat treatment as in the experiment. The values of the parameters used for the numerical solution are given in the figure. Both the experimental result and the theoretical one are represented as the changes relative to the values at room temperature when the specimen is furnace-cooled. The close agreement between the two shows the adequateness of our model and the approximation. By quenching the specimen from 450°C or above, the ordering in it takes place in the course of cooling by the aid of excess vacancies, and below 200°C the vacancy migration is prevented by the shortage of vacancies. Between 250 and 430°C the equilibrium state of order is brought to room temperature by quenching, as is assumed in the general treatment in Section II. A similar behavior of the electrical resistivity in the Cu–Zn system \( (10) \), also shown

![Fig. 4. Variations of resistivity as a function of quenching temperature. The results for Cu–Zn alloys were obtained by Lang et al.\textsuperscript{(10)} Dashed curve represents our calculated relative change of short range order parameter.](image-url)
Short-Range Order and Vacancies in Alloys

Fig. 5 Variations in resistivity (a) and short range order parameter (b) with rising temperature for furnace-cooled specimen. S and P2 denote single crystal and polycrystal, respectively. P1 denote the polycrystal initially deformed by drawing and then annealed at 360°C for 42.5 h.

in Fig. 4, may be explained on the same footing as described here.

The relative changes of the resistivity in the furnace-cooled single and poly-crystalline specimens of Cu–15.3 at%Al, when the temperature is raised at a constant rate, are given in Fig. 5, together with the corresponding results of our calculation. A close resemblance between the experimental results and the theoretical ones allows us for an interpretation that the furnace-cooled specimens are not in a thermal equilibrium, but that as the temperature is raised the atoms begin to move through vacancies to develop short range order approaching the equilibrium, and then the specimens begin to disorder as the temperature becomes higher. The observed difference between the curves for the single and polycrystals is satisfactorily explained as due to the difference in the dislocation density.

Figure 6(a) shows the calculated change of specific heat in the quenched specimen as the temperature is raised at a constant rate, showing the two exothermic stages and the one endothermic, which correspond to the ordering by the aid of quenched-in excess vacancies, the further ordering by thermal vacancies, and the disordering to follow the increasing temperature. The same feature is observed in the specific heat of Cu–15.5 at%Al quenched from 350°C(9), as shown in Fig. 6(b).

The effect of isochronal annealing to the
Fig. 7 Change of lattice parameter obtained experimentally (a), and calculated change of short range order parameter (b) as functions of isochronal annealing temperature $T_A$. The specimen was quenched from $T_A$ before the measurement.

The lattice constant of Cu–18.6 at% Al is given in Fig. 7(a), where the lattice constant is obtained from the bulk density of the specimen as a function of the final quenching temperature. The specimen, initially quenched from 400°C, undergoes the step-annealing, namely the heat treatment of raising the temperature by 25°C on annealing at each temperature for 15 min until the temperature reaches $T_A$, from which the specimen is quenched for the measurement. The result of the calculation following the same thermal procedure shows a qualitative agreement with the observed one. The results of similar experiment on the filed or cold-worked specimens are also reproduced by the numerical solutions of eqs. (6) and (7), with an appropriate choice of a large dislocation density.

IV. Conclusion

From the analyses described in the foregoing sections we conclude that in binary substitutional alloys such as αCu–Al the ordering proceeds only through vacancies, which are created and annihilated at dislocations and grain boundaries, migrating through the lattice inbetween. By applying the general kinetic equation for the process of ordering in isothermal annealing, we obtain the vacancy formation energy $E_f$ between 0.90 and 1.10 eV for αCu–Al, depending slightly upon the alloy concentration. The linearized kinetic equation, which is valid only over a limited range of the short range order parameter, can account for the changes of some physical quantities under various heat treatments, if we assume the vacancy migration energy between 0.65 and 0.70 eV. The result for the concentration dependence of the vacancy formation and migration energies will be discussed elsewhere by one of the present authors (C. K.). The actual form of the rate function $G(x, T)$ should be obtained by a theory based on a specific model for the elementary process of vacancy migration, and this is also under study by the present authors.

REFERENCES