

THE 4TH INTERNATIONAL CONFERENCE ON ALUMINUM ALLOYS

ISOTHERMAL PRECIPITATION IN A PRECIPITATION-HARDENING ALLOY

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Abstract

While the kinetics of the nucleation and growth with hard impingement has been studied rather thoroughly similar studies for the soft impingement reaction is largely lacking. The reason for this is that the latter reaction is much more complicated to simulate. In the present investigation the precipitation of Mg_2Si -particles in an Al-1.26 wt% Mg_2Si -Alloy has been investigated isothermally. The rate of growth of the precipitates has been determined by the rate of diffusion of the Mg- and Si-atoms. Ternary diffusion is included in the model. The kinetics with different nucleation conditions has been compared to site saturation and Johnson-Mehl-Avrami kinetics. The results obtained show that the transformation curves deviates somewhat from the teoretical values. The deviation increases when the particles are not randomly distributed in the material. When a transient nucleation rate is simulated which is probably the most realistic one, it is difficult to give approximate values of the transformation kinetics. The use of binary approximations to ternary diffusion problems have also been discussed. For quasibinary alloys the use of a mean diffusion coefficient is the best and almost an exact approximation. As the concentration deviates from a quasibinary composition, the use of an average diffusion coefficient is still the best approximation, as long as the deviation from a quasibinary composition is not too large. As the deviation from a quasibinary composition increases, the use of the diffusion coefficient of the element opposite of the one in excess gives the best approximation to a ternary treatment of the diffusion problem.

Introduction

One of the ultimate objectives within the field of science and technology of materials is to predict technological properties of the material from the knowledge of their microstructure. A comprehensive and up-dated presentation of this approach is given in for instance Cahn and Haasen (1). In a more limited sense, for a material in which a phase transformation is taking place during a heat treatment, one aims at an equation relating one technological property under consideration (say strength σ) to the fraction transformed, thus:

$$\sigma = F(X)$$

(1)

where X is defined most often as the volume fraction transformed versus the total available volume fraction. Very often one is interested in the evolution of σ with time. A prerequisite for establishing the relationship given in (1) is that the relationship

$$X = X(t) \quad (2)$$

is known with acceptable accuracy. If this is not the case the effort becomes rather qualitative. Thus an essential step in establishing relationship (1) is to establish relationship (2). Most work has been done on the isothermal transformations. However, the non-isothermal transformations are in industrial respect frequently of equal importance, thus:

$$X = X\left(t, \frac{dT}{dt}\right) \quad (3)$$

Also, great efforts have been made to convert the rather extensive information collected during the years related to the isothermal transformations to the non-isothermal case. The approach sketched above has long traditions within the field of heat treatment of steels (for example (2)).

Very many of the phase transformations of industrial importance are nucleation and growth transformations. When the transformation occurs by a completely random nucleation of the new phase with a nucleation rate \dot{N} and by hard impingement of the growing crystals, equation (2) can be written in the following way:

$$dX = (1 - X)dX' \\ X' = \int_0^t \dot{N}(t, \tau) \left[\int_{\tau}^t \dot{G}(t, T) \right]^3 dt \cdot d\tau \quad (4)$$

For this particular case equation (4) is an exactly correct expression of equation (2). In the case of soft impingement of growing precipitates this is not the case and several approximate expressions have been suggested, (3). These approximations have been compared with each other, but how well they describe the experimental results are difficult to judge because they contain several adjustable parameters.

The most commonly used expression for equation (4) even for these transformations is:

$$X = \frac{v(t)}{V_{\max}} = 1 - \exp\left(-\left(\frac{t}{\tau}\right)^n\right) \quad (5)$$

Here $v(t)$ is the volume of the precipitates formed after an ageing time t , and V_{\max} is the maximum volume of precipitates that can form at the temperature used. When site saturation occurs $n = 3/2$ and $n = 5/2$ when the nucleation rate is constant with time. When the nucleation rate is increasing with time $n > 5/2$ while $n < 5/2$ when the nucleation rate is decreasing with time. τ is a scaling time, the magnitude of which depends on the diffusion coefficient, the nucleation rate or the nucleation site density. The kinetics of the transformation is sensitive to the magnitude of n . One finds for $t_{0.99}$, the time taken before 99% of the transformation is completed:

$$\frac{dt_{0.99}}{dn} = -t_{0.99} \ln \ln \left(\frac{100}{n^2} \right) \quad (6)$$

Thus if an n -value of 1.4 or 1.3 is used instead of 1.5, $t_{0.99}$ is increased by approximately 8% or 17%, respectively. Thus, for a simulation of such transformations to be reliable the value of n needs to be as reliable as possible.

A rigorous treatment of the soft impingement transformation requires the solution of a very complicated diffusion problem. In order to obtain reliable results, numerical methods have to be used. In the present study a computer modelling of the growth of precipitates in a supersaturated solution has been carried out and the results have been compared with some approximate solutions.

Computer Simulations

The results presented in the present paper are all related to isothermal, diffusional transformations with soft impingement. The non-isothermal case will be published elsewhere (4).

The growth of spherical Mg_2Si - particles in a unit volume of a quasibinary AlMgSi -alloy was simulated under various nucleation conditions of the particles. In the first run all the particles were assumed to be nucleated at $t = 0$. The N nucleation sites ($10^7/\text{mm}^3$) were distributed at random within the unit volume. The unit volume was then subdivided into N Vorronoi-cells, each such cell associated with one particle. The size distribution, $f(v)$ of the Vorronoi-cells can not be calculated analytically, but there exist several numerical calculations of this distribution (5). This distribution can be expressed in an approximate way by the following mathematical expression (6):

$$f(v) = \frac{(kN)^k}{\Gamma(k)} v^{k-1} \exp(-kvN) \quad (7)$$

Here k was found by the numerical calculation to be 6.18 ± 0.11 but the exact value was believed to be 6. In the present simulation $k = 6$ is used. Γ is the gamma-function. In technological alloys the nucleation sites are not always randomly distributed within the material. In such cases the size distribution of the Vorronoi-cells will not be given by equation (7). In the second run this condition was simulated by retaining the site saturation condition but using a log normal cell distribution instead of the distribution given by equation (7):

$$f(R) = \frac{1}{R \ln \sigma_g \sqrt{2\pi}} \exp \left(-\frac{(\ln R - \ln R_g)^2}{2(\ln \sigma_g)^2} \right) \quad (8)$$

where R is the radius of the cell, R_g is the geometric mean and σ_g is the geometric standard deviation of the distribution. In the third run the particles were assumed to nucleate at a constant frequency \dot{N} (1/unit volume · unit time). In order to handle this case, some additional simplifications have to be introduced: At $t = 0$, a number $N_0 = \dot{N}_{\text{eff}} \Delta \tau V_0$ was nucleated in the total volume where \dot{N}_{eff} is the effective nucleation frequency and $\Delta \tau$ is the effective nucleation time. The

effective nucleation frequency is related to the nucleation frequency simply by: $\dot{N}_{eff} = \dot{N} \Delta t / \Delta \tau$. The total volume was divided into N_0 sub-volumes of equal sizes $v_0(0) = (V_0/N_0)$ and of spherical shape with a particle in its centre. These particles were allowed to grow for a period of time Δt . At this time, N_1 new particles were nucleated. These particles were allowed to nucleate only in that part of the total volume where the supersaturation was approximately unaffected by the growing particles. The reason for this restriction is that the nucleation rate is very sensitive to the degree of supersaturation (3). In the results presented here a reduction of 10% of the initial supersaturation was allowed without effecting the nucleation rate. For a larger reduction the nucleation rate was put equal to zero. Thus $N_1 = \dot{N}_{eff} \Delta \tau V_1$ particles were formed where V_1 is the volume where the supersaturation is larger than 90% of the initial supersaturation. The volume V_1 was now distributed equally between all particles. Thus, the size of the cells associated with the particles nucleated at $t = \Delta t$ is $v_1(\Delta t) = V_1 / (N_0 + N_1)$ while the size of the cells associated with the particles formed at $t = 0$ will be $v_0(\Delta t) = (V_0 - V_1) / N_0 + V_1 / (N_0 + N_1)$. All the particles were now allowed to grow for a time Δt and the same procedure was then repeated until the supersaturation was reduced to below 90% in the total volume of the material, after which the remaining part of the transformation occurs by growth only of the particles.

Quite often the growth of particles in ternary alloys is approximated by binary diffusion where the diffusion coefficient of the slowest diffusing element is used. The legacy of this approximation was studied in some details in the fourth run. The rate of growth of each particle within its cell was assumed to be controlled by long distance diffusion of Mg- and Si-atoms towards the particle. The cells were assumed to be spherical and closed with the spherical particle in the centre. These assumptions have been evaluated and found to be very good approximations (7). The diffusion problem was solved by taking account of ternary diffusion (8) and the movement of the particle/ matrix interface was also included in the calculation (7). Equilibrium was assumed to be established at the interface and the interface concentration was found from a revised AlMgSi-phase diagram (9). The magnitudes of the diffusion constants of Mg and Si in the ternary alloy have been found in a separate investigation (10).

Results and Discussion

The results of the first run are shown in Fig. 1. The transformation kinetics was simulated at several temperatures: from 524 °C, which is only one degree below the solvus temperature of the alloy down to 400 °C. As can be seen, all the curves have a very similar shape. In the early stages of the transformation, when the volume fraction formed is between 10^{-6} - 10^{-2} the slopes n of the lines are all very close to $\frac{3}{2}$. This is also to be expected because in this region very little impingement of the depleted zones has occurred, and all the particles are to a very good approximation growing truly in an infinitely large crystal. With increasing volume fraction formed the n -values of all the curves are decreasing continuously. In table 1 the n -values for the lines in Fig 1 in the interval 1-90% and 1-99% are given. As can be seen, all the n -values are less than $\frac{3}{2}$, which is the value predicted by the Johnson-Mehl-Avrami (J.M.A.)-approximation and are systematically becoming steeper with increasing undercooling. At temperatures close to the solvus temperature the n -value is as low as 1.34 in the range 1-99%. At large supersaturations the approximation $n = \frac{3}{2}$ must be considered to be an acceptable one.

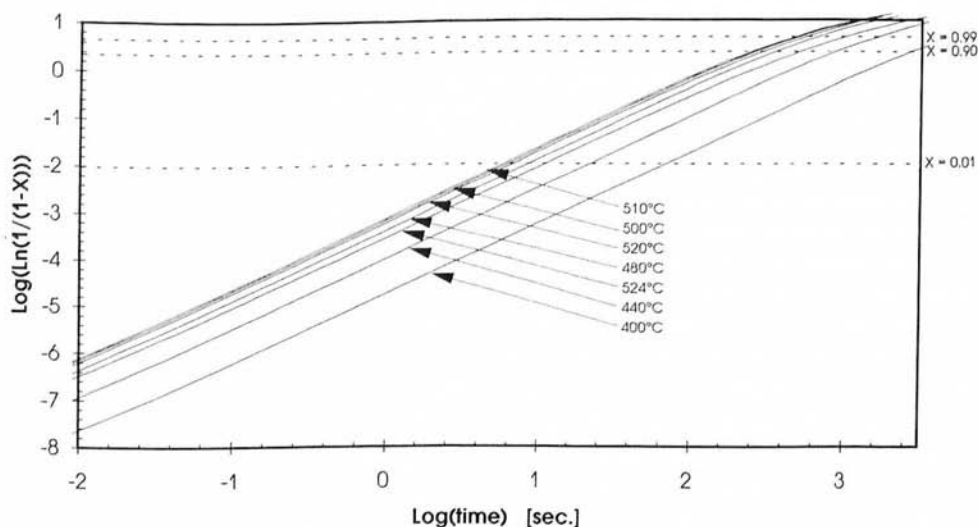


Figure 1. Isothermal transformation curves for several temperatures. The n -values (slopes) for the curves are shown in table I

Table I. Average n -values of the curves in Fig. 1 in the regions 1-90% and 1-99% transformed.

	400°C	440°C	480°C	500°C	510°C	520°C	524°C
1-90 %	1.474	1.470	1.458	1.448	1.440	1.416	1.410
1-99 %	1.425	1.420	1.408	1.400	1.392	1.377	1.340

The results of the second run are given in Fig. 2. The results at only one temperature (500 °C) are presented. As can be seen, a non-random distribution of the particles has a rather dramatic effect on the transformation kinetics. When the Vorronoi cell volumes have a log normal distribution, which implies that the particle size distribution is also log normal when the transformation is complete, the n -value in the interval 1-99% is as low as 1.2. The J.M.A.-approximation of $\frac{3}{2}$ can in this case not be considered an acceptable one.

On the other hand, when the particles are completely uniformly distributed in the lattice, which means that all the particles are of equal size, a n -value of $\frac{3}{2}$ is a very good approximation. The n -value in this case is even closer to $\frac{3}{2}$ than the value obtained in the first run.

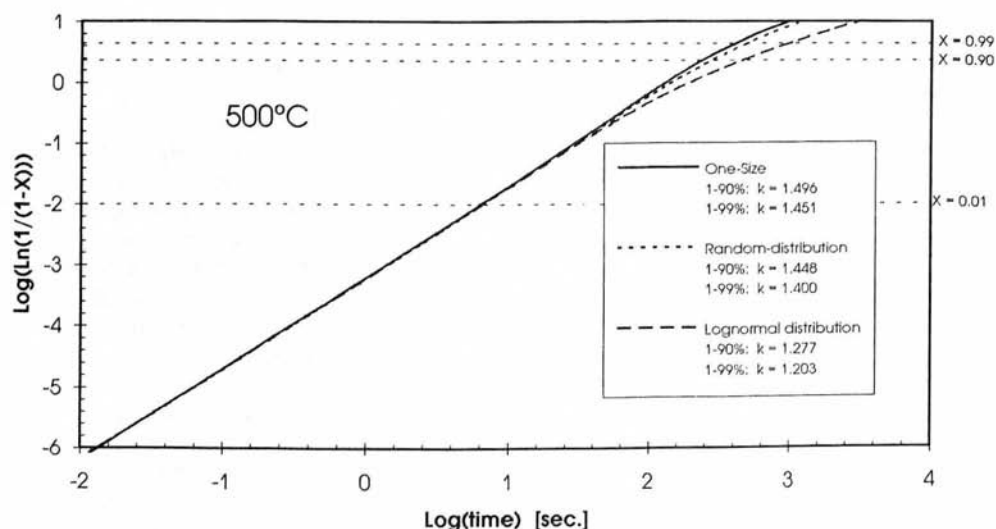


Figure 2. Transformation kinetics with the size distributions of the cells according to eqs. (7) and (8) and when all cells are of equal size.

The results of the third run are shown in Fig. 3 and compared with the site saturation case from the first run under the condition that an equal number of particles was formed during the transformation in both cases. In this case the J.M.A.-approximation yields $n = \frac{3}{2}$ while the simulated values in the interval 1-90% and 1-99% are 1.94 and 1.88 respectively. This demonstrates that the J.M.A.-approximation is not acceptable in this case.

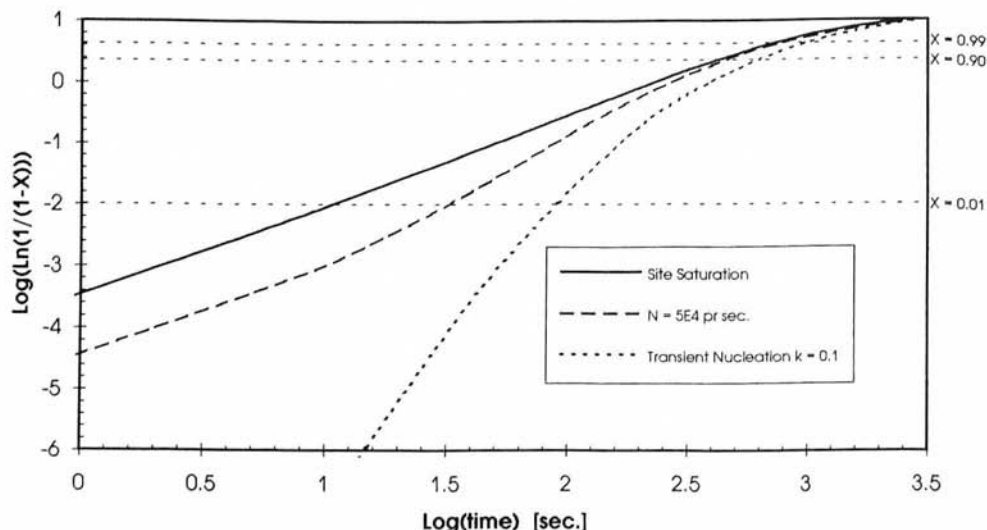


Figure 3. Site saturation nucleation kinetics compared with constant nucleation rate and transient nucleation conditions. In the two first cases the total number of nuclei was the same.

When a transient nucleation rate is simulated, with $t_0=0.1 \cdot t_{0.99}$, very large n -values ($n \sim 6$) are obtained. In this case, which is probably the most realistic one, an approximate value of n can not be given.

In Figs. 4a and b the results from a simulation with simultaneously diffusion of Mg and Si (ternary diffusion) are compared with different approximations using binary diffusion. In the case of a quasibinary composition of the alloy (Fig. 4a) an approximation using the mean value of the Mg and Si is very accurate. As can be seen, the use of the slowest diffusing element is a poor approximation. In Fig. 4b a case with excess silicon content (0.80 wt% Mg, 0.80 wt% Si) is simulated. In this case the use of a mean value of the diffusion coefficients is not as good as for a quasibinary alloy composition. However, the use of the slowest diffusing element (Si) is the poorest approximation, and also inferior to the use of the fastest diffusing element (Mg). In case of excess magnesium concentration the use of a mean diffusion coefficient is still the best, but in this case the use of the diffusion coefficient of Si gives a better approximation than the use of the diffusion coefficient of Mg. In general: For quasibinary alloys the use of a mean diffusion coefficient is the best and almost an exact approximation. As the concentration deviates from a quasibinary composition, the use of an average diffusion coefficient is still the best approximation, as long as the deviation from a quasibinary composition is not too large. As the deviation from a quasibinary composition increases, the use of the diffusion coefficient of the element opposite of the one in excess gives the best approximation to a ternary treatment of the diffusion problem.

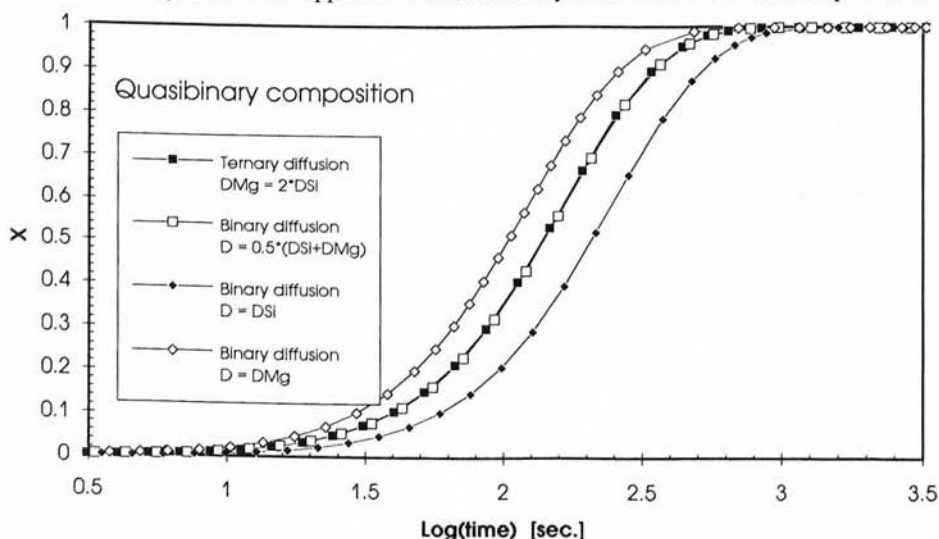


Figure 4a. Ternary diffusion compared with different approximations using binary diffusion for a quasibinary alloy.

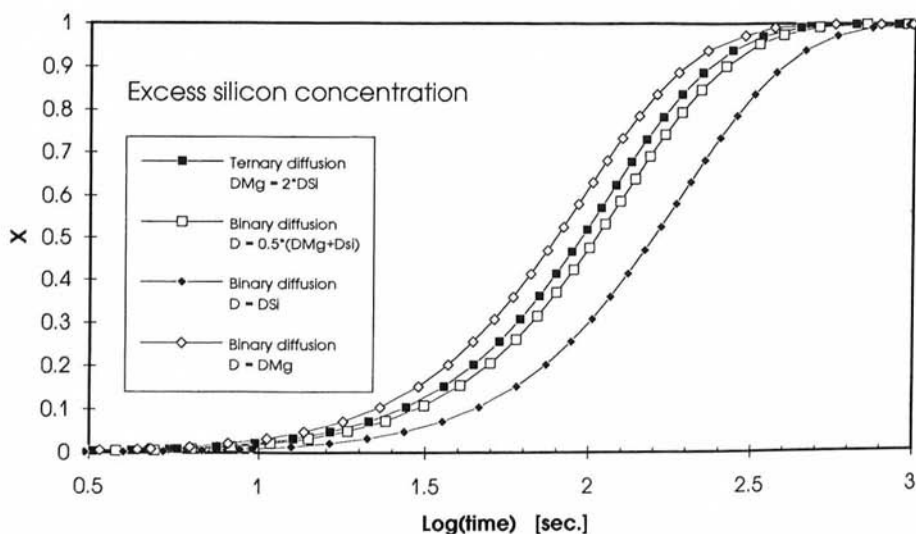


Figure 4b. Ternary diffusion compared with different approximations using binary diffusion for an alloy with excess silicon content.

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