DIFFUSIVE REACTION DURING MECHANICAL ALLOYING OF INTERMETALLICS

A. K. Bhattacharya and E. Arzt
Max-Planck-Institut für Metallforschung
Seestrasse 92, 7000 Stuttgart 1, Germany

Introduction

Diffusion plays a dominant role in the evolution of microstructure during various types of metallurgical processes. During mechanical alloying, the role of diffusion under the compositional gradients is also the primary mechanism through which alloying of the species takes place. Modelling of diffusion in mechanical alloying has been considered by Courtney et al. (1) in a simplified form for the case of homogenization only. However, the formation process of many intermetallics has high values of negative enthalpy of mixing and thus, the process of mixing may be strongly influenced by the reaction rates between the two species. For this reason, the model of diffusion, while considering mechanical alloying of these intermetallics, should consider the interaction of diffusion and the resulting reaction. In this paper we deal with the formulation of such processes and present some conclusions based on the computed preliminary results.

Model and Analysis

The process to be described here deals with the formation of some intermetallics having high negative enthalpy of mixing by mechanical alloying from their constituent powders (e.g. Ni and Al to form NiAl). During this process, we consider the absorption of one species by another through which it can diffuse and with which it can also react chemically. Effectively, this combined phenomenon will give rise to some of the diffusing substance being immobilized after reaction as diffusion progresses. It is assumed that the product itself is a non-diffusing entity. Therefore, the governing differential equation for such a diffusive reaction is,

$$\frac{\partial^2 c}{\partial x^2} - \frac{1}{D}\frac{\partial c}{\partial t} - \frac{k}{D}c = 0 \qquad (1)$$

where D is the diffusion coefficient, k is a reaction rate constant, c is the composition of the diffusing substance and t is the time. We have considered here only an irreversible first order reaction between two species a and b to form a single phase reactant product r, thus giving rise to the rate of removal of the diffusing substance as kc.

During mechanical alloying, physical mixing of the species takes place by repeated forging and fracturing of the compacts made of an agglomeration of powder particles. We will model these compacts as collections of flattened particles as depicted in Fig.1. Here, we consider alloying of two elemental powders, and the particles are considered to be arranged in an alternate plate-like fashion. This parallel-plate geometry is used for classical treatment of finite diffusion problems (2) and considerably simplifies the analysis. The geometry in Fig.1 considers a particle of the minor constitutent of thickness λ in the compacted powder to be surrounded by the particles of the major constituent of thickness $(L-\lambda)$. x-coordinate is the distance perpendicular to the plates starting at the mid-point of the plate with minor constituent. This particular distribution of the powders is assumed to be uniform throughout the powder compact. Therefore, symmetry conditions apply at x=0 and x=(L-λ)/2. The composition c has been normalized from zero to unity so that c_a=0 and c_b=1. Thus, if the compositions of the major and minor constituent particles are c_a and c_b, respectively, then the normalized concentration profile in the region is as shown in Fig.2. The parallel-plate geometry also permits us to describe a mean composition ($\bar{c}$) of the compact as, $\bar{c} = \lambda / L$.

Therefore, the initial conditions at the beginning of mechanical alloying are,

$$c=c_b=1, \quad 0 \le x \le \lambda / 2 \qquad (2a)$$

$$c = c_a = 0, \quad \lambda/2 \le x \le L/2 \tag{2b}$$

The boundary conditions are,

$$\frac{\partial c}{\partial x} = 0 \quad \text{at } x = 0 \text{ and } L/2 \tag{3a}$$

$$\frac{\partial c}{\partial x} \text{ and } c \text{ (at } x = \lambda/2) \text{ are continuous functions} \tag{3b}$$

The resulting solution for concentration c inside the zone, $\lambda/2 \le x \le L/2$, is,

$$c(x,t) = \frac{1}{2}\exp(-kt)\left[\begin{array}{l} \sum\limits_{n=0}^{\infty} \operatorname{erfc}\left(\dfrac{2nL - \lambda + 2x}{4\sqrt{Dt}}\right) + \sum\limits_{n=0}^{\infty} \operatorname{erfc}\left(\dfrac{2L(n+1) - \lambda - 2x}{4\sqrt{Dt}}\right) \\ - \sum\limits_{n=0}^{\infty} \operatorname{erfc}\left(\dfrac{2nL + \lambda + 2x}{4\sqrt{Dt}}\right) - \sum\limits_{n=0}^{\infty} \operatorname{erfc}\left(\dfrac{2L(n+1) + \lambda - 2x}{4\sqrt{Dt}}\right) \end{array}\right] \tag{4}$$

We get the concentration at x=L/2 as,

$$c\left(\frac{L}{2}, t\right) = \exp\{-\Omega\xi\}\left[\sum\limits_{n=0}^{\infty} \operatorname{erfc}\left(\frac{(2n+1)/\bar{c} - 1}{4\sqrt{\xi}}\right) - \sum\limits_{n=0}^{\infty} \operatorname{erfc}\left(\frac{(2n+1)/\bar{c} + 1}{4\sqrt{\xi}}\right)\right] \tag{5}$$

where $\xi = Dt/\lambda^2$, is a diffusion parameter and $\Omega = k\lambda^2/D$, is a reaction parameter. In all these equations, k is given as (3),

$$k = A \cdot \exp\left(-\frac{E}{RT}\right) \tag{6}$$

and, D represents an effective value to include the low temperature diffusivity and is given as (4),

$$D = D_L \cdot \exp\left(-\frac{Q_L}{RT}\right) + \beta b^2 \rho D_C \cdot \left(-\frac{Q_C}{RT}\right) \tag{7}$$

Here, A and E are the frequency factor and enthalpy of reaction, respectively. D_L, D_C and Q_L, Q_C are the diffusion pre-exponent and activation energy of lattice and core diffusion, respectively. b is the Burgers vector, ρ is the dislocation density and β is a core diffusivity factor.

<u>Results and Discussion</u>

The calculated results for the composition at the location x=L/2 are presented in Figs.3 and 4 as a function of the diffusion parameter ξ. These plots are made for two average compositions ($\bar{c}$) of 0.5 and 0.25, and for different values of the reaction parameter Ω. As indicated before, the composition scale should be considered as normalized between c=0 and 1.

Let us first consider the case of diffusion in the absence of any reaction (Ω=0) in Fig.3. This will signify the case of homogenization only between the two species. The composition c at x=L/2 reaches within 1% of its average composition of 0.5 at a ξ value of about 0.4 (point A in Fig.3). We now consider the data for Ni diffusing into NiAl (5) given in Table 1. Here we have assumed that the activation energy for core

diffusion is 50% of the activation energy for lattice diffusion. Davis et al. (6) simulated the movements of 15 balls with a charge ratio of 6:1, with estimated velocity of 6 m/sec. If we consider that an average of 1000 particles (7) are involved in a typical powder compact, then their calculation showed that an estimated number of 5 impacts took place for each particles in one minute. Calculations (1, 8) have shown that the duration of an impact event with a velocity of 6 m/sec is of the order of 10^{-5} sec. Therefore, we can estimate that during one minute of mechanical alloying at this speed, the compact will experience a total time of 10^{-4} sec during which it will experience a reasonably high temperature caused by the impact events. Calculations (8) have shown that during mechanical alloying at a velocity of 6 m/sec, a contact temperature of the order of 1000 K could be achieved in the case of niobium. For the purpose of our present diffusion and reaction calculation, we assume that the Ni+Al powder mixture will see a temperaure of 950 K during such impact events. This obtains a D/λ^2 value of 3/sec, if we consider a layer thickness $\lambda=1$ μm. We thus find an actual diffusion time of $0.4/(3/\text{sec})=0.133$ seconds, for the composition to reach the average value of 0.5. This translates to an alloying time of 0.133 sec/(10^{-4} sec/min) = 22 h. Therefore, in this particular case of diffusion without reaction, we can consider the alloying to be completed after 22 hours.

Let us now consider the case where we also consider the reaction process to form NiAl from the elements Ni and Al. Using transition theory (9), a typical value of the reaction frequency factor A is found to be 10^{13} /sec. The activation energies of reaction to form many intermetallics usually lie in the range of 10^5 - 2.5×10^5 J/mole (10). In the absence of any available published value of E for forming NiAl, we consider $E=2.25\times10^5$ J/mole. This gives rise to a reaction parameter $\Omega=1.33$. This indicates that the state of alloying in this case is at point B (Fig.3), instead of at point A for the case of diffusion only. We also observe that now the criteria for alloying should be the time at which the final composition c will approach zero, indicating the total consumption of this element at the completion of reaction. Proceeding along the extrapolated curve of $\Omega=1.33$, we note that now the ξ parameter should be approximately 3. This represents a diffusion time of 1 sec. Thus, the criterion of complete reaction leads to a large extension in the alloying time when compared with the time determined from the homogenization (diffusion only) criterion alone. In this case, the diffusion being much more rapid, the composition of the diffusing substance and the transformed material are uniform throughout the layer, and thus the reaction rate is the controlling mechanism for alloying.

Now, we consider a lower activation energy of $E=2\times10^5$ J/mole. In this case, we calculate the value of Ω to be 32. Approximate concentration profile with $\Omega=32$ is also shown in Fig.3. We observe that due to fast reaction, the concentration reaches nearly zero value at an approximate ξ value of 0.25, which is less than the ξ value for nearly complete homogenization with no reaction. Thus, when the reaction is very rapid, we can assume that the transformed material is always in equilibrium with the component free to diffuse, and thus diffusion, being slower, should be the rate controlling mechanism for mechanical alloying.

Conclusions

We have presented a model and analysis for diffusion along with reaction, based on a planar model, that can take place while mechanical alloying intermetallics with high negative heat of mixing. The model also considers, in principle, the effect of dislocation accumulation which takes place due to large amounts of plastic deformation, causing enhancement of the diffusion coefficient due to extra mobility along the dislocation cores. The analysis indicates that from this model, we can estimate the mechanical alloying time from the starting elemental properties. It also indicates that the presence of chemical reactions can dramatically alter the completion of mechanical alloying.

References

1. T. H. Courtney, J. C. Malzahn Kampe, J. K. Lee and D. R. Maurice, Diffusion Analysis and Applications, p 225, eds. A. D. Romig and M. A. Dayananda, TMS Minerals, Metals and Materials Society, Warrendale, Pennsylvania (1989)
2. J. Crank, The Mathematics of Diffusion, Oxford University Press, London, UK (1956).
3. R. E. Weston and H. A. Schwarz, Chemical Kinetics, Prentice Hall, Englewood Cliffs, New Jersey (1972)
4. W. D. Nix and J. C. Gibeling, Flow and Fracture at Elevated Temperatures, ed. R. Raj, ASM, Metals

Park (1985)
5. G. F. Hancock and B. R. McDonnell, Phys. Stat. Sol. (a), 4, 143 (1971)
6. R. M. Davis, B. McDermott and C. C. Koch, Met. Trans., 19A, 2867 (1988)
7. P. S. Gilman and J. S. Benjamin, Ann. Rev. Mat. Sci., Vol. 13, p 279, eds. R. A. Huggins, R. H. Bube
and D. A. Vermilyea, Annual Reviews Inc., Palo Alto, California (1983).
8. A. K. Bhattacharya and E. Arzt, submitted to Scripta Met.
9. S. W. Benson, Thermochemical Kinetics, p 75, John Wiley and Sons, New York (1968)
10. H. C. Li and J. J. Moore, J. Mat. Sci. 25, 1159 (1990)

TABLE 1
Diffusion Data For Ni in NiAl

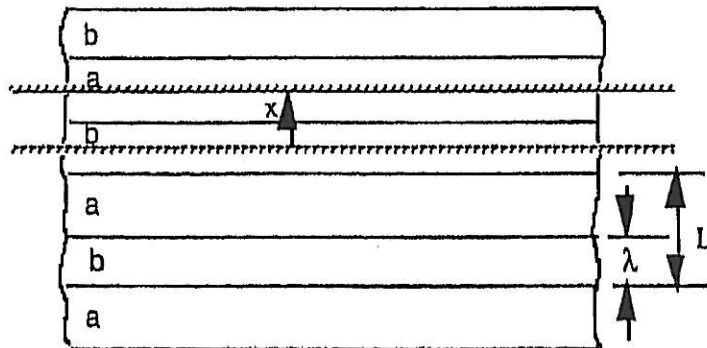|	
D_L, m^2/sec	4.46×10^{-4}
D_C, m^2/sec	1.2×10^{-3}
Q_L, kJ/mol	307
Q_C, kJ/mol	155
ρ, 1/cm^2	10^{14}

FIG.1 - Schematic morpholgy of layered powder particles (a and b), evolving in mechanical alloying.
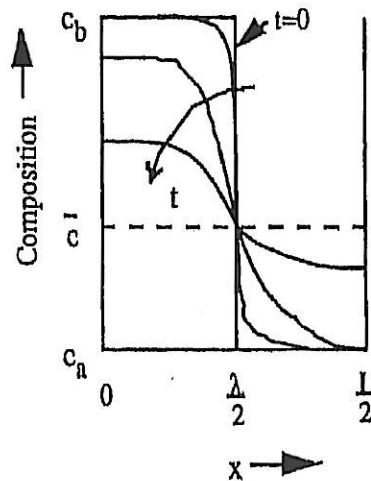

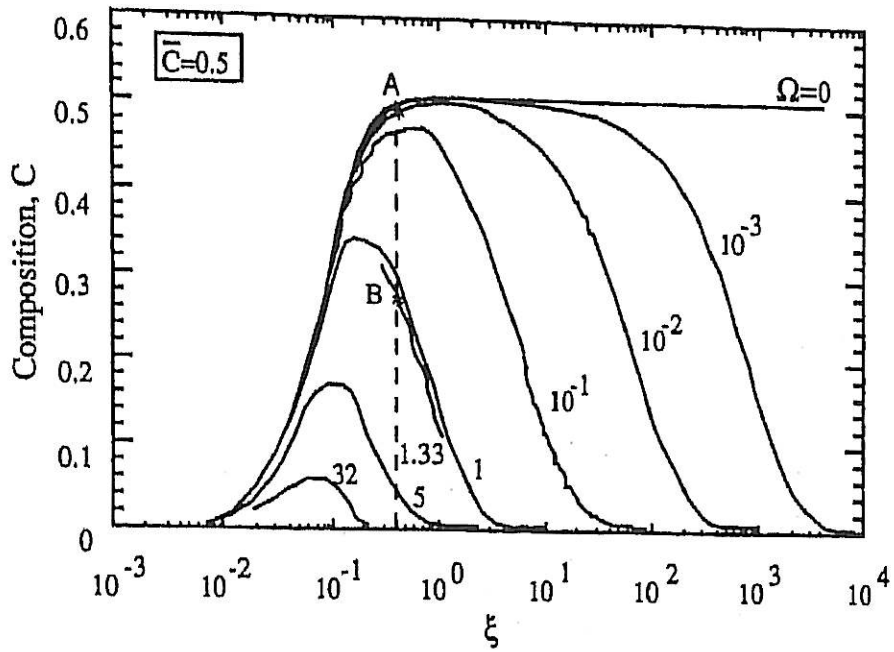FIG.2 - Concentration-distance profile as a function of time

FIG.3 - Composition-time history at various values of the reaction parameter Ω. Here, $\bar{c}$=0.5
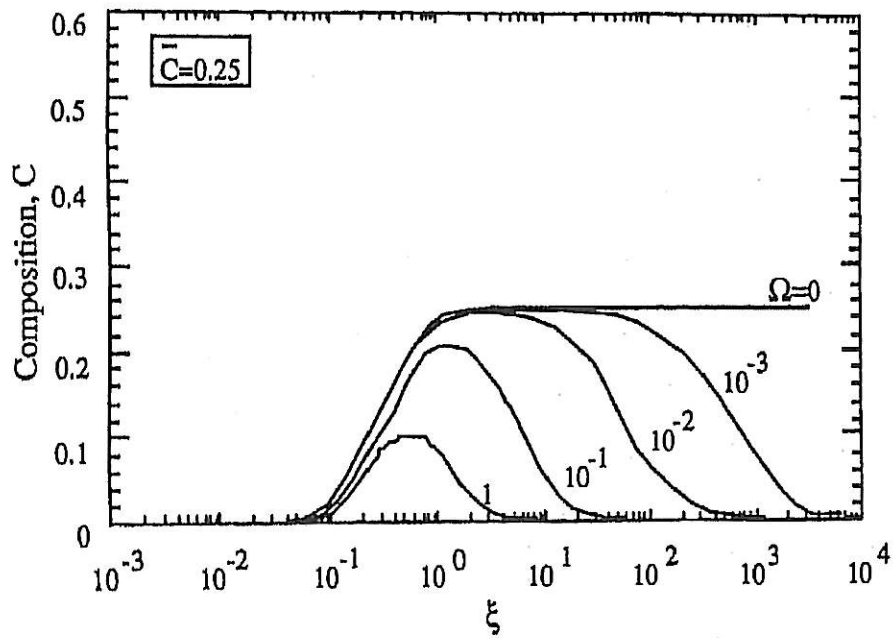

FIG.4 - Composition-time history at various values of the reaction parameter Ω. Here, $\bar{c}$=0.25