MATHEMATICAL MODELLING OF THE MECHANICAL ALLOYING KINETICS

S. K. PABI, D. DAS, T. K. MAHAPATRA and I. MANNA
Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Kharagpur
721302, India

(Received 20 January 1997; accepted 10 January 1998)

Abstract—A rigorous mathematical model, based on the modified iso-concentration contour migration method, has been developed to predict the kinetics of diffusive intermixing in a binary miscible system in the course of mechanical alloying (MA). The present model considers the variation of diffusion coefficient with composition, and interface shift due to both interdiffusion and mechanical deformation. Comparison of the kinetics predicted by the present model with the relevant experimental data from Cu–Ni and Cu–Zn shows that the effective mass transport operative in MA attains a rate intermediate between that for volume or grain boundary diffusion. An effective temperature for diffusion ($T_e$) has been proposed to simulate the observed alloying kinetics. $T_e$ is a function of composition but is not related to the adiabatic temperature rise at the point of ball-powder collision. Finally, the ratio of $T_e$ to the corresponding liquidus temperature for all the composition studied lies between 0.4 and 0.5.

1. INTRODUCTION

Nanostructured materials have received wide attention in the recent times as they may possess metastable microstructure with novel ranges of property [1–3]. Mechanical alloying (MA) by high energy ball milling is an easy and inexpensive route of producing nanostructured materials in bulk quantities with excellent scope of microstructural and process control [4–10]. In MA of ductile metals, the powder particles trapped between the colliding balls and vial undergo simultaneous deformation, fragmentation, and cold welding [8, 11] resulting into agglomerates of multilayered structures with clean interfaces [11–15]. Intermixing in such an aggregate during high energy ball milling often leads to the extension of solid solubility limit, and formation of nanostructured alloys, intermetallic compounds and amorphous phases [8, 16–18].

In the past, several attempts have been made to model the process/mechanism of MA [8, 18–22]. But only a few studies have been reported on mathematical modelling of the kinetics of MA [23–26]. During high energy ball milling, alloying may take place through (at least) two different mechanisms, namely, gradual diffusive intermixing and discontinuous additive mixing [27, 28]. The present model concerns the kinetics of alloying through the former mechanism only. Schultz et al. [23] have developed a simple kinetic model for solid state amorphization in Ni–Zr by MA. It has been assumed that Ni disperses rapidly along the boundaries of Zr grains of experimentally determined minimum size, and subsequently, undergoes bulk diffusion towards the center of the Zr particles leading to solid state amorphization. The kinetic analysis is therefore reduced to solving the diffusion equation for a Zr particle surrounded by a semi-infinite medium of Ni. Dupeux et al. [24] have considered the chemical interdiffusion characteristics within the multilayered structure generated during MA as equivalent to that in sandwich specimens of alternate polycrystalline slices of Ni bonded to stoichiometric Ni$_3$Al. Similar simplistic solution for homogenization in MA has also been presented by Courtney et al. [25]. However, all these models [23–25] make several simplifying assumptions in solving the mass balance equation and fail to consider the change in the diffusion field width caused by deformation during MA.

Martin and coworkers [21, 29, 30] have suggested that phase transformation in an externally driven system such as high energy ball milling needs to be analyzed from the point of view of a nonequilibrium dynamical situation. Bellon and Averback [31] have proposed that mass transport during MA may take place by two simultaneously operating mechanisms, namely, atomic transport due to shear along randomly selected glide planes as well as thermally activated diffusion of the constituent atoms. If the former process is dominant, the atomic mobility term in this approach may not be related to the melting/liquidus temperature of the system. Such a model may provide an explanation for alloying induced by ball milling in the immiscible systems.

During MA in ductile and miscible (completely/partially) systems, deformation leads to a change in the thickness of the constituent phases, that in turn distorts the concentration profiles. Moreover, the
interface also shifts due to concurrent intermixing of the constituent atoms diffusing at different rates. As a result, the MA kinetics transforms into a special moving boundary problem. In this paper, a rigorous numerical solution of this problem has been presented. The present model simultaneously takes into account the variation of the interdiffusion coefficient \((D)\) with composition \((C)\), and interface shift due to both diffusion as well as deformation. The results predicted by the model have been compared with the relevant experimental data from the Cu–Ni and Cu–Zn systems to yield a measure of the enhanced/effective mass transfer rate operating during MA.

2. THE MODEL

The present model on MA kinetics is based on a modified version of the iso-concentration contour migration (ICCM) method [32], developed earlier to estimate the rate of diffusion controlled dissolution in a two-phase planar and multilayered aggregate. This modified ICCM (henceforth to be referred as the MICCM) method is capable of considering the deformation induced changes in diffusion distances while calculating the alloying kinetics. Here the extent or rate of deformation of the constituent phases need not be identical. For this purpose, the diffusion equations have been suitably transformed to express the distance \((X)\) as a function of concentration \((C)\) and time \((t)\), such that \(C\) is an independent variable. As the solute concentration at the interface remains constant in a diffusion controlled alloying process, this transformation converts the moving boundary problem into a static boundary one, even in the presence of mechanical deformation accompanying the MA process. Here, \(X\) is computed at any \(t\) in two discrete steps, at first to consider diffusive intermixing, and subsequently, to incorporate the constraints of concurrent deformation accompanying MA.

2.1. Calculation of the diffusional mass transfer

Formation of a layered structure during MA of ductile ingredients has been reported by several investigators [11–15]. Figure 1 schematically shows the cross-section of such a layered structure composed of uniformly sized and homogeneous plates of A and B phases. The broken lines represent the location of the symmetry planes signifying no net mass transfer across them. In view of the symmetrical and repetitive configuration, a sandwich structure consisting of two adjacent halves of the A and B layers may constitute a representative element for numerical analysis. The concentration profile in such an element of initial half width, \(W\) \((=W_A+W_B)\) at \(t = 0\) in the course of MA is schematically illustrated in Fig. 2. The volume fraction of A at the beginning of MA (i.e. \(t = 0\)) is \(W_A/W\) (Fig. 2(a)). Figures 2(b) and (c) schematically illus-
trate how the respective interdiffusion and superimposed deformation affect the distance-concentration profile and interface shift with respect to the original position of the interface. Since \( W_A \) or \( W_B \) is much smaller than their respective lengths, the scheme of mixing may be considered as a one-dimensional diffusion problem having the field equation:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left( D \frac{\partial C}{\partial X} \right) \tag{1}
\]

where, \( C \) is the dependent variable and \( D \) the diffusion coefficient. Since the concentration along an iso-concentration contour is constant,

\[
dC = \left( \frac{\partial C}{\partial X} \right) dX + \left( \frac{\partial C}{\partial t} \right) dt = 0 \tag{2}
\]

and therefore,

\[
\left( \frac{\partial C}{\partial t} \right) = -\left( \frac{\partial C}{\partial X} \right) \left( \frac{\partial X}{\partial t} \right). \tag{3}
\]

It may be readily shown that,

\[
\frac{\partial}{\partial X} \left( D \frac{\partial C}{\partial X} \right) = \left( \frac{\partial D}{\partial C} \right) \left( \frac{\partial X}{\partial C} \right)^2 - D \left( \frac{\partial^2 X}{\partial C^2} \right) \left( \frac{\partial X}{\partial C} \right)^3. \tag{4}
\]

Substitution of equations (3) and (4) to the field equation (1) with proper subscripts and superscripts yields the following set of coupled partial differential equations for the A-phase:

\[
\frac{\partial X}{\partial t} = D_A \left( \frac{\partial^2 X}{\partial C_A^2} \right) \left( \frac{\partial X}{\partial C_A} \right)^2 - D_A \left( \frac{\partial C_A}{\partial C_A} \right) \left( \frac{\partial X}{\partial C_A} \right)^{-1} \tag{5}
\]

and for the B-phase:

\[
\frac{\partial X}{\partial t} = D_B \left( \frac{\partial^2 X}{\partial C_B^2} \right) \left( \frac{\partial X}{\partial C_B} \right)^2 - D_B \left( \frac{\partial C_B}{\partial C_B} \right) \left( \frac{\partial X}{\partial C_B} \right)^{-1} \tag{6}
\]

where, \( D_A \) and \( D_B \) are the interdiffusion coefficients, and \( C_A \) and \( C_B \) the compositions of A and B, respectively. Since the dimension of the sandwich element may change due to deformation, the interface between A and B phases representing the concentration invariant location is taken as the reference (\( X = 0 \)) in the computation. Therefore, the boundary conditions for finite geometry of the sandwich element are:

\[
\frac{\partial X}{\partial C_A} \rightarrow \infty, \quad \text{at} \quad X \rightarrow -W_A, \quad \tau \geq 0 \tag{7}
\]

\[
\frac{\partial X}{\partial C_B} \rightarrow \infty, \quad \text{at} \quad X \rightarrow W_B, \quad \tau \geq 0 \tag{8}
\]

It may be pointed out that \( W_A \) and \( W_B \) do not remain constant in the course of MA. But \( W_A/W_B \) would not be affected, if the shear strain in both the phases are identical. The present model, however, allows the strain to be unequal in the two constituent phases. The condition of diffusional mass balance across the interface can be written as:

\[
\frac{\partial S}{\partial t} = \frac{1}{C_{SA} - C_{SB}} \left[ D_B \left( \frac{\partial C_B}{\partial X} \right)_{X=0} - D_A \left( \frac{\partial C_A}{\partial X} \right)_{X=0} \right] \tag{9}
\]

where, \( C_{SA} \) and \( C_{SB} \) are the respective compositions of the A and B phases at the interface.

Computations have been carried out on a distance-concentration grid as shown in Fig. 3, which also illustrates the grid nomenclature. Here the respective composition ranges of the A and B phases have been divided into \( n \) and \( r \) equally spaced intervals, where \( n = (g - e) \). According to the finite difference method of calculation, the respective derivatives of equations (5), (6) and (9) at a given time \( t_1 \) may be expressed as:

\[
\frac{X_{i+1}^{n+1} - X_i^n}{\Delta t} = 4D_A \left[ \frac{X_{i+1}^{n} - 2X_i^n + X_{i-1}^{n}}{(X_i^{n+1} - X_i^{n})^2} \right] - \frac{D_{A,n+1} - D_{A,n}}{X_i^{n+1} - X_i^{n+1}} \tag{10}
\]

\[
\frac{X_{i+1}^{n+1} - X_i^n}{\Delta t} = 4D_B \left[ \frac{X_{i+1}^{n} - 2X_i^n + X_{i-1}^{n}}{(X_i^{n+1} - X_i^{n+1})^2} \right] - \frac{D_{B,n+1} - D_{B,n}}{X_i^{n+1} - X_i^{n+1}} \tag{11}
\]

where \( X_i^n \) is the distance of the contour \( G_i \) from the A/B-interface (cf. Fig. 3) at an instant \( t_1 = n \Delta t \), \( n \) being an integer and \( \Delta t \) the time increment of \( t \). If \( |\Delta S| \) is extent of increment in \( W_B \) at \( t_2 = (n + 1) \Delta t \) due to diffusion alone, then

\[
\frac{\Delta S}{\Delta t} = \frac{2}{(C_{SA} - C_{SB})} \times \left[ \frac{D_B \Delta C_B}{X_i^{n+1} - 4X_i^{n+2} + 3X_i^{n+3}} + \frac{D_A \Delta C_A}{X_i^{n+1} - 4X_i^{n+2} + 3X_i^{n+3}} \right] \tag{12}
\]

It is evident from equations (10)–(12) that a unique value of \( D \) (say, \( D_i \)) may be assigned to each concentration grid point (\( G_i \)) during computation that automatically takes care of the variation of \( D \) with \( C \). The stability conditions of the algorithm and method of initiation of calculation in the present model are analogous to that in the ICCM model [32]. In the present finite difference formulation, the boundary conditions (equations (7) and (8)) can be incorporated by fitting a parabola to the last three grid points. Thus, for the A-phase:

\[
X_{i+1}^{n+1} = \frac{(\sqrt{2}X_{i+1}^{n+1} - X_{i+1}^{n+1})}{(\sqrt{2} - 1)} \tag{13}
\]

and for the B-phase:

\[
X_{i-1}^{n+1} = \frac{(\sqrt{2}X_{i-1}^{n+1} - X_{i-1}^{n+1})}{(\sqrt{2} - 1)}. \tag{14}
\]
As none of the contours of the B-phase can physically go beyond $W_B$, (i.e. $X_1^{n+1} > W_B$), a grid point $G_{r+1}$ is discarded, as soon as the $X_1^{n+1}$, exceeds $W_B$. In this situation, the value of $X$ at the last grid point $X_1^{n+1}$ is computed by fitting a parabola to $X_1^r$, $X_1^{r-1}$ and $X_1^{r-2}$. Thus,

$$X_1^{n+1} = X_1^n + D^B \Delta t/(W_B^n - X_1^n).$$

Similarly the grid point $G_g$ is ignored when $X_1^{n+1} > W_A^n$ in A, and consequently,

$$X_1^{n+1} = X_1^n - D^A \Delta t/X_1^{n-1}.$$  

In Fig. 3, curve-a schematically shows the distance–concentration profile at a given time $t_1$ and curve-b after interdiffusion and consequent change in $W_A$ and $W_B$ at time $t_2$. Here $W_A$ and $W_B$ are the half-widths of A and B phases at $t_1$, respectively. The new half widths $X_1^{n+1}$ after interdiffusion is redefined as $X_2^{n+1}$, such that $X_2^{n+1} = (X_1^{n+1} + \Delta S)$ and $X_2^{n+1} = (X_1^{n+1} + 1 + \Delta S)$ for the A and B phase, respectively.

2.2. Superimposed effect of deformation on intermixing

Figure 2(c) schematically shows the reduction in the widths of A and B phases following the impact of the colliding balls on the layered structure and consequent modification in the concerned concentration profiles. Plastic deformation is expected to expedite intermixing of the constituents atoms at the interface between the adjacent layers and thereby, reduce the composition difference across the interface ($\Delta C = C_{SA} - C_{SB}$). The $\Delta C$ is a function of the transient/metastable solubility limits of the phases concerned. In this regard, it may be noted that a considerable extension of solid solubility limit by extensive deformation in ball milling has been observed in Ni–Al [33, 34], but not in Cu–Zn [35]. On the other hand, atomic transport from the interface to the interior of a layer has to take place by diffusion, which may be enhanced by deformation induced “mechanical interdiffusion”, as proposed by Rouff and Balluffi [36]. The mechanical deformation changes the relative position of the iso-concentration profiles. For instance, the point $P$ having any particular concentration $C$ located at a distance $x_1$ from the interface (Fig. 2(b)) would be shifted by uniform shear to a position $P'$, located at a distance $x_1$ from the same interface (Fig. 2(c)). As a consequence, the concentration–distance profile within a layer appears steeper due to deformation at that instant (cf. Fig. 2(c) vis-à-vis Fig. 2(b)). It may be pointed out that the change in composition profile during a given interval of time is essentially the resultant of the contributions rising out of diffusion (Fig. 2(b)) and deformation (Fig. 2(c)). While deformation tends to make the profile steeper, concurrent diffusion would tend to flatten the same. In any case, the concentration–distance profile becomes shallower with the progress of MA. For instance, curve-a (shown by broken line in Fig. 4) schematically represents the resultant concentration profile at time $t'$. At a later instant of time $t'$ ($> t$), the same profile becomes shallower.
In a distance–concentration plot (Fig. 3), the position of a given iso-concentration line after deformation in the interval \( (t_2 - t_1) \) during MA may easily be determined by multiplying \( X_{2i+1}^{n+1} \) by a scaling factor. For phase A, the scaling factor for the time interval \( (t_2 - t_1) \) is defined as: 
\[
Z_A = \frac{W_{t_2}^A}{W_{t_1}^A},
\]
where \( W_{t_1}^A \) and \( W_{t_2}^A \) are the widths of the A-layer before and after deformation, respectively. The \( Z_B \) for phase-B can be defined in a similar manner. Figure 5 shows the iso-concentration contour at \( t_2 \) before (curve-a) and after (curve-b) deformation. Accordingly, the new position of the contour at any grid point \( G_i \) in A and B-phase after deformation are \( X_{2i+1}^{n+1} = X_{2i}^n + \eta_A \) and \( X_{2i+1}^{n+1} = X_{2i}^n + \eta_B \), respectively. It may be pointed out that \( \frac{\partial X}{\partial C} \rightarrow \infty \) at the symmetry planes, and therefore, remains unchanged by the multiplication with \( \eta_A \) or \( \eta_B \). Hence, the boundary conditions (equations (7) and (8)) imposed by the finite geometry remain unaffected by the deformation process.

In numerical computation, the simultaneous deformation and interdiffusion are taken into account by incorporating a finite extent of dimensional change after solving the equations (10)–(14) at every \( \Delta t \) interval. After computation of \( X2 \) values at the \( (n+1) \)th time step, these are taken as the new value of \( X1 \) before solving the equations (10)–(14) for the next time step. When the number of workable grid points in any phase drops to less than three, the concentration profile in it is taken to be linear for introducing one new grid point at the midpoint between two nodes. The computation is terminated either when the width of a given phase measures less than \( 10^{-3} \) times its initial width, or composition gradient disappears in both the phases. Finally, the average composition of each phase at a given \( t \) has been computed by dividing the area under the \( X \) vs \( C \) plot by the corresponding instantaneous phase width.

3. EXPERIMENTAL

Two Cu–Ni alloys of nominal compositions Cu\(_{50}\)Ni\(_{50}\), and Cu\(_{20}\)Ni\(_{80}\) were produced by ball milling pure (>99.5 wt%) elemental powders of Cu and Ni of –325 mesh size in a Fritsch Pulverisette Experiments were conducted at...
5/2 high energy planetary ball mill. Milling was carried out at a mill speed (Ω) of 300 rpm in toluene medium using hardened chrome steel (Fe-12 wt% Cr-2 wt% C) container and balls of 10 mm diameter with a ball to powder ratio of 10:1.

The milled powders were characterized at various stages of milling by X-ray diffraction (XRD) analysis obtained from a Phillips PW 1710 diffractometer with Co–Kα radiation. The crystallite size (i.e. coherence length) was determined from the XRD line profile analysis of the (220) reflection by variance method [37, 38]. The extent of Ni dissolved in Cu (say, CuNi) and vice versa (NiCu) were determined by the peak shift analysis of the Cu and Ni peaks with respect to the standard data for the same reported in the literature [39]. The morphology and microstructure of the milled product were examined with a CAM SCAN2 scanning electron microscope (SEM).

4. RESULTS AND DISCUSSION

4.1. Crystallite size

Figure 6 shows the variation of crystallite size or coherence length (d) for Cu and Ni as a function of t for Cu50Ni50 and Cu20Ni80 blends. In either case, d for both Cu and Ni decreases with an increase in t and merges with each other after about 20 h. Finally, d reaches a minimum (dmin) of 31 and 18 nm for Cu50Ni80 and Cu20Ni80, respectively (Fig. 6). It has been pointed out by Eckert et al. [40–42] that dmin attainable under a given milling condition depends on the extent of recovery and solid solution hardening of the alloy in the course of MA. It is known that Cu–Ni system exhibits an f.c.c. structure over the entire composition range and addition of Cu to Ni produces a typical solid solution hardening in a polycrystalline alloy with grain size r1m [43]. Similar solid solution hardening may account for the smaller dmin in Cu50Ni50 as compared to that in Cu20Ni80. However, the present data are at variance with the recent observation of solid solution softening of Cu alloyed nanocrystalline Ni by Shen and Koch [44].

4.2. Solid solubility

It is known that the relative position of the XRD peaks from a single phase alloy is a function of the composition of the alloy. In the present study, the XRD peaks of Ni and Cu undergo a gradual shift towards each other as t increases. The extent of shift is more for Cu peaks than that in Ni, indicating faster enrichment of Ni in Cu than the reverse. Cu–Ni being an isomorphous system, this may be attributed to the faster diffusion coefficient of Ni in Cu, than that of Cu in Ni [45]. The gradual merger of the Cu and Ni peaks and continuous variation of d with t for both suggest that the diffusive intermixing mechanism is operative in the present system [27, 28]. It may be noted that the enthalpy of mixing (ΔHM) for Cu–Ni alloys (in the solid state) is only about 2 J/mol [46, 47], which is favorable for gradual diffusive intermixing [27].

In order to compare the experimental data on the variation of CuNi vs t with the predictions of the MICCM model, the experimental data on the variation of d for Cu and Ni (Fig. 6) has been used in the computation as the input data for d as a function of t. It implies that the lower limit of the layer thickness corresponds to the coherence length determined by XRD analysis, and hence, computation would predict the lower limit of the time required for intermixing. It may be mentioned that a possible change in the average diffusion field width caused by any extensive penetration of shear bends of different constituents can also be reflected in the measured value of d, that has been used as an
input. A sharp composition gradient at the interface between the A and B regions depicted in Fig. 2 is, however, not expected in an isomorphous system like Cu-Ni. In order to apply the present MICCM formulation to the Cu-Ni system, it is assumed that the respective Ni contents at different temperatures and at different composition nodes [48, 49]. At a given T, D vs C values have been fitted to a fourth order polynomial to determine D for a given concentration node in Fig. 3.

Computer analysis [8, 20, 50] has shown that the localized temperature at the point of impact between the ball and powder does not exceed 500 K. Furthermore, the experimental results of ball milling of steel powders with martensitic structure have evidenced that the local temperature rise should not exceed 538–553 K [16, 19]. If the alloying is assumed to take place by volume diffusion at T = 553 K (i.e. maximum attainable T during MA), the kinetics of MA predicted by the MICCM model (curve-2 in Fig. 7) in terms of the variation of CuNi with t are more than two orders of magnitude slower than the corresponding experimental data (i.e. curve-1 in Fig. 7). Therefore, volume diffusion does not seem to make any significant contribution to the process of MA. However, it is important to point out that the normalized temperature (T/C128) operative in the milling temperature must be selected with an accuracy of ±10 K to minimize the deviation of the predicted result from the experimental data. Table 1 shows that T/C128 is a function of the composition of mechanically alloyed powders. However, it is important to point out that the normalized temperature ratio (T/C128) operative in the milling temperature (T/C128=555 K, matches well with the experimental data of curve-1 in Fig. 7).

In order to derive a better understanding of the kinetics of intermixing, volume diffusivity (D/C128) values at different T have been used as the input along with the experimentally determined data on d as a function of t for Cu50Ni50 and Cu70Ni30 (Fig. 6) to simulate the variation of CuNi with t in each composition in the course of MA. The temperature at which the theoretical predictions by MICCM model shows best agreement with the experimental data on the variation of CuNi as a function of t, may be defined as the effective temperature of diffusive alloying (T/C128). Thus, T/C128 reflects a measure of the enhanced interdiffusivity (D/C128) operative in the process of MA. For Cu50Ni50 composition, curve-3 calculated for T/C128=755 K, matches well with the experimental data of curve-1 in Fig. 7. Similar calculation for Cu70Ni30 yields T/C128=785 K (curve-3 in Fig. 8). It is interesting to note that a moderate deviation from T/C128 (say, ±40 K) yields a significant change in the alloying kinetics (curve-2 and curve-4 in Fig. 8). Therefore, T/C128 must be selected with an accuracy of ±10 K to minimize the deviation of the predicted result from the experimental data. Table 1 shows that T/C128 is a function of the composition of mechanically alloyed powders. However, it is important to point out that the normalized temperature ratio (T/C128) operative in the milling temperature (T/C128=555 K, matches well with the experimental data of curve-1 in Fig. 7).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ω rpm</th>
<th>T1 (K)</th>
<th>T/C128 (K)</th>
<th>T/C128 (K)</th>
<th>θ/C128</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu50Zn50</td>
<td>200</td>
<td>1217</td>
<td>505</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>Cu50Zn50</td>
<td>300</td>
<td>1217</td>
<td>520</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>Cu50Zn50</td>
<td>300</td>
<td>1170</td>
<td>560</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Cu50Ni50</td>
<td>300</td>
<td>1580</td>
<td>755</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>Cu50Ni50</td>
<td>300</td>
<td>1670</td>
<td>785</td>
<td>0.47</td>
<td></td>
</tr>
</tbody>
</table>

Earlier kinetic studies on cluster assembled nanocrystalline Cu have yielded exceptionally high self diffusivity values in these materials [2, 52, 53]. Therefore, it is of interest to find out whether the rate of mass transfer operative in MA reaches the level of concerned grain boundary chemical diffusivity (D gb). Using the extrapolated D gb values of Cu-Ni system at 373 K [45], the kinetics predicted by MICCM model (curve-4 in Fig. 7) is found to be more than an order of magnitude faster than the corresponding experimental data (curve-1 in Fig. 7). Thus, the actual atomic transport rate in MA seems to be faster than that for volume diffusivity, but appreciably slower than the same for grain boundary diffusion at the milling temperature.

4.3. Effective temperature for alloying

In order to derive a better understanding of the kinetics of intermixing, volume diffusivity (D/C128) values at different T have been used as the input along with the experimentally determined data on d as a function of t for Cu50Ni50 and Cu70Ni30 (Fig. 6) to simulate the variation of CuNi with t in each composition in the course of MA. The temperature at which the theoretical predictions by MICCM model shows best agreement with the experimental data on the variation of CuNi as a function of t, may be defined as the effective temperature of diffusive alloying (T/C128). Thus, T/C128 reflects a measure of the enhanced interdiffusivity (D/C128) operative in the process of MA. For Cu50Ni50 composition, curve-3 calculated for T/C128=755 K, matches well with the experimental data of curve-1 in Fig. 7. Similar calculation for Cu70Ni30 yields T/C128=785 K (curve-3 in Fig. 8). It is interesting to note that a moderate deviation from T/C128 (say, ±40 K) yields a significant change in the alloying kinetics (curve-2 and curve-4 in Fig. 8). Therefore, T/C128 must be selected with an accuracy of ±10 K to minimize the deviation of the predicted result from the experimental data. Table 1 shows that T/C128 is a function of the composition of mechanically alloyed powders. However, it is important to point out that the normalized temperature ratio (T/C128) operative in the milling temperature (T/C128=555 K, matches well with the experimental data of curve-1 in Fig. 7).

In order to verify the proposed hypothesis on T/C128 and θ/C128, the alloying kinetics for the Cu–Zn blends (earlier reported) have been compared with the predictions of the MICCM model to obtain the corresponding T/C128 and θ/C128 values. For simplification of the present analysis, it is assumed that the β-phase is present in the MA product since t = 0. The volume fraction of β at t = 0 can be
estimated from the nominal composition of the blend. Furthermore, it is assumed that the compositions of $x$ and $\beta$ at the $x$-$\beta$ interface during MA may be obtained from concerned equilibrium diagram [55].

For the present computation, the data on the variation of $d$ with $t$ for $x$ in the Cu–Zn system (reported in [34, 35]) has been utilized. The bulk diffusivity values in $x$ and $\beta$ phases are available in the literature [56]. Using these data, the variation of fusivity values in (reported in [34, 35]) has been utilized. The bulk diffusion co-efficient of Ni is enhanced by several orders of magnitude in amorphous NiZr [58] and crystalline Ni–Al [59] during ball milling possibly indicates the dominant role of structural defects in the mass transfer process during plastic deformation concomitant with the process of MA. In this regard, earlier studies have reported that the diffusion coefficient of Ni is enhanced by several orders of magnitude during beam irradiation may increase the configurational entropy, which is equivalent to a rise in the temperature of the system to $T'$ ($> T = $ ambient temperature).

Furthermore, it was proposed that $T'$ is related to $T$ through the following relationship:

$$T' = T \left(1 + \frac{D_{\text{bal}}}{D_{\text{chim}}} \right) \tag{17}$$

where, $D_{\text{bal}}$, and $D_{\text{chim}}$ are the ballistic and chemical interdiffusion coefficients, respectively. It may be pointed out that $D_{\text{bal}}$ is exponentially related with temperature, while $D_{\text{chim}}$ is considered to be temperature independent [57]. In an attempt to extend the applicability of equation (17) to MA, $T'$ may be considered as equivalent to $T_{\text{eff}}$ (obtained from Table 1) and $T = 323$ K, i.e. the approximate temperature inside the most common mills [8]. This gives $D_{\text{bal}}/D_{\text{chim}} = 0.4 - 1$ for the $T_{\text{eff}}$ data presented in Table 1. If $T$ in equation (17) corresponds to the temperature at the point of ballpowder impact, it would have higher values ($\sim 538–553$ K [8, 16, 19]), which would further reduce the ratio of $D_{\text{bal}}$ to $D_{\text{chim}}$. Therefore, it appears, that if $D_{\text{bal}}$ is correlated with $T_{\text{eff}}$ through equation (17) (assuming $T' = T_{\text{eff}}$), it would not account for the orders of magnitude enhancement in the diffusivity ($D_{\text{eff}}$) encountered in MA.

In the MA process, microstructural refinement takes place as a result of sustained shear, repeated fracture and cold welding of particles [8, 11]. Hellstern et al. [4] have shown that the evolution of microstructure in MA takes place in several stages. All these factors make dynamic modelling of the MA process a formidable task. On the other hand, the present model yields a measure of the enhanced mass transfer rate in MA, which is supported by several experimental observations [23, 58–60]. This possibly indicates the dominant role of structural defects in the mass transfer process during plastic deformation concomitant with the process of MA.

In this regard, earlier studies have reported that the diffusion coefficient of Ni is enhanced by several orders of magnitude during beam milling possibly due to a transient increase in free volume during plastic deformation. Hart [61] has shown that the bulk diffusion coefficient can be enhanced by dislocation short-circuiting, if a tracer atom visits many dislocations during the time of the experiment. Earlier, Balluffi and Ruoff [36] have concluded that...
short-circuiting through moving grain boundaries and dislocations are responsible for the enhancement of diffusivity during plastic deformation. In general, the dislocations or grain boundaries sweeping through the crystals [62–64], excess vacancies created by deformation, or cooperative displacement of atoms by shear along randomly selected glide planes [31] may separately or in combination account for the enhanced mass transport rate during MA. The present study indicates that this enhanced diffusion rate may be correlated with the melting temperature of the system. However, further investigation is warranted to identify the precise contribution and mechanism responsible for this enhanced diffusion rate. Finally, it is apparent from the present study that the crystallite size of the constituents has to be reduced to nanoscale (<100 nm) even in an isomorphous system like Cu–Ni for achieving a significant extent of alloying by high energy ball milling (Figs 6–8).

5. CONCLUSIONS

(1) A rigorous mathematical model of mechanical alloying (MA) in ductile miscible systems has been developed using a modified iso-concentration contour migration method. The model takes into account the variation of diffusion coefficient with composition, interface shift due to interdiffusion between adjacent phases, and change in of crystallite size of the constituent phases in the course of milling.

(2) The predictions of the model, when compared with the experimental data of MA for the Cu–Ni and Cu–Zn systems, indicate that volume diffusion has insignificant contribution to alloying. On the other hand, the rate of mass transport in MA seems to be slower than that for grain boundary diffusion. Thus, it appears that the effective mass transport operative in MA attains a rate intermediate between that for volume and grain boundary diffusion.

(3) An effective temperature for diffusive alloying ($T_{\text{eff}}$) has been proposed to simulate the observed alloying kinetics. $T_{\text{eff}}$ does not appear to have any direct correlation with the localized temperature rise at the point of ball-power impact.

(4) $T_{\text{eff}}$ is a function of the alloy composition. However, a change in milling speed from 200 to 300 rpm seems to have marginal effect on $T_{\text{eff}}$ for the Cu$_{70}$Zn$_{30}$ blend.

(5) The normalized temperature ratio for all the Cu–Ni and Cu–Zn alloys studied is found to lie between 0.4 and 0.5. Thus, the effective mass transfer rate in MA seems to be related to the liquidus temperature of the systems studied.

Acknowledgements—The work is sponsored by the Department of Science and Technology, Government of India (Grant No.III.4(23)92-ET). The authors are thankful to C. Abromeit (HMI, Berlin) for a stimulating discussion.

REFERENCES

32. Pabi, S. K., Phys. status solidi (a), 1979, 51, 281.