

NON-EQUILIBRIUM DIFFUSION MASS TRANSFER DURING MECHANICAL ALLOYING AND ITS EFFECT ON SUBSEQUENT SHS

B. B. Khina

Physico-Technical Institute, National Academy of Sciences, 10 Kuprevich St., Minsk, 220141, Belarus

Mechanically activated self-propagating high-temperature synthesis (MA-SHS) is currently a subject of extensive experimental investigation because it gives an opportunity to control the structure and composition of final products and produce nanograined powder materials with unique properties [1-5]. Seemingly, after mechanical activation (MA) of a charge mixture the conversion degree, SHS temperature and combustion wave velocity are supposed to increase because MA produces composite (lamellar) particles due to fracturing/cold welding in a comminuting device (vibratory or planetary ball mill, attritor, etc.), thus increasing significantly the contact surface area and decreasing the characteristic size of reactants. However, numerous experimental studies have revealed that the degree of chemical conversion really increases but both the SHS temperature and the combustion velocity decrease noticeably [1-5]. In some cases, the SHS temperature even appears to be below the melting point of a metallic reactant, thus truly the solid-state combustion becomes possible [3-5]. The observed effects are typically attributed to the accumulation of non-equilibrium point defects (vacancies and interstitial atoms) during MA and release of stored energy of cold plastic deformation during heating in the SHS wave [4, 5]. But in the latter case, the SHS temperature must increase, which contradicts the experimental data. Besides, the diffusion coefficients of vacancies and interstitials are the order of magnitude higher than that of lattice atoms, and severely cold-worked metals contain a high density of dislocations which act as volume-distributed sinks for point defects. Hence, relaxation of non-equilibrium defects may occur during fast heating to the ignition temperature in the SHS wave and they will not affect the phase and structure formation mechanisms during the SHS itself.

The author believes that the reasons for the changes of the SHS wave behavior after MA can be revealed only by analyzing the physical processes that occur during the MA itself, in particular solid-state diffusion. It is known that diffusion mass transfer in binary metallic systems is substantially enhanced by intensive periodic plastic deformation: the apparent diffusion coefficients can reach a value typical of liquid metals ($\sim 10^{-5}$ – 10^{-4} cm²/s) and even higher [6]. This effect plays an essential part in Mechanical Alloying (MA), which is used as a versatile means for producing a wide range of far-from-equilibrium materials (supersaturated solid solutions, amorphous and quasi-crystalline phases, nanostructures). However, despite a large amount of experimental results (see reviews [7-9] and literature cited therein), the physical mechanism of this intricate phenomenon is not well understood, and a comprehensive model of solid-state interdiffusion in the conditions of MA has not been developed so far. Moreover, the very role of the diffusion process in MA is hotly debated in literature. In some papers [10, 11], the role of diffusion in MA is even completely rejected basing on the classical diffusion theory which, however, does not account for the process-specific factors. On the contrary, in a number of works [12-14] a qualitative analysis of physical reasons for accelerated diffusion during MA is presented. In few modeling attempts only separate aspects are studied, e.g., diffusion along curved dislocation pipes [15] or a change in the geometry of an elementary diffusion couple due to deformation [16]. Moreover, virtually in all of the modeling works the values of the parameters involved in the models are estimated by the data fitting to obtain a match between the results of the calculated and experimental data, thus their physical meaning might have been lost.

In this work, a new, rigorous mathematical model for solid-state interdiffusion in a binary substitutional system A-B under the conditions of periodic plastic deformation during MA is developed [17,18]. The model includes the basic physical factors that affect diffusion, such as the generation of non-equilibrium point defects by gliding screw dislocations during deformation and their relaxation in periods between impacts. The interaction of edge dislocations with point defects and cross-link effects (due to high values of the non-diagonal Onsager coefficients) are considered.

Calculations are performed with realistic data (e.g., quasi-equilibrium self-diffusion coefficients known in literature for a particular binary system) and the process parameters typical of MA in laboratory vibratory (shaker) mill SPEX-800. A repeated “deformation-relaxation” cycle is considered. The results of modeling,

which was performed for different situations arising within this approach, reveal the physical mechanism of substantial enhancement of solid-state interdiffusion by periodic plastic deformation. It is unambiguously demonstrated that within the frame of the developed model, the formation of supersaturated solid solutions (SSS) with high concentration of non-equilibrium point defects (vacancies and interstitial atoms) can occur in a reasonably short processing time in a milling device. The enhancement of solid-state interdiffusion is due to a synergetic effect and competition of several “elementary” physical processes such as the generation of equilibrium vacancies during shear deformation, their accumulation because of insufficiently high relaxation rate in intervals between collisions, increase of local diffusion coefficients due to high vacancy concentration, cross-term influence of diffusion fluxes of atoms and vacancies, and interaction of diffusion fluxes with phase boundary A/B.

Basing on the computer modeling results conclusions are drawn about the physical reasons responsible for the observed influence of MA on subsequent SHS. First, the SSS formation during MA decreases the heat release during SHS and, therefore, the combustion temperature because of the excess enthalpy of mixing associated with SSS. Second, a gently sloping concentration profile facilitates the formation of the product phase (e.g., intermetallic compound) at lower temperatures (as known in [19-21], in the field of a steep concentration gradient the nucleation of an intermediate phase is suppressed for both thermodynamic and kinetic reasons). In other words, the processes of deformation-enhanced interdiffusion that take place during MA can substantially change the conditions for the new phase nucleation upon subsequent heating in the SHS wave. These factors, in combination with a small lamellae thickness in composite particles, constitute possible physicochemical reasons for the effects observed in MA-SHS.

References

- [1] Charlot F., Gras C., Bernard F., Niepce J.C., Gaffet E. (1999) *Acta Materialia*, Vol. 47 pp. 2113-2123
- [2] Anselmi-Tamburini U., Maglia F., Doppio S., Monagheddu M., Cocco G., Munir Z.A. (2004) *Journal of Materials Research*, Vol. 19, pp. 1558-1566.
- [3] Korchagin M.A., Grigor'eva T.F., Barinova A.P., Lyakhov N.Z. (2000) *Doklady Physics*, Vol. 45 pp. 205-207.
- [4] Korchagin M.A., Grigor'eva T.F., Bokhonov B.B., Sharafutdinov M.R., Barinova A.P., Lyakhov N.Z. (2003) *Combustion, Explosion and Shock Waves*, Vol. 39 pp. 43-50.
- [5] Korchagin M.A., Grigor'eva T.F., Bokhonov B.B., Sharafutdinov M.R., Barinova A.P., Lyakhov N.Z. (2003) *Combustion, Explosion and Shock Waves*, Vol. 39 pp. 51-58.
- [6] Larikov L.N., Falchenko V.M., Mazanko V.F., Gurevich S.M., Kharchenko G.K., Ignatenko A.I. (1975) *Doklady Akademii Nauk SSSR*, Vol. 221 pp. 1073-1075 (in Russian).
- [7] Bakker H., Zhou G.F., Yang H. (1995) *Progress in Materials Science*, Vol. 39 pp. 159-241.
- [8] Suryanarayana C. (2001) *Progress in Materials Science*, Vol. 46 pp. 1-184.
- [9] Khina B.B., Froes F.H. (1996) *Journal of Metals (JOM)*, Vol. 48 No. 7 pp. 36-38.
- [10] Shtremel' M.A. (2002) *Metal Science and Heat Treatment*, Vol. 44 pp. 324-327.
- [11] Shtremel' M.A. (2004) *Metal Science and Heat Treatment*, Vol. 46 pp. 146-147.
- [12] Farber V.M. (2002) *Metal Science and Heat Treatment*, Vol. 44 pp. 317-323.
- [13] Skakov Y.A. (2004) *Metal Science and Heat Treatment*, Vol. 46 pp. 137-145.
- [14] Nechaev Y.S. (2001) *Izvestiya Akademii Nauk. Seriya Fizicheskaya*, Vol. 65 pp. 1507-1514 (in Russian).
- [15] Rabkin E., Estrin Y. (1998) *Scripta Materialia*, Vol. 39 pp. 1731-1736.
- [16] Mahapatra T.K., Das D., Manna I., Pabi S.K. (1998) *Acta Materialia*, Vol. 46 pp. 3501-3510.
- [17] Khina B.B., Solpan I., Lovshenko G.F. (2004) *Journal of Materials Science*, Vol. 39 pp. 5135-5138.
- [18] Khina B.B., Lovshenko G.F., Konstantinov V.M., Formanek B. (in press) *Metal Physics and Advanced Technologies* (in Russian).
- [19] Desre P.J., Yavary A.R. (1990) *Physical Review Letters*, Vol. 64 pp. 1533-1536.
- [20] Gusak A.M., Gurov K.P. (1992) *Solid State Phenomena*, Vol. 23-24 pp. 117-122.
- [21] Khusid B.M., Khina B.B. (1991) *Physical Review B*, Vol. 44 pp. 10778-10793.