

# Modelling accelerated solid-state diffusion under the action of intensive plastic deformation

B. B. KHINA\*

*Physico-Technical Institute, National Academy of Sciences of Belarus, Minsk 220141, Belarus*

*E-mail: khina@lenta.ru*

I. SOLPAN

*Technical University of Moldova, Chishinau, Moldova*

G. F. LOVSHENKO

*Mogilev State Technical University, Mogilev, Belarus*

A mathematical model of accelerated solid-state diffusion during mechanical alloying (MA) in a binary substitutional system A-B is developed. An individual lamellar particle formed due to fracturing/cold welding during a preliminary stage of MA is considered. Interdiffusion occurs via the vacancy mechanism. During the plastic deformation, jog dragging by moving screw dislocation generates non-equilibrium point defects (vacancies and interstitial atoms), which can diffuse, interact with edge dislocations and recombine. To evaluate the point defect generation rate, a simple Hirsch-Mott theory is employed. Numerical simulation has been performed for a repeated "deformation-rest" cycle at 100°C using realistic parameter values. The influence of non-equilibrium vacancies on the atomic diffusion is evaluated. It reveals itself via the increase of partial diffusivities of substitutional atoms and through the cross-link terms in the matrix of interdiffusion coefficients. The incoherent phase boundary between parent phases (pure elements) is considered as a sink for non-equilibrium vacancies. Due to interplay of these factors, substantial alloying by solid-state diffusion is observed after a reasonable time of MA (4000 s). © 2004 Kluwer Academic Publishers

## 1. Introduction

Accelerated solid-state diffusion in metals under cold intensive periodic plastic deformation (IPPD) was observed in a wide range of strains and strain rates [1] including those typical of mechanical alloying (MA) in different milling devices [2]. An apparent diffusion coefficient estimated from experimental data reaches the value of  $D \geq 10^{-5} \text{ cm}^2/\text{s}$  [1] which is close to that in liquid metals. Deformation-enhanced interdiffusion is usually attributed to the generation of non-equilibrium vacancies and accumulation of lattice strain, and is supposed to play an essential part in MA (see, e.g., reviews [3–5] and literature cited therein).

Despite extensive experimental [1, 3–6 and many other] and theoretical [7–10 and other] research, the mechanism of metastable phase formation during MA is not well understood yet, and the role of diffusion is hotly debated [6–8 and other]. Most developed are theories based on the concept of mechanical reactive mixing in interfacial regions formed by codeformation [7, 8 and other work]. The main role is ascribed to energy transfer during collisions, formation of "fresh" contact

surfaces by shear deformation and chemical affinity of the components.

A thorough theory of deformation-enhanced diffusion taking into account particular physical mechanisms has not been developed so far. For example, in Ref. [9] alloying during MA was ascribed to pipe diffusion along curved dislocation ignoring volume diffusion and point defects. In theoretical work [10], the role of deformation was reduced to thinning of an elementary diffusion couple and a trivial one-dimensional diffusion equation was used; the values of diffusion coefficients were taken at an arbitrarily chosen "effective" temperature (up to 825 K for Cu-Ni system) which was varied to fit the calculated results to experimental data.

In connection with the above, the goal of this research is to develop a rigorous model of accelerated diffusion under IPPD taking into account basic physical factors (e.g., point defect generation etc.) and perform computer simulation using realistic values of parameters.

## 2. Formulation of a model

An early stage of MA in a binary system is examined when composite particles consisting of alternating

\*Author to whom all correspondence should be addressed.

lamellas of metals A and B have formed due to fracturing and cold welding, the layer thickness is  $L = 0.5\text{--}0.1 \mu\text{m}$  [2–5]. At this stage, the formation of nano-sized grains has not occur yet, and the dominating mechanism of plastic deformation is the dislocation glide. An elementary diffusion couple “phase 2 (based on metal B)/phase 1 (based on metal A)” of thickness  $L$  is considered. Diffusion in both phases occurs via the vacancy mechanism. Phase transformation and nucleation of a new phase in the field of a steep concentration gradient can be suppressed [11, 12], thus we consider only atomic diffusion. Since the impacts experienced by a particle are chaotic, we imply that the shape and size of the elementary diffusion couple do not change, and reduce the role of deformation to the generation of point defects.

According to the mechanistic model of MA [2], for a vibratory SPEX mill the strain rate is  $\varepsilon' \sim 10^3 \text{ s}^{-1}$  and the maximal pressure during collision is  $p \sim 1 \text{ GPa}$ . Hence the ballistic effects, which are noticeable at  $p \sim 100 \text{ GPa}$  [13], can be neglected. Then the dominating mechanism of the point defect generation is jog dragging by gliding screw dislocations during shear deformation. Non-equilibrium vacancies can substantially increase the diffusion coefficients of atoms A and B. Besides, the interaction of diffusion fluxes of lattice atoms and vacancies becomes important due to cross-terms in the matrix of Onsager coefficients [14]. During diffusion, vacancies and interstitials can recombine in the volume and interact with edge dislocations which act as volume-distributed sinks for non-equilibrium point defects.

Mathematical formulation of the above physical model is based on certain issues of the theories of strain-enhanced diffusion in metals [15] and diffusion in irradiated alloys [16 and other work]. Evolution of the concentrations of lattice atoms B, excess vacancies and interstitial atoms A and B (denoted as  $v$ ,  $A_i$  and  $B_i$ , correspondingly) is described as

$$\begin{aligned} \partial c_B / \partial t = & \partial (D_{BB} \partial c_B / \partial x + D_{Bv} \partial c_v / \partial x) / \partial x - p_i c_B \\ & + z_{Bi} D_{Bi} c_{Bi} \rho_e + k_{iv} \Delta c_v c_{Bi} \end{aligned} \quad (1)$$

$$\begin{aligned} \partial c_v / \partial t = & \partial (D_{vB} \partial c_B / \partial x + D_{vv} \partial c_v / \partial x) / \partial x + p_v \\ & - z_v D_v \Delta c_v \rho_e - k_{iv} \Delta c_v (c_{Bi} + c_{Ai}) \end{aligned} \quad (2)$$

$$\begin{aligned} \partial c_{Ai} / \partial t = & D_{Ai} \partial^2 c_{Ai} / \partial x^2 + p_i c_A - z_{Ai} D_{Ai} c_{Ai} \rho_e \\ & - k_{iv} \Delta c_v c_{Ai} \end{aligned} \quad (3)$$

$$\begin{aligned} \partial c_{Bi} / \partial t = & D_{Bi} \partial^2 c_{Bi} / \partial x^2 + p_i c_B - z_{Bi} D_{Bi} c_{Bi} \rho_e \\ & - k_{iv} \Delta c_v c_{Bi} \end{aligned} \quad (4)$$

where  $c_i$  is the concentration of  $i$ -th species,  $\Delta c_v = c_v - c_v^0$  where  $c_v^0$  is the equilibrium vacancy concentration,  $D_{ij}$  ( $i, j \equiv A, B, v$ ) are interdiffusion coefficients,  $D_{Ai}$ ,  $D_{Bi}$  and  $D_v$  are the self-diffusivities of point defects,  $p_i$  and  $p_v$  are the interstitial and vacancy production rates,  $k_{iv}$  is the recombination coefficient of vacancies and interstitials, factors  $z_j$  ( $j \equiv v, Ai, Bi$ ) characterize the effectiveness of edge dislocations as sinks for point defects, and  $\rho_e \approx 0.5\rho$  is the density of edge dislocations where  $\rho$  is the total dislocation

density. The concentration of lattice atoms A is determined from the balance condition  $c_B + c_A + c_v = 1$ . In Equations 3 and 4 the diffusivities of interstitials are assumed constant.

Boundary conditions to Equations 1–4 at the edges  $x = 0$  and  $x = L$  of the diffusion couple (the centers of phase layers 2 and 1, correspondingly) look as

$$\partial c_j / \partial x|_{x=0,L} = 0, \quad j \equiv A, B, v, A_i, B_i \quad (5)$$

The incoherent phase boundary 2/1 (at  $x = G = L/2$ ) can be treated as a localized sink for non-equilibrium vacancies, and hence an additional boundary condition to Equation 2 is posed

$$\partial c_v / \partial x|_{x=G} = c_v^0 \quad (6)$$

The dependencies of lattice diffusivities in Equations 1 and 2 on the vacancy concentration are determined on the basis of the theory of diffusion in the presence of excess vacancies [14]:

$$\begin{aligned} D_{BB} = & D_B^* c_v / c_v^0, \quad D_{AA} = D_A^* c_v / c_v^0, \\ D_{vv} = & D_v + D_{AA} \\ D_v = & [c_B D_B + c_A D_A^*] / c_v^0, \quad D_{Bv} = -D_B^* c_B / c_v^0, \\ D_{vB} = & D_{AA} - D_{BB} \end{aligned} \quad (7)$$

where  $D_A^*$  and  $D_B^*$  are self-diffusion coefficients of atoms A and B, which are measured in the conditions of equilibrium vacancy concentration. In formulas 7 the thermodynamic factor for diffusion [14]  $g = 1 + \partial(\ln \gamma) / \partial(\ln c)$  is ignored, where  $\gamma$  is the activity coefficient, i.e. phases 2 and 1 are treated as ideal solid solutions.

In the most simple case, the rates of point defect production by jog dragging ( $p_i$  and  $p_v$ ) can be determined using the Hirsch-Mott theory [17] which gives a lower-level estimate

$$p_j = 0.5b\varepsilon'(f_j \xi \rho / 2)^{1/2}, \quad j \equiv v, i \quad (8)$$

Here  $b$  is the Burgers vector,  $\xi \approx 0.5$  is the fraction of forest dislocations,  $f_v$  and  $f_i$  are the portions of vacancy and interstitial producing jogs which are formed on gliding screws due to intersection with forest dislocations,  $f_v + f_i = 1$ ; it is usually considered that  $f_v > f_i$ .

### 3. Justification of parameter values for simulation

For calculations, we considered a repeated “deformation-rest” cycle at a constant temperature of  $100^\circ\text{C}$ . The space-time scale has been chosen from the results of mechanistic modeling of MA [2, 18] for a SPEX 8000 shaker mill with the oscillation frequency of 20 Hz, i.e. 40 pulses per second, hence the cycle duration is  $t_c = 0.025 \text{ s}$ . The duration of deformation is  $t_d \sim 10^{-4} \text{ s}$  [2, 18], then the rest period is  $t_r = 0.0249 \text{ s}$ . During deformation, parameters  $p_v$  and  $p_i$  are determined by Equation 8, and in the rest

period they are set to 0. The thickness of the diffusion couple is  $L = 0.1 \mu\text{m}$  [2–5, 18]. The strain rate can reach  $10^3 \text{ s}^{-1}$  [2, 18]; we take  $\varepsilon' = 10 \text{ s}^{-1}$  as a reasonable lower estimate. For cold-worked metals, the dislocation density is  $\rho \sim 10^{10}\text{--}10^{12} \text{ cm}^{-2}$ ; we assume  $\rho = 10^{11} \text{ cm}^{-2}$  and take the ratio  $f_v/f_i = 2$ .

The Al (metal B)/Cu (metal A) diffusion couple is considered as a model system. The values of equilibrium diffusion parameters at  $T = 373 \text{ K}$  are calculated using reference data [19]. For Al:  $D_{\text{Al}}^* = 2 \cdot 10^{-20} \text{ cm}^2/\text{s}$ ,  $D_{\text{Cu}}^* = 7.8 \cdot 10^{-20} \text{ cm}^2/\text{s}$  and  $b = 2.86 \cdot 10^{-8} \text{ cm}$ ; for Cu:  $D_{\text{Cu}}^* = 6.6 \cdot 10^{-29} \text{ cm}^2/\text{s}$ ,  $D_{\text{Al}}^* = 8.6 \cdot 10^{-29} \text{ cm}^2/\text{s}$  and  $b = 2.55 \cdot 10^{-8} \text{ cm}$ . Taking  $D_0 = 5 \cdot 10^{-25} \text{ cm}^2/\text{s}$  as a representative value, the characteristic diffusion time in equilibrium conditions is estimated as  $t_0 \sim L^2/D_0 = 5 \cdot 10^{10} \text{ h}$ , which is enormously large.

The equilibrium vacancy concentration is  $c_v^0 = \exp[-\Delta_f H_v/(k_B T)]$ , where  $\Delta_f H_v$  is the enthalpy of vacancy formation and  $k_B$  is the Boltzmann constant [14];  $\Delta_f H_v = 0.76 \text{ eV}$  for Al and  $1.17 \text{ eV}$  for Cu [20]. This gives  $c_v^0 = 5.4 \cdot 10^{-11}$  for Al and  $1.6 \cdot 10^{-16}$  for Cu at  $T = 373 \text{ K}$ .

According to estimates based on Ref. [16], in fcc metals the diffusion coefficient for interstitials is by 7–8 orders of magnitude higher than that for vacancies. For modeling, we assume  $D_{\text{Ai}}, D_{\text{Bi}} \sim 10^3 D_v$ . The values of factors  $z_j (j = v, \text{Ai}, \text{Bi})$  are of the order of unity and  $z_{\text{Ai}}, z_{\text{Bi}} > z_v$  [16 and other work]. The recombination coefficient  $k_{\text{iv}}$  is estimated basing on theory [21]:  $k_{\text{iv}} \approx 8 \cdot 10^7 \text{ s}^{-1}$  for Al and about  $2 \cdot 10^6 \text{ s}^{-1}$  for Cu at  $T = 373 \text{ K}$ .

#### 4. Numerical results and discussion

Nonlinear partial differential Equations 1–4 were solved numerically using finite-difference methods. On each temporal step, the diffusion coefficients were recalculated according to Equation 7, and difference analogues of Equations 1–4 were solved jointly. The iterative procedure was continued until the solution converged, and then a transition to the next temporal layer was performed.

The results of computer simulation of IPPD-enhanced diffusion during MA with the above listed data values are presented in Fig. 1. It is seen that substantial alloying of metal B (Al) with metal A (Cu) occurs within a relatively short milling time, 4000 s (Fig. 1a). This is connected both with increased diffusion coefficient of metal A due to high vacancy concentration and the interaction of the concentration gradients of different species via the cross-link terms in the diffusion equations. The interplay between these two factors may have a selective effect on the diffusion of atoms A and B.

Accumulation of vacancies, which is especially noticeable in phase 1 (Fig. 1b), is due to the fact that during the rest period relaxation of non-equilibrium vacancies, which are generated during deformation, do not proceed in full. After a certain time (about 1200 s for the situation considered) a steady-state concentration profile of vacancies is established. From Equations 1 and 5 it is seen that due to cross-terms the

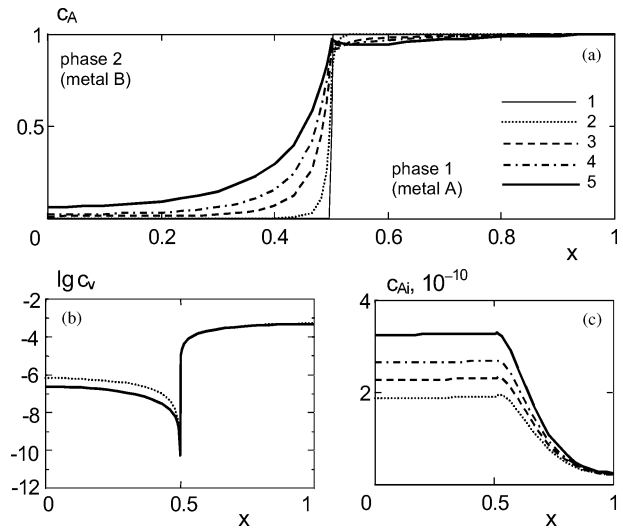


Figure 1 Calculated concentration profiles of atoms A (a), vacancies (b) and interstitials A (c) at different time instances:  $t = 0$  (line 1),  $t = 250 \text{ s}$  (line 2), 3,  $t = 1250 \text{ s}$  (line 3),  $t = 2000 \text{ s}$  (line 4),  $t = 4000 \text{ s}$  (line 5).

counterflow of vacancies accelerates diffusion of atoms while the co-flow decelerates it. The fluxes of vacancies in both phases are headed to the phase boundary (Fig. 1b). This accelerates the fluxes of foreign substitutional atoms, which have crossed the boundary, and retards the diffusion of base atoms towards the boundary. This results in a small peak on the concentration profile of atoms A near the boundary (Fig. 1a). Therefore, in addition to the above-stated factors, the interaction of diffusion fluxes with the phase boundary is important.

The concentration of interstitial atoms A is small as compared with vacancies, and in phase 1 is lower than in phase 2 (Fig. 1c). The latter is connected with recombination of interstitials with vacancies whose concentration is substantially higher in phase 1 than in phase 2.

#### 5. Conclusions

Computer simulation within the frame of a newly developed rigorous model of IPPD-enhanced diffusion with realistic parameter values has demonstrated a possibility of substantial alloying during a relatively short time of MA. The enhancement of diffusion is ascribed to the interplay of several factors: (i) increase of diffusion coefficients due to excess vacancies generated by jog dragging by gliding screw dislocations during shear deformation, (ii) slow relaxation of non-equilibrium vacancies inside the phase layers during the rest periods, (iii) interaction of diffusion fluxes through cross-link terms  $D_{ij}$ , and (iv) interaction of diffusing species with the phase boundary. The vacancy fluxes directed to the phase boundary may have a selective effect on the diffusion of substitutional atoms A and B. Besides, the accumulation of excess vacancies and interstitials leads to lattice distortion which can decrease the activation energy for diffusion and yet more enhance the intermixing of atoms.

The developed macrokinetic model can be combined with mechanistic models [2] and theories of plastic

deformation for a more comprehensive modeling of MA processes.

### References

1. L. N. LARIKOV, V. M. FALCHENKO, V. F. MAZANKO, S. M. GUREVICH, G. K. KHARCHENKO and A. I. IGNATENKO, *Dokl. Akad. Nauk SSSR* **221** (1975) 1073.
2. T. H. COURTNEY, *Rev. Particulate Mater.* **2** (1994) 63.
3. P. S. GILMAN and J. S. BENJAMIN, *Ann. Rev. Mater. Sci.* **13** (1983) 279.
4. J. S. BENJAMIN, *Mater. Sci. Forum* **88–90** (1992) 1.
5. C. C. KOCH, *Ann. Rev. Mater. Sci.* **19** (1989) 121.
6. Y. A. SKAKOV, *Mater. Sci. Forum* **343–346** (2000) 597.
7. P. BUTYAGIN, *J. Mater. Synth. Process.* **8** (2000) 205.
8. F. DELOGU and G. COCCO, *ibid.* **8** (2000) 271.
9. E. RABKIN and Y. ESTRIN, *Scripta Mater.* **39** (1998) 1731.
10. T. K. MAHAPATRA, D. DAS, I. MANNA and S. K. PABI, *Acta Mater.* **46** (1998) 3501.
11. P. J. DESRE and A. R. YAVARI, *Phys. Rev. Lett.* **64** (1990) 1533.
12. B. M. KHUSID and B. B. KHINA, *Phys. Rev. B* **44** (1991) 10778.
13. A. M. GUSAK and I. N. BUSHIN, *Metallofizika* **18** (1996) 68.
14. K. P. GUROV, B. A. KARTASHKIN and U. E. UGASTE, "Mutual Diffusion in Multiphase Metallic Systems" (Nauka, Moscow, 1981) p. 74.
15. R. W. BALLUFFI and A. L. RUOFF, *J. Appl. Phys.* **34** (1963) 1634.
16. R. A. JOHNSON and N. Q. LAM, *Phys. Rev. B* **13** (1976) 4364.
17. F. R. N. NABARRO, Z. S. BASINSKI and D. B. HOLT, *Adv. Phys.* **50** (1964) 193.
18. D. MAURICE and T. H. COURTNEY, *Metall. Trans. A* **21** (1990) 289.
19. "Metals Reference Book", edited by C. I. Smithells (Butterworth, London, 1976) p. 339.
20. B. S. BOKSHTEIN, "Diffusion in Metals" (Metallurgiya, Moscow, 1978) p. 92.
21. K. MANSUR, *J. Nucl. Mater.* **83** (1979) 109.

*Received 11 September 2003  
and accepted 27 February 2004*