MODELING OF DIFFUSION
IN MECHANICAL ALLOYING

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MODELING OF DIFFUSION
IN MECHANICAL ALLOYING

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SUMMARY

Mechanical Alloying (MA) is a ball milling process where a powder mixture placed in a ball mill is subjected to high-energy collision from the balls. The process leads to repetitive plastic deformation, fracturing and cold welding of the powders.

Diffusion is a fundamental process during mechanical alloying. In this thesis, a mathematical model, taking into consideration the critical factors which influence the diffusion process during MA, has been developed to predict the kinetics of diffusive intermixing in a binary miscible system during MA.

This model divides the MA process into three stages:

1) At the initial stage, the powder particles are cold-welded together to form a laminated structure. The chemical composition of the composite materials varies significantly.

2) At the second stage, the laminated structure is further refined as fracture takes place. The thickness of the lamellae is decreased. Although dissolution may have taken place, the chemical composition of the powders may still not be homogeneous. A very fine crystalline size can be obtained.

3) At the final stage, the lamellae become finer and eventually disappear. A homogeneous composition is achieved for all the powder particles, resulting in a new alloy with the composition corresponding to the initial powder mixture.

In view of the symmetrical and repetitive configuration of these layered structures, a sandwich structure consisting of two adjacent halves of the A and B layers
may constitute a representative element for numerical analysis. With periodically repeated deformation in MA, the process of diffusion and homogenization continues till the final stage where the average A element concentration is roughly the same in both A and B composite layers. The lamellar structure gradually disappears till A-B alloy is formed. Taking into the relative factors of the SPEX ball milling process, a mathematical model could be setup to predict the diffusion process and result during MA.

During the ball milling process, a change in the lattice parameter is an indication of the diffusion process of the two different elements. For ball milling of Ni$_3$Al, the status of the diffusion process is experimentally studied through the calculation of the change in lattice parameter by using the XRD method.

Comparison between the kinetics predicted by the present model with the relevant experimental data from Ni-Al shows that changes in composition and completion time of diffusion are in good agreement.
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Chapter 1

Introduction

Mechanical Alloying (MA) is a high-energy ball milling process employed to synthesize materials with homogeneous microstructure and novel properties. This method was originally devised by Benjamin et al. [1-3] in the late 1960s to produce oxide-dispersion strengthened nickel-based superalloy. During the last decade, the MA technique has been developed into a non-equilibrium process to produce materials such as intermetallic compounds, amorphous phase and nanocrystalline materials, materials that are difficult to be prepared by conventional methods.

In this process, a powder mixture placed in a ball mill usually at room temperature is subjected to high-energy collisions from the balls [4]. The two most important events involved in the process are the repeated welding and fracturing of the powder mixture [5-7].

Since the first experimental result reported, and especially after the discovery of the formation of metastable phase by ball milling, MA has attracted considerable attentions from materials scientists, not only due to the unique properties of products and promising commercial applications but also due to the usual physical phenomena involved. An increasing demand in the improvement of the properties of novel materials produced by MA to particular applications, and the improvement of the MA systems and apparatus designs for commercial scaling necessitate the development of mathematical models of MA. Modeling and computer simulation are based on
Chapter 1  Introduction

theoretical concepts and a formal mathematical description of the process. However, theoretical works in this area are very limited.

Based on the analysis of the available literature, all of the theoretical/modeling work can be subdivided into mechanistic, atomistic, thermodynamic, and kinetic models.

(1) Mechanistic Models

Developed in the past few years by Maurice and Courtney [8-11], Hashimoto and Watanabe [12], and others, these models consider the plastic deformation / cold welding of powders in a ball mill (“local” models) and the ball dynamics in a milling device (“global” models). Such an approach is based on the concept of Hertzian collision and employs certain results of the plastic deformation, theory of welding, and empirical relationships for work hardening. The underlying assumptions are well justified because the deformation during a collision occurs at high rates of $10^3 - 10^4 \text{ s}^{-1}$, but is less than those observed in the dynamic loading of metal powders, the impact velocity ($v \approx 1-3\text{ m/s}$) being substantially lower (compared with $v \approx 1,000 \text{ m/s}$ at dynamic processing)[13-14]

Starting with the mechanical properties of the materials and the characteristics of the materials and the characteristics of the mill, these models yield the plastic strain and strain rate, local-temperature rise due to a collision, particle hardness due to work hardening, the lamellar thickness, and the impact frequency and velocity. The results of modeling (in particular, the lamellae thickness, average particle size, and micro-hardness) are in reasonable agreement with experimental data for many alloy systems. The main disadvantage of mechanistic approach is that it is not linked with phase
transformation and chemical interaction in the particles undergoing repetitive plastic deformation.

(2) Atomistic Models

These models are based on the molecular dynamic (MD) approach and direct simulation of the atomic and defect structure of metastable solid phases [15-17]. The interaction of similar and dissimilar atoms in the crystal lattice is described using the Lennard–Jones potential. The key of these models is centralized at the consideration of solute atoms or crystal–lattice defects. Because of the rearrangement of atoms in the lattice (e.g., destruction of the long range order sequence, creation of antisite defects, vacancies, and dislocations), the elastic strain of the crystal lattice caused by the mismatch of atomic sizes and the formation of defects results in stability loss of the crystal lattice and eventually brings about the transition to an amorphous phase.

The atomistic models are capable of describing crystal-to-glass transition in solids under ball milling, solid-state inter-diffusion, hydrogen absorption, and irradiation [18-20]. However, the question of how the solute concentration in a crystalline phase is attained during MA (starting from blended elemental powders) is only marginally addressed.

(3) Thermodynamic Models

Phenomenological thermodynamic description is widely used for the interpretation of experimentally observed solid-state amorphization (SSA) during MA. In this approach, it is implied that because of the non-equilibrium nature of the process, the formation of stable (intermetallic) compounds is disallowed for certain
kinetic reasons, and the metastable equilibrium of terminal solid solutions with the amorphous phase often treated as a super cooled liquid. Research efforts are focused on an adequate description of thermodynamic functions of metastable phases.

Intrinsic in the thermodynamic approach is the absence of phase-formation kinetics. The development of kinetic models is important for a deeper understanding of the intricate mechanisms involved in MA.

(4) Kinetic Models

Most of the phenomenological kinetic models used for describing metastable phase formation were originally developed for a crystalline–phase layer growth and solid-state amorphization during thermal annealing of planar-binary multiplayer diffusion couples [21-33]. Early models considered the competitive diffusion controlled growth kinetics of crystalline phases (i.e., they neglected the interface reaction and nucleation barriers). It has been shown that at a certain ratio of the parameters $D\Delta c$ for adjacent phases, where $\Delta c$ is the homogeneity range, and $D$ is the interdiffusion coefficient, a phase will not grow fast enough to appear [21-33]. For thin layers, the interfacial reaction kinetics are more likely to control the growth rate. It has been shown that in the interface-reaction-controlled regime, an immediate phase can be kinetically unstable and will disappear. If the first phase to form in a thin-film diffusion couple is an amorphous phase, it must have attained a certain critical thickness - $X_{\text{critical}}$. However, the nucleation aspects were not addressed in the above models.

These concepts qualitatively agree with experimental data on the formation of the second (intermetallic) phase in thin films. However, all these models do not
consider the generation of defects (i.e., vacancies and dislocations) in metal particles during MA because of repeated plastic deformation. Direct observation of defects during the formation of phase in MA can be found in some works [21-33]. Disorder in intermetallic compounds during ball milling was examined by some people [21-33]. The formation of amorphous phase is also not examined in these models. Such models have only one link to MA - it is assumed that the thickness of the amorphous phase layer in a particle during MA always remains less than $x_{cr}$ because of plastic deformation.

Figure 1-1. A schematic of mechanical alloying modeling
Chapter 1  Introduction

(5) MA modeling as present study

The analyses discussed indicate that there is an obvious gap between the mechanistic and atomistic models of MA. The mechanistic models yielding an adequate description of plastic strain, and other characteristics of metal particle undergoing repetitive deformation/cold welding in a milling device are not linked to the transformation mechanisms, while the atomistic models are, in the most part, not connected to the deformation parameters during MA. The kinetic and thermodynamic models are intended to fill this gap and bring together the most interesting and promising results. This is schematically shown in Figure 1-1. Further progress in this area necessitates the development of novel macro kinetic models linking the plastic strain and generation of defects to the mechanisms and kinetics of metastable phase transformation. In particular, the intermixing of atoms at the interfaces of metals A and B in lamellar particles must be enhanced by the increased concentration of vacancies and dislocations.

Like most reactions in solids, diffusion is a fundamental process during mechanical alloying [34-36]. By analysis of the special characteristics of the ball milling process, three critical factors which influence diffusion in mechanical alloying have been found:

1) decrease in crystalline size which increases the diffusion area, and changes in diffusion mechanism from volume diffusion to grain boundary diffusion;
2) increase in density of defects in alloy which can decrease the activation energy, resulting in an increase in diffusivity; and
3) repeated fracturing and cold-welding of the powder particles which enable the powder particles to be always in contact with each other with atomically clean surfaces and minimized diffusion distance.

In the present study, a mathematical model based on the consideration of the three critical factors above has been developed to predict the kinetics of diffusive intermixing in a binary miscible system in the course of mechanical alloying. Comparison between the kinetics predicted by the present model with the relevant experimental data from Ni-Al shows that changes in composition and completion time of diffusion are in good agreement.
Chapter 2

Literature Review

2.1 Introduction

Mechanical alloying is a process of the repeated cold welding and fracturing of powder particles, which enables the powder particles to be always in contact with each other with atomically clean surfaces and with minimized diffusion distance. Microstructurally, the MA process can be divided into three stages:

1) At the initial stage, the powder particles are cold-welded together forming laminated structure. The chemical composition of the composite particles varies significantly within the particles and from particle to particle.

2) At the second stage, the laminated structure is further refined as fracture takes place. The thickness of the lamellae is decreased. Although dissolution may have taken place, the chemical composition of the powders may not be homogeneous. A very fine crystalline structure can be obtained.

3) At the final stage, the lamellae become finer and eventually disappear. A homogeneous composition is achieved for all the powder particles, resulting in a new alloy with the composition corresponding to the initial powder mixture.

Diffusion is a fundamental process during mechanical alloying. As in a normal diffusion process, its occurrence always decreases Gibbs free energy of the bulk materials. Diffusion ceases when a minimum Gibbs free energy is reached. There are two common mechanisms by which the atoms can diffuse through a solid. The operative mechanism depends on the type of sites occupied in the lattice. Substitution
atoms usually diffuse by a vacancy mechanism, whereas smaller interstitial atoms migrate by forcing their way between the larger atoms interstitially. These mechanisms also hold in the formation of new alloys using the mechanical alloying technique, even though the latter is normally carried out at room or sub-ambient temperature. Mechanical alloying minimizes the effect of product barriers on the reaction kinetics and provides the conditions required for the promulgation of solid-state reactions at low temperature.

2.2 Diffusion Mechanism

Due to thermal energy, the atoms in a solid vibrate about their rest positions. Occasionally, a particularly violent oscillation of an interstitial atom causes an atom to result in a jump. Such atomic movements generate atomic fluxes and are known as diffusion. Although atoms spend most of their time at the lattice sites, a small fraction of the time spends as atomic fluxes. Fluxes exist in both homogeneous and inhomogeneous materials. The net flux at equilibrium in all directions is zero, and therefore, the atomic fluxes across a plane in the forward and reverse directions are the same. On the other hand, the net flux in a solid which is not in equilibrium is not zero. Consequently, the system tends to return to its equilibrium state. Such diffusion fluxes determine the rates of solute transfer and hence the rates of transformations.

Diffusion flux is defined as the amount of diffusion substance passing through a unit area perpendicular to the diffusion direction per unit time. At constant temperature and pressure, atoms migrate from regions of high chemical potential to those of low chemical potential. Chemical potential gradients induce fluxes. The flux
vanishes when the gradients become zero. Under constant operating parameters, the flux is a function of the chemical potential gradient.

In a binary system, the two fluxes $J_1$ and $J_2$ of two components 1 and 2 can be written as [4]:

$$J_1 = -D_1 \times \left( \frac{dC_1}{dx} \right)$$  \hspace{1cm} (2-1)

$$J_2 = -D_2 \times \left( \frac{dC_2}{dx} \right)$$  \hspace{1cm} (2-2)

where $D_1$ and $D_2$ are diffusion coefficients of component 1 and 2 respectively. The chemical interdiffusion coefficient $D$ can be expressed as [4]:

$$D = N_1D_1 + N_2D_2$$  \hspace{1cm} (2-3)

where $N_1$ and $N_2$ are the fractional concentrations of the two components 1 and 2 respectively.

For a steady state diffusion, concentration of the two components 1 and 2 gradually changes at the interfaces. Diffusion in mechanical alloying process, however, differs from the steady state diffusion since the balance of atom concentration at the interface between two different components may be destroyed by subsequent fracturing of the powder particles. Consequently new surfaces are created by cold welding of different powder particles. The concentration of the diffusing species is important, which affects diffusivity. Large difference in composition at the interface therefore promotes interdiffusion.

In order to move an atom to an adjacent location, the atoms of the parent lattice must be forced apart into higher energy positions. The increase in free energy is referred to as activation energy. Activation energy for diffusion is equal to the sum of
the activation energy to form a vacancy and the activation energy to move the vacancy. The activation energy, $Q$, is therefore,

$$Q = Q_f + Q_m \quad (2-4)$$

where $Q_f$ is the activation energy for creating vacancies, and $Q_m$, the activation energy for moving vacancies. It appears that in most of the mechanical alloying processes, temperature is not a dominating factor since the temperature generated by collision is far from reaching the diffusion temperature. Therefore, factors other than temperature must significantly contribute to the diffusion process.

On microscopic level, atoms rearrange corresponding to the limit of elasticity [35]. There exist various mechanisms on such rearrangement. One such mechanism is the rupture of interatomic bonds and the rearrangement of atoms in the nucleus of dislocation. Dislocation movement and formation of dislocations are obvious manifestation of heavy plastic deformation. The rearrangement of atoms during milling can be analyzed using classical chemical kinetics.

During mechanical alloying, mechanical energy can partially be stored by the creation of dislocations and grain boundaries in the mechanically alloyed material. There are two primary classes of point defects, vacancies and interstitials. If there is sufficient activation energy present, atom can move in crystal lattices from one atomic site to another. When dislocations move along a slip plane, the mechanical energy is transformed into kinetic energy of the atoms which excites the translation mobility of the atoms. All atoms receive additional energy and mobility. As a result of formation of large amount of defects (vacancies are normally generated by thermal energy in thermally induced diffusion process) due to high energy collision of the powder
particles, the total activation energy required by diffusion is lower because part of the activation energy required to form vacancies may or may not be required completely.

In general, diffusivity can be written as:

\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]  

(2-5)

where \( D \) is the diffusion coefficient, \( D_0 \), material constant, \( Q \), activation energy, \( R \), universal gas constant and, \( T \), temperature.

An empirical correlation between \( Q \) and \( T_m \), the melting temperature, may be described by the following equation [6]:

\[ Q = 33.7T_m \]  

(2-6)

where \( Q \) is in joules, and \( T_m \) has the unit K.

Substituting Equation (2-4) into Equation (2-5), Equation (2-5) can be rewritten as:

\[ D = D_0 \exp\left[-\left(\frac{Q_f + Q_m}{RT}\right)\right] \]  

(2-7)

Equation (2-7) establishes that at the same value of \( D \), decrease in activation energy, such as that to create vacancies, is equivalent to increase in temperature. Therefore, it is possible to lower activation energy significantly by lowering \( Q_f \). It is believed that the lowering in activation energy plays an important role in the mechanical alloying process. In thermal induced diffusion, lattice defects may be annealed out very rapidly to result in a decrease in diffusion coefficient. Defects probably contribute little to the increase in homogenization kinetics in such diffusion process. However, the density of defect during mechanical alloying increases with mechanical alloying duration and therefore it significantly contributes to homogenization kinetics, which help to complete the diffusion process.
Bhattachary and Arzt [37] proposed a model for the calculation of diffusion. In their model, powder particles are considered to be an alternate plate-like fashion. This simplification of alternate structure has experimentally been observed as layered composite structure during intermediate stage of milling. In the equation, diffusivity includes two parts as formulated in the following equation:

\[
D = D_l \exp\left(\frac{-Q_l}{RT}\right) + \beta b^2 \rho D_c \exp\left(\frac{-Q_c}{RT}\right)
\]  \hspace{1cm} (2-8)

where \(D_l\) and \(D_c\) are respectively the material constants for the lattice and the core, \(Q_l\) and \(Q_c\) are respectively the activation energies of the lattice and core diffusion, \(b\), Burgers vector, \(\rho\), dislocation density and \(\beta\), a core diffusivity factor. In principle, the model considers the effect of dislocation accumulation which takes place as a result of large amount of plastic deformation causing enhancement of the diffusion coefficient due to extra mobility along the dislocation cores. The rate change in dislocation density with impact strain is [37]:

\[
\frac{d\rho}{d\varepsilon} = \frac{1}{100b} \sqrt{\rho}
\]  \hspace{1cm} (2-9)

where \(\varepsilon\) is the deformation strain. Diffusivity can be calculated if dislocation density is known. The dislocation formed during collision effectively act as pipes which allow atoms to diffuse along them with diffusion coefficient \(D_p\). The contribution of dislocations to the total diffusive flux through the powder particles depends on the density of dislocations. The apparent diffusivity \(D_{app}\) is a function of the cross sectional area of the dislocation pipes. The ratio of \(D_{app}\) to \(D_l\) can be written as:

\[
\frac{D_{app}}{D_l} = 1 + A \frac{D_p}{D_l}
\]  \hspace{1cm} (2-10)
where $A_p$ is the cross-sectional area of pipe per unit area of particle.

Butyagin [38] has indicated that there are two main differences in mechanical treatment and chemical processes. The first difference is that the activation energy is influenced by the elastic stress while the second one is that the energy librated after the transition of the barrier is the sum of the enthalpy of the process and activation energy of the barrier. Mechanical milling promotes the atoms to jump over the barrier by an exothermic process. In many cases, the height of the barrier is commensurable with the energy of interatomic bonds and energy released during the rearrangement of atoms. Some factors are important for the mechanochemical solid-state reaction. These factors can be divided into two groups. The first group may be characterized by an “extensive”, namely, specific surface area, particle size distribution and shape of particles, etc. It is also found that the stored enthalpy increases with prolonged mechanical alloying duration. The decrease in transition temperature from ordered $\gamma'$ to disordered $\gamma''$ is the result of the increase in stored energy when mechanical alloying duration is increased [37].

2.3 Thin Film Solution

If an inhomogeneous single-phase alloy is annealed, matter flows in a manner which will decrease the concentration gradients. If the specimen is annealed long enough, it will become homogeneous and the net flow of matter will eventually cease. Given the problem of a flux equation for this kind of a system, it would be reasonable to take the flux across that plane. For example, if the x-axis is taken parallel to the
concentration gradient of component 1 the flux of component 1 \((J_1)\) along the gradient can be given by the equation [5]

\[
J_1 = -D_1 \left( \frac{\partial C_1}{\partial X} \right),
\]

(2-11)

where \(D_1\) is called the diffusivity. This equation is called Fick’s first law and fits the empirical fact that the flux goes to zero as the specimen becomes homogeneous.

If a steady state does not exist, that is, if the concentration at some point is changing with time, Fick’s second law of diffusion must be used [5].

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left( D \frac{\partial C}{\partial X} \right)
\]

(2-12)

Imagine that quantity of a solute ‘\(\alpha\)’ is plated as a thin film on one end of a long rod of solute-free material. If a similar solute-free rod is welded to the plated end of this rod (without any diffusion occurring) and the rod is then annealed for time \(t\) so that diffusion takes place, the concentration of solute along the bar can be given by [5]

\[
c = \frac{\alpha}{2\sqrt{\pi Dt}} \cdot \exp \left(-\frac{x^2}{4Dt}\right)
\]

(2-13)

where \(x\) is the distance in either direction normal to the initial solute film. To confirm Equation (2-13) to be correct, two steps are necessary. First, differentiation shows that it is indeed a solution to Equation (2-12). Second, the equation satisfies the boundary conditions of the problem since

\[
\text{for } |x| > 0 \quad c \rightarrow 0 \text{ as } t \rightarrow 0
\]
for $x = 0 \rightarrow \infty$ as $t \rightarrow 0$

yet the total quantity of solute is fixed since

$$\int_{-\infty}^{\infty} c(x, t) dx = \alpha$$

(2-14)

For the mechanical alloying of ductile-ductile A-B alloy, since A and B form layered structure and the diffusion time is very short, about 100 seconds [37], the thin film solution can be used.

2.4 Grain Boundary Diffusion

2.4.1 Introduction

Grain boundary (GB) diffusion plays a key role in many processes occurring in engineering materials at elevated temperatures, such as Coble creep, sintering, diffusion-induced GB migration (DIGM), different discontinuous reactions, recrystallization and grain growth [39]. On the other hand, GB diffusion is a phenomenon of great fundamental interest. Atomic migration in a GB should be treated as a correlated walk of atoms in a periodic quasi-2D system with multiple jump frequencies [40, 41]. It should be noted that many fundamental properties of random walkers, such as the return probability $p_r$ depend on the dimensionality of the system (e.g. $p_r=1$ in 1D and 2D systems and $p_r<1$ in 3D systems [42]). GB diffusion is sensitive to the GB structure and chemical composition, and on the other hand it can be studied by modern radiotracer methods without disturbing the GB state. Due to these
unique features, GB diffusion measurements can be used as a tool to study the structure and physical properties of GBs.

Although the fact that GBs providing high diffusivity ('short circuit') paths in metals has been known since the 1920–1930s, the first direct proof of GB diffusion was obtained in the early 1950s using autoradiography [43]. The autoradiographic observations were followed by two important events, the appearance of the famous Fisher [44] model of GB diffusion, and the development and extensive use of the radiotracer serial sectioning technique. It was largely due to these events that GB diffusion studies were put on quantitative grounds and GB diffusion measurements became the subject of many investigations. During the four decades after Fisher, the experimental techniques for GB diffusion measurements have been drastically improved and have been extended to a wide temperature range and a broad spectrum of metallic, semiconductor and ceramic materials. On the other hand, the Fisher model, being still the foundation of GB diffusion theory, has been subject to careful mathematical analysis and extended to many new situations encountered in either diffusion experiments or various metallurgical processes. The fundamentals and recent achievements in the area of GB diffusion have been recently summarized by Kaur, Mishin and Gust [45]. A complete collection of experimental data obtained up to the end of the 1980s can be found in the handbook of Kaur, Gust and Kozma [46].

2.4.2 Basic Equations

Most mathematical treatments of GB diffusion are based on Fisher’s model [44], which considers diffusion along a single GB. According to Fisher's model, the
GB is represented by a high-diffusivity, uniform, and isotropic slab embedded in a low-diffusivity isotropic crystal perpendicular to its surface (Figure 2-2). The GB is described by two physical parameters: the GB width, $\delta$, and the GB diffusivity $D_b$. It is assumed that $D_b >> D$, where $D$ is the volume diffusivity. One more physical parameter, the GB segregation factor, will be introduced later.

Figure 2-1. Schematic geometry in the Fisher model of GB diffusion [44].

In a diffusion experiment, a layer of foreign atoms or tracer atoms of the same material is created at the surface and the specimen is annealed at a constant temperature $T$ for a time $t$. During the annealing, the atoms diffuse from the surface into the specimen in two ways, directly into the grains and, along the GB. In turn, the atoms which diffuse along the GB eventually leave it and continue their diffusion in the lattice regions adjacent to the boundary, thus giving rise to a volume diffusion zone around the boundary. Mathematically, this diffusion process is described by a set of two coupled equations [44]:

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) \quad (2-15)$$
where $|x| > \delta/2$, and
\[
\frac{\partial c_b}{\partial t} = D_b \frac{\partial^2 c_b}{\partial y^2} + \frac{2D}{\delta} \left( \frac{\partial c}{\partial x} \right)_{x=\delta/2} \tag{2-16}
\]

These equations represent diffusion in the volume, and along the GB, respectively. Here $c(x, y, t)$ is the concentration of the diffusing atoms in the volume and $c_b(y, t)$ is their concentration in the boundary. The second term in the right-hand side of Equation (2-16) takes into account the leakage of the atoms from the GB to the volume. The solution of Equations (2-15) and (2-16) should meet a certain surface condition (see below) and natural initial and boundary conditions at $x$ and $y \to \infty$.

Fisher [44], considered a constant source condition at the surface:
\[
c(x, 0, t) = c_0 = \text{const.}
\]

This condition can be established by depositing a layer of the diffusant with thickness $h$ such that $h >> (Dt)^{1/2}$. The constant source condition also applies when diffusion occurs from a gas phase. Suzouka [47, 48] introduced a so-called instantaneous source, or thin layer condition:
\[
c(x, y, 0) = M\delta(y), \quad \text{and} \quad \left( \frac{\partial c}{\partial y} \right)_{y=0} = 0 \tag{2-17}
\]
where $M$ is the amount of diffusant deposited per unit area of the surface, and $\delta$ is Dirac's delta-function. This surface condition suggests that the initial layer of the diffusant is completely consumed by the specimen during the diffusion experiment, i.e.
\[
h << (Dt)^{1/2}. \tag{2-18}
\]

In modern diffusion experiments, the thin layer condition is established more often than the constant source condition. This tendency is explained by the desire of the experimentalists to work with extremely thin radiotracer layers which would not
disturb the structural or chemical state of the GBs during the experiment. Of course, this imposes more strict requirements on the specific radioactivity of the diffusant and the sensitivity of the detection technique.

2.4.3 Classification

A GB diffusion experiment is a complicated process that involves several elementary processes, such as direct volume diffusion from the surface, diffusion along the GBs, partial leakage from the GBs to the volume, and the subsequent volume diffusion near the GBs. In a fine-grained polycrystalline sample, diffusion transport between individual GBs can also play an important role. Depending on the relative importance of such elementary processes, one can observe essentially different situations, or regimes of kinetics. In each regime there are one or two elementary processes that essentially control the overall kinetics. Each regime prevails in a certain domain of diffusion- temperatures, times, grain sizes and/or other relevant parameters. The knowledge of all possible regimes is extremely important for both designing diffusion experiments and interpreting their results. This is because the diffusion characteristics that can be extracted from the penetration profile depend on the kinetic regime and should therefore be identified a priori.
Harrison's [49, 50] introduces three regimes of diffusion kinetics, called type A, B and C (Figure 2-3).

(1) Type A kinetics

The A regime is only observed in the limiting case of high temperatures, and/or very long heating durations and/or small grain sizes. In such conditions the volume
diffusion length, \((Dt)^{1/2}\), is greater than the spacing \(d\) between the GBs and the volume diffusion fields around neighbouring GBs overlap each other extensively. Thus, the condition of type A kinetics is:

\[
(Dt)^{1/2} \gg d
\]  

(2-19)

Under this condition, an average tracer atom visits many grains and GBs during the anneal time \(t\). On a macroscopic scale, the whole system of a homogeneous medium appears to obey Fick's law with some effective diffusivity \(D_{\text{eff}}\). According to Hart [51], \(D_{\text{eff}} = fD_b + (1 - f)D\), where \(f\) is the volume fraction of GBs of a polycrystal, i.e. \(f = q\delta/d\), \(q\) being a numerical factor depending on the grain shape (\(q = 1\) for parallel GBs). If there is GB segregation of the diffusing atoms, \(f\) should be multiplied by \(s\), resulting in \(f = qs\delta/d\) [45]. The diffusion profile measured in the A regime follows a Gaussian function (instantaneous source) or an error function (constant source), and the only quantity determined from the profile is \(D_{\text{eff}}\). Since \(D_b \gg D\), \(D_{\text{eff}}\) is generally larger than \(D\), which explains why the diffusivity measured on polycrystals is often larger than the true value of \(D\). If \(d\) is very small, \(D_{\text{eff}}\) is dominated by the first term, and \(D_{\text{eff}} \approx qs\delta D_b/d\).

(2) Type B kinetics

If the temperature is lower, and/or the diffusion duration is shorter, and/or the grain size is larger than in the previous case, diffusion is dominated by the so called B regime. The condition of this regime is:

\[
s\delta \ll (Dt)^{1/2} \ll d
\]  

(2-20)

Here again, GB diffusion takes place simultaneously with volume diffusion around the GBs, but in contrast to the A regime the volume diffusion fields of
neighbouring GBs do not overlap each other (Figure 2-3). Individual GBs are thus isolated, and the solutions worked out for an isolated GB are also valid for the polycrystal.

The above condition implies that $\alpha \ll 1$. It is additionally assumed for the B regime that $\beta >> 1$, which means that the tracer penetrates along the GBs much deeper than in the volume [52]. Then, the penetration profile has a two-step shape shown schematically in Figure 2-3. The GB-related tail of the profile depends on the dimensionless variable $\omega$ only, the physical reason being the quasi-steady character of GB diffusion in this case. The triple product $s \delta D_b$ is the only quantity that can be determined in the B regime. In this regime, Equations (2-19) and (2-20) can be applied for the processing. The conditions of the B regime are the most commonly encountered in GB diffusion measurements. For reasonable anneal times, the B regime comprises the widest and the most convenient temperature range.

(3) Type C kinetics

If diffusion is carried out at lower temperatures and/or shortening anneal times, there will be no volume diffusion. Diffusion only takes place along the GBs, without any essential leakage to the volume (Figure 2-3). In this regime, called type C, $(Dt)^{1/2} \ll s \delta$. This relation shows that the criterion for the C regime is $\alpha >> 1$. In practical conditions, the regime is identified as C if $\alpha > 10$. The concentration profile in the C regime is either a Gaussian function (instantaneous source) or an error function (constant source) with the diffusivity $D_b$. If the profile is measured experimentally (which is extremely difficult to implement, because the amount of tracer diffused into the sample is very small), $D_b$ can separately be determined from $s$ and $\delta$. 
If the profile is accurately measured in a wide concentration range, the B and C regimes can be distinguished from the shape of the profile, and not only from the $\alpha$-value. This is illustrated in Figure (2-4), where the C regime profile for GB self-diffusion in Ag was measured using the carrier-free radiotracer $^{105}$Ag [53].

In order to measure this profile in a wide concentration range, a carrier-free $^{105}$Ag radiotracer layer was implanted at the ISOLDE/CERN facility. After a microtome sectioning, the radioactivities of the sections were determined using a well-type intrinsic Ge $\gamma$-detector with a high sensitivity and extremely low background. The tail of the profile shows a downward curvature when plotted as $\log \bar{c}$ versus $y^{6/5}$ (B regime format, lower scale) but becomes a straight line when plotted as $\log \bar{c}$ versus $y^{2}$ (C regime format, upper scale).
Fig. 2-3. A typical penetration profile of GB self-diffusion in polycrystalline Ag measured in the C regime ($\alpha=17$) [53].

2.5 Diffusion Through Dislocations

In a recent paper [54], Schwarz proposed a model for MA based on diffusion of solutes along dislocation cores. It is assumed that in ball milling, the exchange of atoms between two "cold-welded" elemental particles occurs via pipe diffusion along dislocations terminating at the interface. A further assumption is that the pipe diffusion occurs during relatively long times, of the order of hundreds of seconds, between the collision events involving trapping of particles between two colliding balls or between a ball and a vial wall. Upon a stress pulse associated with ball impact, some or all dislocations in a powder particle are displaced leaving behind a string of solutes and
are available as "diffusion pumps" again. As suggested by Schwarz, this mechanism of repetitive periods of "pumping" of solutes across the interface leads to the formation of extended solid solutions or amorphous alloys and can explain the major features of MA. As a result, the solute penetration depth as estimated by Schwarz using the parameters for pipe diffusion is only of the order of tens of nanometers. Schwarz also suggested that the incubation time often observed in MA experiments is required to refine the powder down to this particle size (tens of nanometers).

There are different mechanisms of interaction between dislocations and solute atoms (elastic, chemical, and electrostatic), the elastic interaction due to the size mismatch between solute and matrix atoms usually giving the major contribution to the interaction energy [55]. This energy is determined by the hydrostatic component of the elastic stress around the dislocation line. The hydrostatic component is the largest for a pure edge dislocation and the smallest for a pure screw dislocation, the elastic interaction energy in the latter case being determined by the anharmonicity effects which are generally small [56]. The accelerated diffusion along the dislocation lines occurs mainly in the core region, where the continuum elastic theory cannot be applied. However, it was shown [55] that using the equations of linear elasticity and assuming \( r_0 = (2/3)b \), where \( r_0 \) and \( b \) are the distance between the dislocation core and the solute atom and the magnitude of the dislocation Burgers vector, respectively, one can get a reasonable agreement between calculated and experimentally measured interaction energies. Therefore, to demonstrate the effect of dislocation curvature on the diffusion along the dislocation line, the equations of linear elasticity should be used. The variable edge component of the Burgers vector along the mixed curved
dislocation gives rise to variable interaction energy, which provides an additional driving force for diffusion. Here it is assumed that the variation of interaction energy along a curved dislocation is due to the variation of the edge component of the Burgers vector only. The magnitude of the interaction, i.e. the binding energy, will be sufficiently large even for a purely screw component. So that a string of solutes can be formed at the dislocation if the solute is supplied from an external source. This assumption is supported by the observation of yield points on deformation curves, which implies that solutes can effectively pin the screw portions of the dislocation loops [55].

It was shown that the elastic stress from a curved dislocation can be divided in two parts, one of which corresponds to the stress from an infinite straight dislocation tangent to the curved dislocation, and the second, non-local one, is caused by the curvature [57]. The ratio of the non-local term to the local one at a distance $r$ from the dislocation core scales approximately as

$$\frac{r \ln(8 \rho/r)}{2 \rho}$$

where $\rho$ is the radius of curvature. It can be seen from the expression (2-21) that for $\rho >> r$ this ratio is small and the non-local effects can be neglected. The geometry of the model is shown in Figure 2-5 a. An obvious reason for acceleration of the rate of solute penetration by pipe diffusion is the fact that solute atoms are supplied from both ends of a curved dislocation. In order to isolate the effect of curvature, they also calculate the total amount of the solute diffused into a dislocation in the geometry of Figure 2-5 b, in which the solute is supplied into the straight dislocation segment of the same length as the curved one, from both ends. In both cases they neglect the image force
arising due to the presence of a free surface [55], because its averaged amplitude scales as $1/\rho$, which for $r<<\rho$ is much smaller than the elastic stress from the dislocation itself scaling as $1/r$. The solute atoms are distributed around the dislocation inhomogeneously. However, only consider the maximum interaction energy, which corresponds to the maximum solute concentration in the dislocation core was considered. In this approximation, and for $r_0 = (2/3) b$, the interaction energy $W$ per mol of solute is given by

$$W = -\frac{G\Delta\omega(1 + \nu)}{2\pi(1 - \nu)} \sin \varphi$$  \hspace{1cm} (2-22)

where $G$, $\nu$ and $\Delta \omega$ are the shear modulus, the Poisson's ratio and the difference of atomic volumes between the solute and the matrix, respectively. $\varphi$ is the angle of diffusion solute geometry as shown in Figure (2-5). The energy $W$ contributes to the chemical potential of solute atoms, $\mu_s$. The difference between the latter and the chemical potential of matrix atoms is known to be the driving force for interdiffusion in the substitutional solid solutions. In the approximation of ideal solutions (where the free energy of mixing is caused by the entropy terms only) the diffusion equation for the molar concentration of solute $c$ can be written in the form:

$$\frac{\partial c}{\partial t} = -\text{div} \left( \frac{Dc(1-c)}{RT} \text{grad} \left[ RT \ln \left( \frac{c}{1-c} \right) + W \right] \right)$$  \hspace{1cm} (2-23)

where $t$ and $D$ are the time and the diffusion coefficient along the dislocation line, respectively, and $RT$ has the usual meaning. It is implied that the pipe diffusion corresponds to a regime in which outward diffusion from the core is negligible. This is a reasonable assumption for the temperatures, at which the MA is usually carried out,
even if heat release due to ball impact is considered. Combining (2-22) and (2-23) and using the polar coordinates one obtains the diffusion equation of the form

\[ \frac{\partial c}{\partial t} = \beta \frac{\partial^2 c}{\partial \rho^2} - \alpha(1 - 2c) \frac{\partial c}{\partial \phi} \cos \phi + \alpha c(1 - c) \sin \phi \]  

(2-24)

where

\[ \alpha = \frac{DG\Delta \omega(1 + \nu)}{2\pi(1 - \nu)RT\rho^2} \text{ and } \beta = \frac{D}{\rho^2} \]  

(2-25)

Figure 2-4. The geometry of the model of diffusion along a curved dislocation:

(a) Both the acceleration of diffusion and the difference in geometry are taken into account in calculating the solute concentration at the depth corresponding to the point A.

(b) The total amount of the solute diffused into the curved and the straight dislocation lines with the same length and the same boundary conditions is calculated.
The above estimates were based on linear elasticity calculations which do not apply in the dislocation core regions. In view of the fact that they provide a prevalent contribution to the total diffusion flux, one cannot expect a high numerical accuracy of the results. However, the calculations were aimed at showing the relative effect of dislocation curvature, and it is expected that more accurate, atomistic computations will certainly not change the sense of the effect predicted and probably its order of magnitude either. As Fiore and Bauer [58] indicated it in their review paper: "The objection... to the use of linear isotropic elasticity to estimate the binding enthalpy have been exclaimed since the time of original papers of Cotrell and Bilby. However, the success of this elasticity analysis in accounting for the results of experimental binding energy studies indicates that some confidence might be placed in it." In fact, recent atomistic calculations by Smith, Najafabadi and Srolovitz [59] give us additional confidence in the above linear elasticity based estimates. They considered a dissociated \((a_0/2)[110]\) dislocation in a Ni-Cu solid solution and calculated the Cu concentration profile around it. The calculations revealed a strong dependence of the maximum Cu concentration in the core region on the type of interatomic potential used. The maximum Cu concentration calculated with the embedded atom method (EAM) interatomic potential specially optimized for the Ni-Cu system exceeded the concentration calculated with the help of general EAM potential for Ni-Cu by a factor of 3. Therefore, at the present state of our knowledge it is very difficult, if not impossible, to perform precise quantitative calculations of the solute segregation to the dislocation core. In this situation, the linear elastic model used provides a reasonable estimate for the effect. Indeed, a comparison between atomistic calculations and the
linear elasticity result based on the size effect, i.e. involving the hydrostatic component of stress, can be made using Fig. 6 of Ref. [59]. For the general EAM potential the solute concentrations calculated using the two approaches only differ by a factor smaller than 2, which indicates that our linear elastic analysis may give the right quantitative estimate of the effect in this case. For the optimized potential the discrepancy between the two approaches is larger. However, for the regions of tensile stress, the calculated Cu concentration is always higher than that predicted by the linear elastic analysis. Because in the linear approximation, the hydrostatic stress is only produced by the edge component of the dislocation Burgers vector [60], this should increase the overall driving force for diffusion along the curved dislocation. It is thus believed that the prediction of a strong enhancement of diffusion due to the curvature effect will sustain an atomistic simulations test.
3.1 Diffusion Model

3.1.1 Introduction

To better understand and finally be able to control the MA process, many models have been proposed including mechanistic, atomistic, thermodynamic and kinetic models. Since diffusion is a fundamental process during MA, it is important to illustrate the mechanism of diffusion in the MA process.

To propose diffusion model for MA, the special characteristics of diffusion in MA has been summarized in Chapter 2. There are three critical factors which influence diffusion in MA:

(a) Decrease in crystalline size increases the diffusion area, and changes the diffusion mechanism from volume diffusion to grain boundary diffusion;

(b) Increase in density of defects in alloy can decrease the activation energy, resulting in an increase in diffusivity; and

(c) Repeated fracturing and cold-welding of the powder particles enables the powder particles to be always in contact with each other with atomically clean surfaces and with minimized diffusion distance.
In this chapter, a mathematical model, based on the consideration of the three critical factors above, has been developed to predict the kinetics of diffusive intermixing in a binary miscible system in the process of mechanical alloying.

3.1.2 The Model

MA is a process of repeated cold welding and fracturing of powder particles, which enables the powder particles to be always in contact each other with atomically clean surfaces and with minimized diffusion distance. Microstructurally, the process can be divided into three stages:

1) At the initial stage, the powder particles are cold-welded together to form a laminated structure. The chemical composition of the composite materials varies significantly.

2) At the second stage, the laminated structure is further refined as fracture takes place. The thickness of the lamellae is decreased. Although dissolution may have taken place, the chemical composition of the powders may still not be homogeneous. A very fine crystalline size can be obtained.

3) At the final stage, the lamellae become finer and eventually disappear. A homogeneous composition is achieved for all the powder particles, resulting in a new alloy with the composition corresponding to the initial powder mixture.

At the initial stage of ball milling, compressive forces due to the collision of balls flatten the powder particles since the materials are generally soft at this stage. For the binary miscible A-B system, for example Ni-Al system, prolonged milling and cold
welding lead to the formation of refined and homogenized layered structures. Diffusion mainly occurs across these composite layers. Figure 3-1 shows a typical lamellar microstructure developed in Ni$_3$Al after 120 minutes of ball milling.

![Figure 3-1. A typical lamellar microstructure developed in ball milling of Ni$_3$Al after 120 minutes.](image)

As diffusion proceeds, the composite layers becomes more and more refined and eventually disappears at the end of diffusion as the final product formed. A homogeneous chemical composition can be achieved leading to the formation of a new alloy with composition corresponding to the starting powder mixture components. In view of the symmetrical and repetitive configuration of these layered structures, a sandwich structure consisting of two adjacent halves of the A and B layers may constitute a representative element for numerical analysis.

During ball milling of A-B alloy, the balls in the vial collide with the powder with force and frequency corresponding to the motion of the milling machine. The collision energy can be transferred to the chemical diffusion between A and B powder composite layers. For SPEX mill, Schwarz [9] approximates the collision time to $t_1 \approx $
$2B / v_s$, where $B$ is the ball diameter and $v_s$ is the speed of a longitudinal acoustic wave in the ball material. For 6mm diameter steel balls, if $v_s$ is 5800 m/s, the impact time $t_1$ should be equal to $2\mu$s, independent of the ball velocity before impact. There is an interval time of $t_2$ between each collision for a given powder particle. The interval time $t_2 \gg t_1$ and is harder to predict. The collision frequency is much shorter than $1/t_2$. For example, in a SPEX mill the collision frequency is about $20s^{-1}$. For any giving collision, each ball can only make contact with a finite number of other balls, less than 12. The area of contact for a ball-to-ball head-on collision is small. Maurice and Courtney [8,9] estimated that in a SPEX mill a given ball must make about 2000 characteristic impacts before each powder particle associated with it is plastically deformed once. Therefore the interval time $t_2$ is about 100s, and the ratio $t_2: t_1$ is $5\times10^6$.

The present model is illustrated in Figure 3-2 where an A-B alloy diffusion process is modeled. A and B represent different constituents and C (X, t) represents the content of A in B, where X represents the lamellar thickness of A (B) alloy. It is assumed that the thickness of the lamellar lineally decreases with milling time. However, the total volume of A and B does not change. The change in diffused matters is equal to the change in the content (A in B) in the diffusion system.

Figure 3-2 (a) shows the initial state of A and B particles after the first collision. Every time when A and B layers are in contact with each other through the collision of the ball, the contact time is about 100 seconds (which is the interval time between the consecutive collision), long enough to let diffusion have enough time to process across the A-B interface. After diffusion, the concentration can approximately be assumed to be homogenous in their respective layers (Figures 3-2. (b) and (c)).
Therefore, in the half of “A” layer, the A composition is reduced to an average concentration level due to the diffusion of element B into A layers, and vice versa. After the interval time, another consecutive collision takes place which results in a new diffusion between A and B with the average concentration difference introduced by diffusion from the previous interval. (Figures 3-2. (d) and (e)). Due to plastic deformation caused by the collision between the ball and the composite layers, the thickness of the layers is reduced to a new dimension after each collision, forming a finer and finer lamellar structure which facilitates the diffusion process by increasing more A-B contact area, and accelerates the diffusion process by introducing grain boundary diffusion (as the grain size gets finer and finer) and dislocation diffusion (as more and more plastic deformation creates denser dislocation).

With periodically repeated deformation in MA, the process of diffusion and homogenization continues till the final stage (Figures 3-2. (f) and (g)) where the average A element concentration is roughly the same in both A and B composite layers. The lamellar structure gradually disappears till A-B alloy is formed.

In this mode of ball milling, only diffusion is considered.
Figure 3-2. The illustration of modeling of A-B alloy diffusion process
3.1.3 Diffusion Flux

Diffusion flux is the amount of diffusion substance passing through a plane of unit area perpendicular to the diffusion direction per unit time. The diffusion flux in MA can be calculated according to the diffusion mode given in section 3.1.2.

During the instance of collision, atoms of A constituent diffuse through A-B interface. The amount of diffusion flux may be represented by Fick’s First Law:

$$J = -D \left( \frac{\partial C}{\partial X} \right)$$  \hspace{1cm} (3-1)

where $D$ is the diffusivity, $C$ is concentration of the diffused constituent and $X$ is the distance away from A-B interface.

Since concentration changes with collision time, the change in concentration has to be considered using Fick’s Second Law:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left( D \frac{\partial C}{\partial X} \right)$$  \hspace{1cm} (3-2)

At a small time interval which is equal to the duration of the collision, the amount of matter flows from A to B can be written as:

$$dN = J \cdot dt = -D \frac{\partial C}{\partial X} \cdot dt$$  \hspace{1cm} (3-3)

Since A and B form a very fine layered structure, thin film solution may be used [61-81],

$$C(X,t) = C_A \left[ \text{erf} \left( \frac{X}{2\sqrt{Dt}} \right) \right]$$  \hspace{1cm} (3-4)

where $C_A$ is the concentration of A in the A-B alloy.
Taking partial derivative with respective to X (for erf function, using derivative in equation (3-6)),

\[
\frac{\partial C(X, t)}{\partial X} = \frac{2C_A}{\sqrt{\pi}} \cdot \frac{1}{2\sqrt{Dt}} \cdot \exp\left(-\frac{X^2}{4Dt}\right) \quad (3-5)
\]

\[
\left(\frac{d}{dy}(\text{erf}(y))\right) = \frac{2}{\sqrt{\pi}} \cdot \exp\left(-y^2\right) \quad (3-6)
\]

At the interface, X = 0,

\[
\frac{\partial C}{\partial X} = \frac{C_A}{\sqrt{D}} \cdot \frac{1}{\sqrt{\pi}} \quad (3-7)
\]

Substitute equation (3-7) into equation (3-3), it follows that,

\[
dN = J \cdot dt = -D \frac{\partial C}{\partial X} \cdot dt = C_A \cdot \sqrt{\frac{D}{\pi}} \cdot dt \quad (3-8)
\]

By integrating diffusion time from 0 to t seconds, the amount of diffused matter can be found as:

\[
N = \int_0^t C_A \cdot \sqrt{\frac{D}{\pi}} \cdot dt = 2C_A \cdot \sqrt{\frac{Dt}{\pi}} = C_A \cdot \sqrt{\frac{4Dt}{\pi}} \quad (3-9)
\]

At the A-B interface, X = 0. For first collision time interval, the diffused matter is equal to:

\[
N_1 = C_A \cdot \sqrt{\frac{4Dt}{\pi}} \quad (3-10)
\]

where \(N_1\) represents the amount of diffused matter across the A-B interface during the time interval between two consecutive collisions.

Because the time interval between consecutive collisions is about 100 seconds, it can therefore be approximately assumed that the concentration is homogenous in the
respective layers. Hence each consecutive collision comes with new contact surfaces.

The concentration of undiffused A in A-B alloy has changed to \((1-N_1)\).

Thus,

\[
N_2 = (1 - N_1) \cdot \sqrt{\frac{4Dt}{\pi}}
\]  

\[\text{...}\]

\[
N_n = (1 - N_{n-1}) \cdot \sqrt{\frac{4Dt}{\pi}}
\]

where \(N_2, \ldots N_n\) represent the diffused matter across the A-B interface during each consecutive collision time interval. As the total volumes of A and B atoms do not change during the diffusion process, the diffused matter also represents the content of A in B layer.

When \(N_1 + N_2 + \Lambda + N_n = \frac{1}{2} C_A\) (\(C_A\) represents the content of A in A-B alloy), half the content of A is diffused into B, which means that a homogenous concentration has been achieved, and the diffusion process has completed to achieve a final A-B alloys.
3.2 Diffusivity

3.2.1 Activation Energy

Diffusive stages have been demonstrated to be relevant for reactions in Ni-Al layers. Figure 3-3 shows the relationship between the activation energy, $Q$, and the composition of bulk and thin film diffusion [64, 65].

![Graph showing the relationship between activation energy and Ni mole fraction.](image)

Fig. 3-3. Activation energy for diffusion and other processes in Ni-Al system as a function of Ni mole fraction. □ Ni volume diffusion; ▄ Ni diffusion in nanocrystalline materials; ■ Al volume diffusion; ▇ Al diffusion in nanocrystalline materials; ◆ volume interdiffusion; ◇ interdiffusion, grain growth, and ordering in nanocrystalline materials; △ grain-boundary or dislocation diffusion.

Through investigation of the figure, the following conclusions can be made:
(1) The highest activation energies for atomic motion in Ni-Al, above 3 eV, pertain to Ni diffusion, or to interdiffusion in bulk-ordered compounds, i.e. stoichiometric NiAl and Ni$_3$Al. For off-stoichiometric NiAl and Ni$_3$Al, $Q$ decreases steadily as a function of composition both in Ni- and Al-rich sides due to the increase in vacancy content in the lattice [64, 65].

(2) For pure Ni, there is a substantial gap between $Q$ for volume diffusion and that for grain-boundary diffusion (3.0 eV vs 1.2–1.4 eV). Values of $Q$ for grain growth of nanocrystalline nickel (1.36 eV–1.6 eV) fall close to the low end of the range. Al diffusion in nanocrystalline Ni has an even lower $Q$ value of 0.93 eV [64, 65].

(3) Studies on the kinetics of ordering of small-grained Ni$_3$Al have provided a $Q$ value of the same order of magnitude as that for grain growth in Ni, i.e. much lower than that for Ni diffusion in the bulk.

(4) The formation of Al$_3$Ni, or the structurally related Al$_6$Ni$_2$ phase, has provided a less ample set of $Q$ values in the range 1.2 eV–1.7 eV [64, 65]. The lower values in the range pertain to nucleation and/or growth in very thin layers, the higher to bulk growth.

(5) $Q$ for tracer diffusion of Ni in Al is of the same order of magnitude as that for self-diffusion of Al along grain boundaries and dislocations but definitely lower than that for self-diffusion of Al in the bulk.

(6) Activation energies for all processes, diffusion, grain growth, ordering, phase formation, occurring in nanocrystalline materials have values comparable with those of defect diffusion (i.e. grain boundaries and dislocations). The contrast between open and full symbols in Figure 3-3 provides a clear impression of this effect. In the
case of thin films, they are considered as nanophases for those having periodicity below 80 nm. From the results on Kissinger analysis of DSC signals, the Al$_3$Ni formation in very thin layers provides an activation energy which is consistent with the definition of a nanophase. Once the layers have grown and Al$_3$Ni$_2$ or NiAl are formed, the activation energies fall well within the ranges obtained with bulk samples.

Available coefficients of interdiffusion of Al$_3$Ni layer growth at temperatures ranging from 650°C to 1000°C agree rather closely and can be represented as $\hat{D} = 2 \times 10^{-4} \exp (-1.5/kT)$ [66]. A recent paper on thin-film couples of Al$_3$Ni reports $\hat{D} = (5-50) \times 10^{-4} \text{m}^2/\text{s}$ and $Q = 1.64-1.76 \text{eV}$ [66] in the temperature range from 330°C to 760°C, growing according to $(\hat{D}t)^{1/2}$.

3.2.2 Diffusivity

Diffusion is a function of diffusivity, $D$, which is temperature dependant and is usually expressed by an Arrhenius type equation:

$$D = D_0 \cdot \exp \left( \frac{-\Delta Q}{RT} \right)$$  \hspace{1cm} (3-13)

where $D_0$ is a material constant, $T$, the temperature, $\Delta Q$, the activation energy for diffusion and $R$, the gas constant.

Diffusion takes place through grain as well as along grain boundary. Therefore the diffusivity is a function of grain and grain boundary diffusion [67]:

$$D_{\text{eff}} = (1 - F)D_g + FD_b$$  \hspace{1cm} (3-14)
where \( D_{\text{eff}} \) is the effective diffusivity, \( D_i \), the coefficient of lattice diffusion, \( D_b \), the coefficient of grain boundary diffusion and \( F \), the area fraction of grain boundaries in a plane perpendicular to the direction of diffusion. If the diameter of the grain is \( d \) and the thickness of the grain boundary is \( \delta \), then \( F \) can be written as:

\[
F = \frac{2 \delta}{d}
\]  
(3-15)

During mechanical alloying, the criterion for lattice diffusion to be transferred into grain boundary diffusion is [67]:

\[
F D_b \geq (1 - F) D_i
\]  
(3-16)

where,

\[
D_b = D_0^b \exp\left(\frac{-\Delta Q_b}{RT}\right)
\]  
(3-17)

and

\[
D_i = D_0^i \exp\left(\frac{-\Delta Q_i}{RT}\right)
\]  
(3-18)

Using the following data for calculation [67]:

\[
Q_i = 126 \text{kJ/mole}, \quad Q_b = 84 \text{kJ/mole}, \quad D_0^i = 1.5 \cdot 10^{-5} \text{m}^2/\text{s} \quad D_0^b = 15 D_0^i,
\]

and \( \delta \equiv 7 \text{Å} \), \( T = 400k \).

If \( d = 100nm \), \( F = 2 \delta / d = 2 \cdot 7 \cdot 10^{-10} / 100 \cdot 10^{-9} = 1.4 \cdot 10^{-2} \), then

\[
\frac{F D_b}{(1 - F) D_i} = \frac{1.4 \cdot 10^{-2} \cdot 15 D_0^i \cdot \exp\left(\frac{-84000}{RT}\right)}{(1 - 1.4 \cdot 10^{-2}) \cdot D_0^i \cdot \exp\left(\frac{-126000}{RT}\right)} = 6.486 \cdot 10^4
\]  
(3-19)

This result indicates that at 400k (which is believed to be the real temperature inside the vial during ball milling) [36] and 100nm grain size (which is believed to be
the beginning of grain boundary diffusion) [1-4], grain boundary diffusion becomes
the most important diffusion in the ball milling process and lattice diffusion can be
ignored when compared to grain boundary diffusion.

On the other hand, the grain size during ball milling continuously decreases
from 100µm to nearly 20 nm. According to Equations 3-14 and 3-15, since the
thickness of the grain boundary δ is almost unchanged as grain size d decreases, the
diffusivity increases continuously. This result is in contrast with Pabi’s model [68],
which assumes that diffusivity is constant during ball milling process.

Figure 3-4. Change in effective crystalline size of Ni$_3$Al with MA time.

From Figure 3-4 [62], the typical change in grain size can be defined into three
stages. At the first stage from 0 to 2h, the effective crystalline size decreases abruptly,
but the powder particle size is not reduced. Some may even grow due to the dominant
effect of cold-welding [69]. Lamellar structure has not been formed at this stage and
Chapter 3  Modeling and Computer Simulations

thus, diffusion is slow and can be taken as lattice diffusion. At stage two from 2h to 20h, the effective crystalline size is reduced from about 100nm to 20nm and can be assumed to be:

\[ d = \text{const} / t \]  \hspace{1cm} (3-20)

where \( d \) and \( t \) represent respectively the grain size and MA time. At this stage, diffusion is mainly controlled through grain boundary and also dislocation. At the final stage from 20 to 40h, the effective crystalline size remains about 20nm while the dislocation density is saturated in the mean time. Diffusion takes place with constant \( D_b \) [70-71].

The value of \( F \) in actual case is higher than that given by this equation because dislocation density increases due to repeated cold-welding and fracturing during ball milling. The influence of dislocations should be considered as diffusion pipes. In the present model, change in dislocation density is assumed to change diffusion barrier, i.e. change in activation energy. By lowering the activation energy, the diffusivity at the same temperature can be increased. Here a factor \( I_d \) is introduced to describe the contribution of dislocation to diffusion:

\[ I_d = \left( D_b + D_{\text{dislocation}} \right) / D_b \]  \hspace{1cm} (3-21)

where \( D_b \) and \( D_{\text{dislocation}} \) represent the diffusivity of grain boundary and dislocation respectively.

Based on Figure (3-4), It is assumed the change in grain size from \( d_{\text{begin}} \) to \( d_{\text{final}} \) as a quadratic function [62],
\[
d_2 = \frac{1}{\rho} d_{\text{begin}} \\
M \\
d_{i+i} = \frac{1}{\rho} d_i 
\] (3-22)

\[
d_{\text{final}} = \frac{1}{\rho} d_{\text{final}-1} = \frac{1}{\rho^{i+1}} d_{\text{begin}} 
\]

where \( i \) is the collision number from the beginning of diffusion, \( d_{\text{begin}}, d_i \) and \( d_{\text{final}} \) represent the grain size at the beginning, after \( i \) times of collision and at the final stage respectively, and \( \rho \) is a constant coefficient.

Because \( D_{\text{eff}} \cong F D_b = (2\delta/d) D_b \propto 1/d \), i.e. diffusivity \( D \) is proportional to the reciprocal value of grain size and is therefore given by:

\[
D_2 = q D_{\text{begin}} \\
M \\
D_{i+1} = q D_i 
\] (3-23)

\[
D_{\text{final}} = q D_{\text{final}-1} = q^{i-1} \cdot D_{\text{begin}} 
\]

where \( i \) is the number of collisions from the beginning of diffusion, \( D_{\text{begin}}, D_i \) and \( D_{\text{final}} \) represent diffusivity at the beginning, after \( i \) times collision and at the final stage respectively, \( q \) is a constant.

In the present model, grain boundary diffusion is a main contribution to MA, it is reasonably assumed that \( \rho \) in (3-22) is equal to \( q \) in (3-33). MA of Ni\(_3\)Al will reduce grain size from the initial 100\( \mu \)m to 20nm after 500 times of impact.

The constants \( \rho \) and \( q \) can therefore be determined as:
3.3 Computer Simulation

3.3.1 Simulation Program

Based on present model and the data obtained from the above analyses, diffusion during MA can be investigated by computer simulation. The simulation program is given in Appendix 1.

In this program, the following equations are employed (ref. to section 3.1.3, Equation 3-4 and 3-10),

The diffusion concentration \( C(x,t) = C/2 \times (1 - \text{erf}(x / 2 \sqrt{D \cdot t})) \)

Diffusion flux \( N = C \times \sqrt{D \cdot t / \pi} \)

Input: The lattice and grain boundary diffusivities - \( D_l, D_b \);

The collision time interval of ball milling - InterTime;

The original and final powder particle size - \( d_1, d_2 \);

Output: The collision times - \( I \)

The diffusion completion time - CompTime

The change of concentration with ball milling time – The curve

\[
q \cong \rho = \left( \frac{d_{\text{begin}}}{d_{\text{final}}} \right)^{\frac{1}{500-1}} \left( \frac{100}{0.02} \right)^{\frac{1}{499}} = 1.017
\]
3.3.2 Simulation Results

Figure 3-5 shows the simulation result of diffusion during MA. From this figure, it can clearly be seen that the diffusion of Al atoms into Ni can be separated into three stages (excluding the diffusion at the beginning 2h of milling, because diffusion can be neglected during this period):

At the first stage from 2 to about 12 hours, the diffusion is slow but increases in speed gradually. Because the grain size has decreased to the range of 100nm, the diffusion process is mainly controlled by grain boundary. As the grain size further decreases, diffusivity increases accordingly. This leads to an increase in diffusion speed. At the same time, dislocation density increases, resulting in an increase in diffusion.

![Graph showing the change in B-solid solution versus milling time for A-B alloy milled at SPEX ball milling.](image)

Figure 3-5. Change in B-solid solution versus milling time (t) for A-B alloy milled at SPEX ball milling.
For the second stage of MA from 2 to 22h, the diffusion speed is the fastest, and the quantities of diffusion form the main part of the total diffusion flux. The diffusion process is mainly controlled by grain boundary diffusion and dislocations. Because the grain size remains almost unchanged, the dislocation density reaches its saturation state and diffusion reaches a stable diffusion.

During the final stage after 22h of ball milling, the diffusion process is mainly controlled by the concentration gradient where the diffusion rate gradually decreases. As the composite concentrations in the initial A and B parts are almost identical, the diffusion rate becomes very slow.
4.1 Materials and Methods

To investigate the diffusion process and its status during mechanical alloying, a fully miscible Ni-Al system was used in this investigation where diffusion and formation of Ni-Al intermetallics were determined.

The interdiffusion was estimated by the change in lattice parameters. When Al atoms diffuse into Ni fcc lattice, the lattice parameters of Ni may change according to the amount of Al diffused.

Figure 4-1. Ni-Al phase diagram [72]. Change in lattice parameter of Ni is measured through the different Al contents in Ni, illustrated as broken line.
Figure 4-1 shows the Ni-Al phase diagram where a number of intermetallic phases can be seen. By measuring the change in lattice parameter of Ni solid solution with different Al contents, the concentration of Al can be determined. Therefore for the present study, Ni alloys with different amounts of Al ranging from 5% to 20% have been prepared. The alloys prepared were first heated to 1200°C. After homogenization for 60 minutes, the alloys were quenched into water to obtain saturated solid solution. The lattice parameter of each Ni (Al) sample was estimated from the X-ray diffraction (XRD) pattern.

The concentration of Al in Ni was then determined by comparing the lattice parameters between the quenched samples and the MAed counterparts.

4.2 Procedures and Equipments

4.2.1 Sintering and Quenching

Ni and Al powders of 99.5wt% purity with –325 mesh particle sizes were mixed according to the atomic compositions of Ni-5%Al, Ni-10%Al, Ni-15%Al and Ni-20%Al. Each specimen was 2g in weight. The powder mixtures were blended for 420 minutes in a container settled onto a V-blender blending machine. The blended powder mixtures were compacted into a 10mm diameter die. The compacts were sintered in the vacuum furnace (1.6×10^{-6} mbar to 4.6×10^{-8} mbar) at 800°C for 4 hours according to the sintering cycle shown in Figure 4-2. The sintered specimens were
finally heated to 1200°C for 1 hour followed by quenching into water [Figure 4-3]. XRD measurement was performed on polished specimens.

The sintering and quenching process is illustrated in Figures 4-2 and Figure 4-3.

![Figure 4-2 Sintering process for Ni-Al powder samples.](image1)

![Figure 4-3 Quenching process for Ni-Al powder samples.](image2)
Figure 4-4 (a) SPEX 8000 mixer/mill in the assembled condition and (b) stainless steel vial set consisting of vial, lid, gasket, and tungsten carbide balls.
4.2.2 Ball Milling

Shaker ball mills are generally used to process small quantity of powder mixture. A typical example of such mill is the SPEX 8000 as shown in Figure 4-4 (a), which was originally developed to pulverize spectrographic samples. It agitates the charge of the powder and mills in three mutually perpendicular directions at approximately 1200 rpm. In comparison to attrition and vibratory ball mills, it has high collision energy. High milling energy can be obtained by using high frequencies and large amplitude of vibration. In the present experiment, with a clamp motion of amplitude of about 5 cm and speed of about 1200 rpm, the ball velocities can be estimated to be of the order of 5 m/s. The stainless steel vial, gasket and tungsten carbide grinding balls for the SPEX mill are shown in Figure 4-4 (b).

MA of Ni and Al of –325 mesh size having a nominal composition of Ni\textsubscript{75}Al\textsubscript{25} was carried out using a SPEX 8000 mixer. Stainless steel vial and 10 mm diameter WC coated balls with a ball to powder weight ratio of 7:1 were employed. The powders were loaded into the stainless steel vial in a LAB MERAUN glove box (Figure 4-5) which was sealed and filled with Ar gas. 3 wt.% of CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{16}CO\textsubscript{2}H was used as process control agent (PCA) to prevent the agglomeration of powders during milling. The milled powder samples were collected for analysis at different stages of milling in the glove box.
4.2.3 XRD Analysis

X-ray measurement was performed on a Shimadzu XRD-6000 diffractometer (Figure 4-6) in a continuous scanning mode using Cr K$_\alpha$ radiation ($\lambda=2.2909$ Å). An acceleration voltage of 40KV and current of 30mA were used. Scan speed of 2°/min and step of 0.02° were chosen. For convenience and accuracy, all powder samples were compressed, polished and stuck onto glass plates. The lattice parameter, grain size and lattice strain of the milled powders were derived from the XRD peaks. In order to determine these parameters accurately, pure silicon powder was used as standard to calibrate the peak position error and instrumental broadening of the XRD machine. The extrapolation function used for lattice parameter calculation in this study is $(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$. 
Figure 4-6  Shimadzu XRD-6000 diffractometer and control/analysis system.
Chapter 5

Results and Discussions

5.1 Lattice Parameter

5.1.1 Sintering and quenching of Ni, Al powders

X-ray diffraction measurements were performed for all samples after sintering and quenching. The lattice parameter was calculated from the diffraction spectra using the XRD peaks of Ni (220). The results are shown in Table 5-1 and Figure 5-1.

Table 5-1. Calculated lattice parameters of samples

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ni-Powder*</th>
<th>Ni-5%Al</th>
<th>Ni-10%Al</th>
<th>Ni-15%Al</th>
<th>Ni-20%Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>76.2472</td>
<td>76.0560</td>
<td>76.0355</td>
<td>76.0152</td>
<td>75.9350</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.5291</td>
<td>3.5366</td>
<td>3.5375</td>
<td>3.5382</td>
<td>3.5391</td>
</tr>
</tbody>
</table>

*Not sintered.

It can be seen from Figure 5-1 that when Al increases from 5% atom to 20% atom, the lattice parameter of Ni linearly increases from 3.5366Å to 3.5391Å. This is because both Ni and Al have fcc structure; they have good miscibility and Al form continuous solid solution with Ni [86]. This liner relation is important.
Figure 5-1. Change in lattice parameter of Ni as a function of Al concentration

(Solid line represents experimental results; chained line represents change in lattice parameter without sintering; and dashed line represents the theoretical results of lattice parameter change with different Al contents in Ni).

From Figure 5-1, it can also be observed that when no Al is added, the lattice parameter of Ni is 3.52911Å, which is not on the extended solid straight line with 5% to 20Al% added. This may be caused by the unsintered Ni powder. The slope of the solid line is:

\[
\frac{3.5391 - 3.5364}{20\% - 5\%} = 0.000164(Å/1\%)
\]

Equation 5-1 indicates that every 1%Al diffused into Ni will cause an increase in the lattice parameter of Ni by 0.000164Å.
As a reference, the JCPDS file for Ni is attached as Appendix B.

5.1.2 Ball Milling of Ni$_3$Al

During the ball milling process, a change in the lattice parameter is an indication of the diffusion process of the two different elements. For ball milling of Ni$_3$Al, the status of the diffusion process is studied through the calculation of the change in lattice parameter by using the XRD method.

Figure 5-2 shows a series of XRD patterns of the Ni$_3$Al powders during ball milling. The curve (a) is the XRD spectrums of starting Ni, Al powder mixtures. And the curve (b) to (f) is the XRD spectrums of the Ni$_3$Al powders collected after different durations of ball milling. The figure shows a shift of Ni (220) peak to lower angles with the progress of ball milling. The Ni (111) and Ni (200) peaks also show similar shift. However no XRD peak shift could be observed from Al diffraction. Because the present XRD pattern is a reduced scale, the Al peaks are not shown here. This observation coincides with some previous work [73]. The reason for the observation is because all Al, Ni and Ni$_3$Al are of fcc structure, and the diffusivity of Al into Ni is tens of thousand times the magnitude of the diffusivity of Ni into Al. Therefore, the main diffusion process in this experiment is that of Al diffusing into Ni, and the lattice parameter of Ni increases continuously till the formation of Ni$_3$Al.
According to the present diffusion model proposed in Chapter 3, it is assumed that only A diffuses into B in an A-B alloy system where internal diffusion is neglected. Here A is the Al atoms, while B, the Ni atoms.

Before 2 h of milling, very few changes could be observed from both the peak positions and the intensities of the XRD patterns. After 2 h of milling, a gradual decrease in intensities of all Al peaks could be observed. At the same time, the peak position of Ni has shifted in the direction of lower angle. The increased Ni lattice
Chapter 5  Results and discussions

parameter is the result of dissolving of Al into Ni lattice. The Al diffraction peaks could still be observed after 22 h of milling, but disappeared after 36 h.

Table 5-2. The calculated lattice parameters for ball milled Ni$_3$Al

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ni, Al-Powder</th>
<th>2h Ball milling</th>
<th>4h Ball milling</th>
<th>8h Ball milling</th>
<th>22h Ball milling</th>
<th>36h Ball milling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θ (deg)</td>
<td>d (Å)</td>
<td>∆d (Å)</td>
<td>∆d (Å)</td>
<td>∆d (Å)</td>
<td>∆d (Å)</td>
</tr>
<tr>
<td>20</td>
<td>76.2472</td>
<td>3.52911</td>
<td>0</td>
<td>0.000054</td>
<td>0.000133</td>
<td>0.000485</td>
</tr>
<tr>
<td>d (Å)</td>
<td>76.2446</td>
<td>3.52916</td>
<td>0.000133</td>
<td>0.000485</td>
<td>0.003592</td>
<td>0.004083</td>
</tr>
<tr>
<td>∆d (Å)</td>
<td>76.2426</td>
<td>3.52924</td>
<td>0.000133</td>
<td>0.000485</td>
<td>0.003592</td>
<td>0.004083</td>
</tr>
<tr>
<td>∆d (Å)</td>
<td>76.2334</td>
<td>3.52960</td>
<td>0.000485</td>
<td>0.003592</td>
<td>0.004083</td>
<td></td>
</tr>
<tr>
<td>∆d (Å)</td>
<td>76.1546</td>
<td>3.53270</td>
<td>0.003592</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>∆d (Å)</td>
<td>76.1421</td>
<td>3.53319</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>*Al% in Ni</td>
<td>0</td>
<td>0.33</td>
<td>0.81</td>
<td>2.96</td>
<td>21.9</td>
<td>24.9</td>
</tr>
</tbody>
</table>

*(Al% in Ni) = ∆d / 0.000164

The calculated lattice parameters of Ni after different times of milling are given in Table 5-2 and Figure 5-3. The amount of aluminum dissolved in Ni lattice was estimated by the method suggested in section 5.1.1, Equation (5-1). According to this method, the lattice parameter of Ni increases by 0.000164 Å for every 1 wt. % of Al diffused into Ni. From Figure 5-3, it can be observed that within the first 2 hours of milling, changes in the Al lattice parameters are small, implying that diffusion of Al in Ni was negligible. The Al content in the Ni lattice is less than 0.5 wt. % before 2 h of milling, suggesting that ball milling has only caused a change in powder particle morphology and refinement of the particle size. With 25 at. % of ductile Al powder in the starting powder mixtures, a lamella structure of Al and Ni is expected to be formed even though the diffusion process may not be dominant. After 8 h of milling, the lattice
parameter of Ni (with the Al content in Ni) increases steadily until 22 h of milling, indicating that the diffusion process between Ni and Al occurs mainly during the period between 8 and 22 h of milling. Before this period, the coefficient of diffusion was very low. This is reasonable, because milling of less than 8 h involves mainly the mixing of Ni and Al powders which is far from homogeneous and the area of activated “atomic scale fresh surface” is negligible for fast diffusion.

![Graph showing Al concentration in Ni versus milling time](image)

**Figure 5-3. Change in Al contents in Ni versus milling time.**

Only fcc phase remained after 22 h of milling. It was found that there was little change in the Al concentration in Ni from 22 to 36 h of milling, and no further change took place after 36 h of milling. Formation of the disordered fcc phase (Ni$_3$Al) at the later stage of ball milling has been reported elsewhere [4], but different explanations of the formation were given. The grain size of this newly formed phase was about 3 nm as calculated according to Williamson-Hall's equation. Pabi et al. [73] ascribed the
inability of the L1$_2$-Ni$_3$Al phase with respect to the disordered fcc solid solution to the lower ordering energy of Ni$_3$Al (5kJ mol$^{-1}$) which provided the driving force for the ordering. Since both Ni and disordered Ni$_3$Al are fcc, under ball milling condition, Ni$_3$Al loses its ordering and distinction with the solid solution of Al in Ni. This explains why formation of disordered Ni$_3$Al in Ni-Al blends containing 75 at. % Ni takes place by gradual enrichment of Ni with Al in a manner similar to the formation of a solid solution. [74]

Through other experiment [73], it was observed that the highest solubility of Al in Ni is about 30 wt.% which is higher than the equilibrium solubility of Al in Ni of about 25 wt.%. MA is a non-equilibrium process that can extend the solubility between elements and therefore produces supersaturated solid solutions. The extended solubility is explainable due to the introduction of a large number of defects during the ball milling process, which leads to a change in the Gibbs free energy-composition curve. From the present study, the upper solubility of Al in Ni is about 30 wt.%. It is noted that even after a large number of investigations in this area, there is no report on the synthesis of ordered Ni$_3$Al directly by MA. The low ordering energy (5kJ mol$^{-1}$), low ordering temperature (638K) [75] and the close packed nature of the crystal structure seem to be the reasons for the easy destabilization of the order in Ni$_3$Al during milling. The extension of Ni$_3$Al in its disordered condition during MA (27.9 at % Al) in comparison with the equilibrium phase field of ordered Ni$_3$Al (25 at % Al) may also be related to the above reasons.
Chapter 5  Results and discussions

5.2 Diffusion Analysis

5.2.1 Grain Boundary Diffusion

Effective crystalline size can be calculated from the broadening of XRD peaks using Scherrer formula:

\[ d = \frac{C \lambda}{\Delta B \cos \theta} \]  \hspace{1cm} (5-2)

where \( d \) is the effective grain size, \( C \), a constant, \( \lambda \), the wavelength of XRD, \( \Delta B \), the difference in full width at half maximum of diffraction peaks, and \( \theta \), the diffraction angle.

Figure 5-4 shows the change in grain size of Ni during SPEX ball milling. At the initial stage from 0 to 2h, the effective crystalline size decreases abruptly, but the powder particle size is not reduced while some even grow due to the dominance of...
cold-welding over fracturing. The lamellar structure has not been formed and thus, diffusion is slow and may be taken as lattice diffusion. At the stage from 2 to 20h, the effective crystalline size changes from about 100nm to 3nm. It can be assumed that d=Const/t where d and t represent the grain size and MA time respectively. At this stage, diffusion is mainly controlled through grain boundary and dislocations. At the final stage from 20 to 36h of MA, the effective crystalline size remains unchanged at about 3nm while the dislocation density is saturated. Diffusion which is mainly controlled by the concentration gradient takes place with constant $D_b$. At this stage, the diffusion rate gradually decreases to a halt. Because the concentration of the composite is getting close to that of the initial Ni and Al lamella, the activation energy derived from the concentration gradient decreases.

5.2.2 Dislocation Diffusion

With longer mechanical alloying time, more defects are generated to form vacancy pipes resulting in an increase in reaction rate by the provision of short circuit diffusion paths.

Following the method for peak shift analysis [76-80], the values of deformation fault probability, $\alpha (=\alpha' - \alpha'')$, where $\alpha'$ and $\alpha''$ are the intrinsic and extrinsic fault densities respectively, have been evaluated assuming the sample milled for 2h as annealed standard. To evaluate the individual values of $\alpha'$ and $\alpha''$, the relation for peak shift containing $\alpha$ has been equated to the peak broadening relation comprising compound fault probability parameter, $1.5(\alpha' + \alpha'') + \beta$, with the values of crystallite
sizes evaluated. Here, $\beta$, the twin fault probability parameter has been assumed to be zero as has been done in earlier studies of many powder samples [76-80].

Using the values of crystallite sizes and strains the values of dislocation density, $\rho$, has been estimated [81] by following the procedures as adopted in some recent X-ray line broadening studied [80, 82]. The relevant relations are

$$\rho = (\rho_D \rho_S)^2$$  \hspace{1cm} (5-3)

where

$$\rho_D (\text{due to domain size}) = \frac{2}{D^2}$$  \hspace{1cm} (5-4)

$$\rho_S (\text{due to strain broadening}) = \frac{(K\varepsilon_L)^2}{b^2}$$  \hspace{1cm} (5-5)

In Equation (5-5), $K = 6\pi$ for Gaussian strain distribution and $b$ is the Burgers vector and its value is $(a/2)^{1/2}$ for [1 1 0] direction of the fcc structure and $(3a/2)^{1/2}$ for [1 1 1] direction of the bcc structure.

Figure 5-2 shows the change in X-ray diffraction patterns of the Ni, Al powder mixtures with increasing milling time up to 36h. The powders milled for longer times needed corrections for slight preferred orientation. The results show the nature of progressive evolution of the microstructure of the milling products in terms of different defect parameters with milling time leading finally to the formation of single phase disordered Ni$_3$Al. Since both Ni and disordered Ni$_3$Al are fcc, under ball milling condition, Ni$_3$Al loses its order and distinction with the solid solution of Al in Ni. To identify and characterize the transformation product a detailed analysis has been done adopting the methodology as explained in the earlier studies [78-80, 82, 84, 85]. A critical study of the results reveal the following important features of the microstructure of the milled blends in terms of the various microstructural parameters:
(1) During the milling process, the elemental blend of Ni (75 at.%) and Al (25 at.%) undergoes severe plastic deformation leading to cold-welding and fracturing of the component powders which in turn results in alloying through material transfer to produce solid solutions.

(2) Prolonged milling leads to complete synthesis of the unreacted elements to Ni-Al which further transforms to Ni$_3$Al as shown by the continuous shifts of the peaks of Ni towards those of Ni$_3$Al phase. Thus, the volume fraction of Ni and Al decreases gradually with milling resulting in the continuous increase in the volume fraction of Ni$_3$Al. Complete transformation to Ni$_3$Al revealing the formation of fully disordered intermetallic compound occurs after about 22h of milling. Following conventional X-ray line broadening analysis, Pabi [83] and Murty [73] have also reported formation of disordered Ni$_3$Al from ball milled powders within a shorter time.

(3) Following the approach adopted in the earlier studies [78-80, 82, 84, 85], by taking an estimation of stacking fault probability, $\alpha$, has been made from peak-shift studies assuming the sample milled for 2h as annealed standard. The results show that increased milling introduces high propensity of faulting in Ni (Al) which gradually approaches the structure of disordered Ni$_3$Al. Combining $\alpha (= \alpha' - \alpha'')$ from peak-shift analysis with the related compound fault probability parameter, \[1.5(\alpha' + \alpha'') + \beta\] from line broadening analyses [86, 87] and assuming the value of twin fault probability, $\beta$ to be zero for powder samples [87], the values of both the intrinsic ($\alpha'$) and extrinsic ($\alpha''$) stacking fault probabilities can also be evaluated. The result shows that the generation of intrinsic stacking faults ($\alpha'$) is more than that of extrinsic ($\alpha''$) in both the phases of the materials. Evidence of occurrence of such high density of faulting also exists in
some recent X-ray peak-shift studies on cold-worked ordered Ni$_3$Al [88] and hot-pressed Ni$_3$Al-based [89] alloys.

From the present study, it is apparent that ball milling introduces high degree of structural defects in Ni (Al). Continuous milling increases the volume fraction of Ni (Al) phase is formed till Ni$_3$Al (disordered) is fully transformed. Severe cold working during mechanical alloying generates larger fraction of nano-crystalline grain structure, higher dislocation densities ($\sim 10^{12-13}$ cm$^{-3}$), higher density of stacking fault and larger strains in this phase.

Assuming the value of the lattice parameter of pure Ni$_3$Al (=0.35668 nm) as that for the present Ni$_3$Al and interpolating the same in Figure 5-2 for Ni-Al plot, the milling time required for its formation could be estimated to be $\sim 36$ h as noted from the abscissa. Further interpolations with this milling time in the abscissa of Figure 5-2 yield the values of the defect parameters for Ni$_3$Al, namely, the values of crystallite size, strain, stacking fault probability $\alpha$, and dislocation density $\beta$.

In the present study, however, milling up to 36 h has revealed no further change in the X-ray diffraction pattern of the synthesized Ni$_3$Al. The only effect of milling was broadening in the peaks promoted by the introduction of increased concentration of defects, showing that the transformation process finally yields only disordered Ni$_3$Al.

5.2.3 Stress-Assisted Diffusion

A potential stress gradient tends to produce a flux of atoms, and this flux must be added to that produced by the concentration gradient to arrive at an equation for the
total flux. For mechanical alloying, as the powder particles are repeatedly deformed, the consideration of stress-assisted diffusion must be introduced.

Shewmon [90] considers a single particle moving at a speed of $V(x, y, z)$ and the gradient of this potential describes the force $F$ on the particle. Thus

$$F = -\nabla V$$

(5-6)

Using the continuity equation for constant $D$

$$\frac{\partial c}{\partial t} = D \nabla \left[ \nabla c + \frac{c \nabla V}{kT} \right]$$

(5-7)

In the mechanical alloying of the present Ni-Al system, however, the total particle volume change (not the shape) in the container is too small to have contributed to diffusion, i.e. $\nabla V \approx 0$. In this situation, diffusion caused by mechanical deformation could be ignored.

5.2.4 Diffusion-reaction

Diffusion up to this point has been discussed without involving additional chemical or nuclear reactions, which can and frequently occur in association with mass diffusion.

Figure 5-5 compares different concentration distribution for various kinetic mechanisms. $X$ is the distance from center to interface; $C_0$ is the start concentration at the center; $C_1$, $C_2$ and $C_{eq}$ represent the concentration distribution for reaction, mixed and diffusion control respectively.

In present study, the application of Fick’s law was strictly limited to binary interdiffusion in media that neither actively consume nor alter the diffusant concentration through some nonconservative reaction.
5.3 Diffusion Modeling

The evolution and formation of Ni$_3$Al were examined using X-ray diffraction patterns (XRD) after each stage of MA. The change in Al content in Ni of Ni-solid solution, which was calculated from the lattice parameter as a function of milling time, was shown in Figure 5-6 as continuous line. Results from the simulation are shown as dashed line (a) and line (b) in the same figure. In the simulation, the following parameters were used:

$$D_{\text{begin}} = 2 \cdot 10^{-18} \text{ m}^2 / \text{s}, \quad d_{\text{begin}} = 100 \mu\text{m}, \quad d_{\text{final}} = 3 \text{nm}, \quad I_d = 1 \text{ for line (a), and } I_d = 1.02 \text{ for line (b).}$$

In this calculation, $I_d$ is defined as the dislocation diffusion factor, and

$$I_d = \frac{(D_b + D_{\text{dislocation}})}{D_b}.$$
According to present model, the grain boundary diffusion dominates during the ball milling process. If the effect of dislocation during the ball milling process is not considered, line (a) could be obtained. It has a similar diffusion curve as that obtained from the experiment, but the diffusion speed is slightly slower. If the decrease in $\Delta G$ due to the attribution of dislocation to diffusion was considered, a more realistic relation represented by line (b) was obtained.

The diffusion process could be separated into three stages as shown in Figure 5-6. The first stage is from 2 to 9h, the concentration of Al in Ni increased very slowly, which agreed with simulation model of lattice diffusion stage. The second stage is
from 9 to 22h, the concentration of Al in Ni increased very fast, in nearly a linear relation with MA time, which agreed with simulation predicted grain boundary diffusion period. Taken into the steadily increase of dislocation density, the experimental concentration change in Figure 5-6 is nearly same as simulation results line (b). After 22h of ball milling, the lamellar structure finally disappeared, the decrease of grain size stopped and the dislocation density also reached a saturation status, thus, diffusion reached a saturated stage.

As shown above, the present simulation model is able to illustrate the key factors involved in the diffusion process during MA, and thus changes in concentration during the process could be predicted.
Chapter 6

Conclusions and Recommendations

6.1 Conclusions

(1) Diffusion is a fundamental process during mechanical alloying, and grain boundary diffusion plays the key role in this process.

(2) A mathematical model to predict the process of diffusion during mechanical alloying has been established. The model takes into three critical factors that influence diffusion in mechanical alloying.

(3) The kinetics of diffusion involved in the mechanical alloying of Ni$_3$Al binary miscible system has been predicted.

(4) New findings such as the different stages of diffusion consideration and changing diffusivities predicted by this diffusion model will help to develop greater understanding in the thermodynamic and kinetic considerations during ball milling.
6.2 Recommendations

(1) Mechanical alloying is a very complicated process. To conduct thoroughly investigation of the diffusion mechanism, microstructure analysis especially during the MA process must be carried out using SEM/TEM and electron energy spectrum etc.

(2) The diffusion model proposed in this thesis has been applied only to a two composition alloying system A-B, and only diffusion process has been considered during MA. For further study, a multi phase diffusion model which including phase transformation and other phenomena could be set up, using similar analyses methods as provided in present studies.
References


34. L. Lu, M. O. Lai and S Zhang, Evolution and characterization of a Ni3Al intermetallic compound during mechanical alloying, Materials and Design, Volume 15, Number 2, 1994.


Appendix A

Computer Simulation Program

/*This program computes the diffusion completion time during Mechanical Alloying

According to the diffusion theory,

The diffusion concentration $C(x,t) = C/2 \times (1 - \text{erf}(x / 2\sqrt{DT}))$

Diffusion flux $N = \int (J \times dt) = \int (D \frac{dC}{dx} \times dt) = C \times \sqrt{D \times t / 3.14159}$

Input: The original crystal diffusion coefficient $D_l, D_b$;
       The collision time interval of ball milling $\text{InterTime}$;
       The original and final powder particle size $d_1$ and $d_2$;

Output: The collision times $I$ during ball milling,
       The diffusion completion time $\text{CompTime}$

-------------------------------------------------------------------*/

#include <iostream.h>
#include <math.h>
#include <stdlib.h>
int main(void)
{
    const double
        Pi = 3.14159;  //arithmetic constant;

    cout << "Please enter the lattice diffusivity Dl:\n";

    double
        Dl; //the lattice diffusivity of A in B powders.

    cin >> Dl;

    cout << "Please enter the grain boundary diffusivity Db:\n";

    double
        Db; //the grain boundary diffusivity of A in B powders.

    cin >> Db;

    cout << "Please enter the average collision interval time InterTime:\n";

    double
Appendix A   Computer simulation program

InterTime;//assuming interval time is the same, and collision time is neglected.

    cin >> InterTime;

    cout << "Please enter the original and final average powder particle size d1 and d2:\n";

    double
        d1, d2; //assuming the powders have homogenized particle size during process;

    cin >> d1 >> d2;

    double
        AreaIncrease = pow((d1/d2),(2/500)), //area increase for each collision;
        DiffIncrease = pow((d1/d2),(1/500)), //diffusivity increase for each collision;
        DiffQuant = sqrt ( Dl * InterTime / Pi ),//diffusion quantity for the first time;
        Sum = DiffQuant,
        I = 1;
Appendix A  Computer simulation program

do
{
    DiffQuant = (1-DiffQuant) * (sqrt(Dl*InterTime / Pi)),
    I++, //to calculate the collision times;
    Sum += DiffQuant; //to calculate the total quantity of diffusions;
    cout << I << Sum;
}

while ( (InterTime * I) < 7200 );

do
{
    Db *= DiffIncrease * 1.02, //dislocation factor Id=1.02;
    DiffQuant = AreaIncrease * (1-DiffQuant) * (sqrt(Db*InterTime / Pi)),
    I++, //to calculate the collision times;
    Sum += DiffQuant; //to calculate the total quantity of diffusions;
    cout << I << Sum;
}

while ( (InterTime * I) < 72000 );

do

\[
\text{DiffQuant} = (1-\text{DiffQuant}) \times (\sqrt{\text{Db} \times \text{InterTime} / \pi}),
\]

\[I++; //to \text{calc}ulate \text{the collision times;}\]

\[\text{Sum} += \text{DiffQuant}; //to \text{calculate the total quantity of diffusions;}\]

\[\text{cout} \ll I \ll \text{Sum};\]

\[\}
\]

\[\text{while ( Sum } < 0.25 );\]

\[\text{double}\]
\[\text{CompTime} = (\text{InterTime} \times I) / 3600;\]

\[\text{cout} \ll "\nThe average collision times per powder are:}\n" \ll I;\]

\[\text{cout} \ll "\nThe diffusion completion time in hours are:}\n" \ll \text{CompTime};\]

\[\text{return} \ 0;\]

\[\} \]
Appendix B

JCPDS File for Nickel

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Nickel syn

Rad. Cukal λ 15405 Filter Ni Beta d-sp

Cutter Int. Diffract 1/λc

Ref. Swanson Tatge Natl Bur. Stand (U.S.) Circ. 539. 1. 13 (1953)

Sys. Cubic S.G. Fm3m (225)

α 3.5238 b c A B C

Ref. Dirl

Dx. 8.911 Dm 88/F30 M. F 8 = 87/0115 / 8

Color: White

Pattern taken at 26 C. Sample obtained from Johnson Matthey Company Ltd. CAS 7440-02-0. Spectrographic analysis show < 0.01% each of Mg, Si and Ca. Cu type. Gold group. gold subgroup. PSC cF4. Melt 5870. Volume(CD) 4376.

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ICPDWIN v. 1.30