Materials Science Forum Vols. 360-362 (2001) pp. 373-378
online at http://www.scientific.net

Experimental Measurement and Theoretical Computation of Milling Intensity and Temperature for the Purpose of Mechanical Alloying Kinetics Description

L.Yu. Pustov, S.D. Kaloshkin, V.V. Tcherdyntsev, I.A. Tomilin, E.V. Shelekhov and A.I. Salimon

Moscow State Steel and Alloys Institute, Leninsky prosp., 4, RU-117936 Moscow, Russia

Keywords: Fe, Kinetics, MA, Milling Intensity, Milling Temperature, Mn

Abstract: The kinetics of phase formation in the $Fe_{50}Mn_{50}$ composition was investigated at different conditions of planetary and vibratory mills. Milling intensity and temperature were measured experimentally using specially developed techniques. The theoretical computation of milling intensity and temperature using computer simulation was conducted for comparison in order to verify the main assumptions of a model. Energy input was calculated, which is necessary for phase transformation in the system under investigation. Good agreement of the γ–(Fe-Mn) phase formation rate with the milling process energy parameters was found.

Introduction

Various empirical criteria have been put forward for the prediction of metastable structures in the final product of metallic, mechanical alloyed systems. These criteria found confirmation in numerous pieces of experimental research, however, the kinetic data often varied significantly, which is related to the different milling conditions applied: type of milling apparatus, milling intensity and temperature.

The nature of the final product and the kinetics of mechanical alloying depend both on physical-chemical features of the initial components and the milling conditions in time and in intensity regime. These parameters are determined by the type of milling apparatus, ball sizes and ball-to-powder mass ratio [1-8]. The milling energy intensity, which is the quantity of mechanical energy transferred to unit of material's mass per unit of time, and milling temperature are the main characteristics of the milling conditions [9-12], and reliable quantitative comparison of experimental data can be realized correctly using at least two of these characteristics.

In the few examples of experimental research [13-16] devoted to the measurement of milling intensity both indirect [15] and direct [16] methods were applied for planetary ball mills (PM). Since the accuracy of indirect methods is low and direct methods face numerous difficulties as well as have limited applicability, theoretical approaches (evaluative dependences and statistic models) are widely used [17-30]. In the most simplistic models [17, 21] the motion of milling balls is described with no intercollisions, while in [19] the milling intensity is determined as the sum of energy quants emanated as result of all collisions during a single revolution. Detailed computer simulation allowed to overcome most of the problems related to simplifying assumptions in evaluative models and to estimate milling intensity and temperature with higher accuracy [29, 30].

In the present research various techniques for the experimental measurement of milling intensity and temperature were tested and the results of the measurements were compared with the data of computer simulations. The influence of milling intensity and temperature on the kinetics of phase formation was investigated during mechanical alloying of the alloy $Fe_{50}Mn_{50}$.

Experimental

Measurement of milling intensity in vibrational mill (VM): Since more than 90 % of the mechanical energy transforms during milling to heat, the milling intensity W was determined by the measurement of the vial heating rate (dT/dt) at the initial moment of time just after the start of operation. The heat capacity of vial and balls ($m \cdot C_p$), was preliminary calculated. Then W was determined by:

$$W = m \cdot C_p \cdot dT/dt \qquad (1).$$

The vial heating rate during mechanical alloying was measured by thermocouples attached to the vial wall (see Fig.1a).

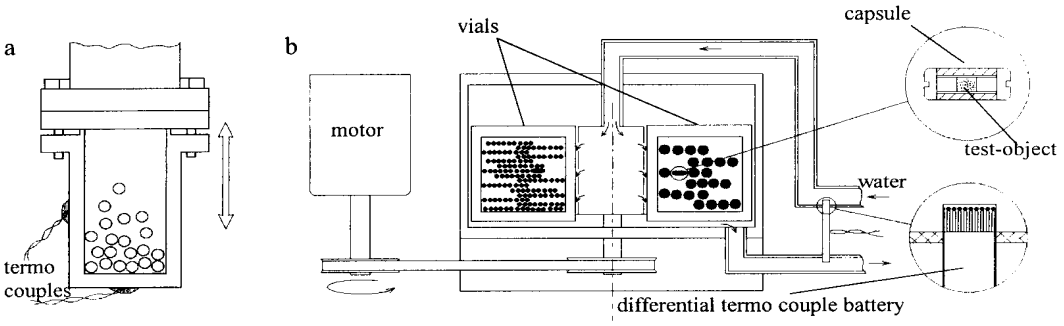

Fig.1 The measurement schemes for temperature and intensity calculations used for vibratory (a) and planetary (b) mills.

Measurement of milling intensity in a planetary mill (PM): When the milling process reached the steady state regime the difference between outlet and inlet water temperatures was related to the milling intensity divided by the mass flow of the cooling water. In order to increase the accuracy of measurements a battery of 10 thermocouples each was mounted into both inlet and outlet water flow (see Fig.1b).

The thermocouple battery was calibrated at normal water flow using an external heater while the vials were stationary. In order to subtract the portion of mechanical energy dissipating due to friction in the mill rotating measurements were also conducted with no balls and powder in vials.

Measurement of milling temperature: The milling temperature was measured by postheating, which occurs after switching off the VM operated in the steady state regime. This effect was measured in a heat-insulated vial, since the milling balls (whose temperature is the milling temperature) transfer heat to the colder vial. The temperature was measured before switching off T_S and at the maximum of the postheating peak T_{AH} ($\Delta T = T_{AH} - T_S$). The heat capacity was calculated for the balls (C_B) and for the effective vial-and-balls system when the VM was switched off (C_E). Then, the milling temperature was calculated as:

$$T_{ма} = \Delta T \cdot C_E / C_B + T_S \qquad (2)$$

For the PM a purpose designed capsule with reference sample was introduced into the vial together with the milling balls and the powder charge. The capsule acted as a milling ball, so that its temperature was equal to the milling temperature. The cylindrical capsule was closed with screws from both ends containing a reference substance with known melting temperature (see Fig.1b). The fusion of reference substance allowed estimating the milling temperature. Reference substances used are cited in Table 1.

Computer simulation: The 2-dimensional model of PM and the 3-dimensional model of VM were used to estimate the milling intensity using assumptions and procedures reported in [29-33]. Positions and velocities of the balls as well as the kinetic energy losses due to inelastic collisions

were calculated after the analysis of «ball-to-ball» and «ball-to-wall» collision in the ball ensemble.

Table 1: Reference substances used to estimate temperature

Substance	naphthalene	Wood's alloy	$Cd_{32.3}Sn_{67.7}$ alloy	Sn	Pb	Zn
Melting temperature, °C	80.8	115	177	232	327	419.5

It was also assumed that the portions of heat, which emerged in collisions were transferred instantly between balls and walls and distribute all over the ball volume causing uniform heating (cooling). This assumption was reasonable, since the high frequency of collisions, the small temperature increments and the high heat transfers are characteristic for the milling apparatuses. The details of the computer simulation were reported in [29 - 33].

Mechanical alloying of the $Fe_{50}Mn_{50}$ alloy: The kinetics of mechanical alloying at different milling intensities and temperatures were studied by means of X-ray diffraction quantitative phase analysis of powders, which were obtained after appropriate co-milling of 99.95 % -pure Fe and 99.9 % -pure Mn during different times. Powder-to-ball charge ratios were 1:10 in both PM and VM. In the latter case milling conditions were invariable (amplitude - 12 mm, vibration frequency –50 Hz, occupancy of vial was about 45 % of maximal occupancy and ball diameter was 4.8 mm), however, milling temperature was governed by external cooling conditions. In the case of PM two rotation speeds (683 and 1237 min^{-1}) and two sorts of milling balls (ball diameter - 4.8 and 8.8 mm) were used to modify the milling intensity at constant vial occupancy of 45 %. X-ray diffraction investigations were on a computer operated DRON-3 diffractometer in $CuK\alpha$ and $CoK\alpha$ radiations. Reduced Rietveld fitting was applied to perform quantitative phase analysis.

Discussion Of Experimental Results

Milling intensity: In Fig.2 and Fig.3 heating curves of temperature versus milling times for VM and PM are shown. For VM the temperature of the external vial wall are shown for different vial occupancies. An approximately linear temperature increase with milling time is observed up-to 30 sec of milling. After a certain time the temperature approaches its steady state value, which is evidence that internal heating and external cooling are in balance. Also, it was found that the presence of milled powder increases the heating rate, while the final steady state temperature is lower. This is most likely related to a higher heat conductivity with powder in comparison with a normal vial atmosphere. A change of powder-to-ball charge ratio does not cause any significant

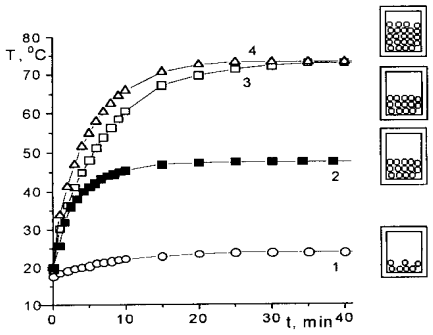

Fig. 2. Heating curves for VM for 20 % (1) 45 % (3) and 70 % (4) occupancies of vial. (2) - 45 % occupancy with fan cooling of vial surface.

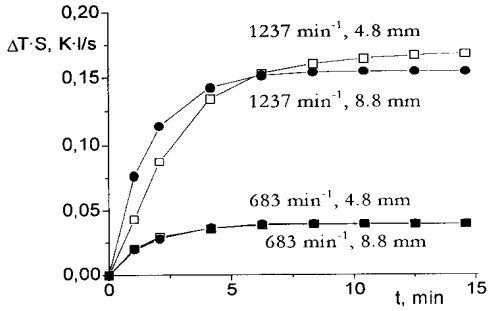

Fig. 3. Heating of cooling water in PM related to unit mass flow of water for different rotation speeds and ball diameters.

variation of either heating rate or final steady state temperature. The temperature of the cooling water in PM scales with milling time in the similar way (see Fig.3). The PM heating-up time (time when the temperature of cooling water approaches its steady state value) tends to be higher for smaller balls and, as it was expected, dramatically increases with rotation speed and number of balls. Nevertheless, the heating-up time is always less for PM (7.5-15 min) than for VM (20 min).

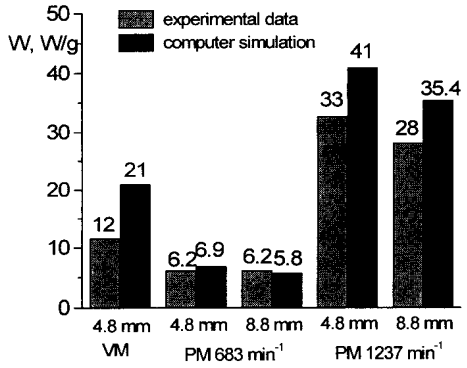

Fig. 4. Experimental and computed values of milling intensity for VM and PM

The experimental values of milling intensity W for VM tend to be lower than the theoretical predicted (see Fig. 4). It is believed that such a discrepancy is caused by the difference in heating rates for the ball ensemble and the vial wall, due to insufficient heat transfer between ball and vial walls. From the fact that the heating rate of the external wall is always lower than that of internal wall, one can conclude the following. The experimental value of the milling intensity may be considered as the lower limit of its true value and that computed values are close to those occurred during milling. In Fig. 4 similar data are given also for PM. It can be seen that the experimental values for lower rotation speeds are in good agreement with the theoretical predicted, while for higher rotation speeds the experimental values are lower than those obtained from computer simulations. Therefore, the intensity can be better estimated from computer simulations.

Milling temperature: The data on milling temperatures at different cooling conditions (fan cooling, heat-insulation of the pivot and heat insulation of the vial) demonstrate the influence of external cooling regimes on the milling temperature in vibratory mills (Fig.5). The lower and upper limits of milling temperature in PM are shown in Fig.6 together with respective theoretical estimations for comparison. It is obvious, that theoretical estimations of the milling temperature are about 100 K higher than the experimental values.

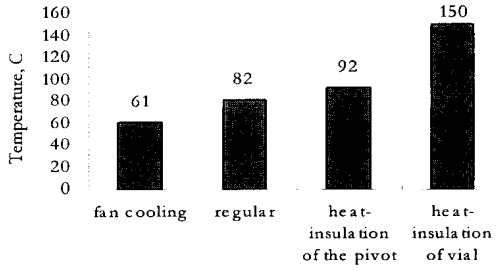

Fig.5.Milling temperature in VM at different external cooling regimes

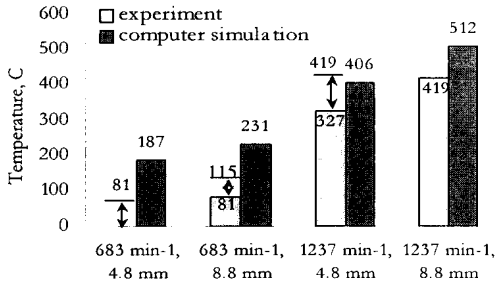

Fig.6. Experimental (lower and upper limits) and calculated values of temperatures in PM

Kinetics of mechanical alloying in Fe-Mn system: During mechanical alloying of the $Fe_{50}Mn_{50}$ alloy a solid state transformation happens:

$$\alpha\text{-Fe} + \alpha\text{-Mn} \rightarrow \gamma\text{-Fe(Mn)} \qquad (3)$$

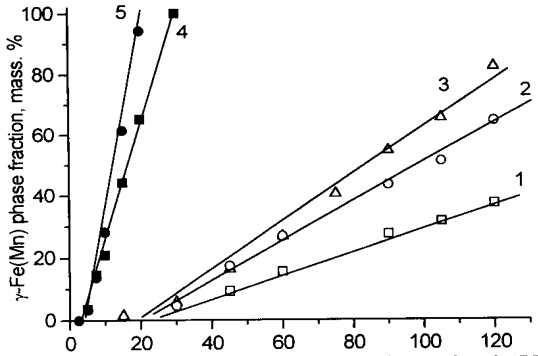

Fig. 7. Kinetics of γ-Fe(Mn) phase formation in VM and PM.

1 - W = 6.9 W, T < 80.8 ^{0}C, E_i = 6.0 MJ/mol (PM)
2 - W = 5.8 W, 80.8 < T 115 ^{0}C, E_i = 3.1 MJ/mol (PM)
3 - W = 21 W, T = 82 ^{0}C, E_i = 2.9 MJ/mol (VM)
4 - W = 41 W, 327 < T < 419.5 ^{0}C, E_i = 3.4 MJ/mol (PM)
5 - W = 35.4 W, T > 419.5 ^{0}C, E_i = 2.1 MJ/mol (PM)

It was shown previously [34], that the kinetics of phase composition changes are firstly decreasing with volume fraction of α-Fe(Mn) and with increasing amount of α-Mn(Fe). After the appearance of the first precipitates of γ-Fe(Mn), the fractions of α-Fe(Mn) and α-Mn(Fe) begin to decrease linearly with linearly increasing volume of γ-Fe(Mn).

Similar curves of linear kinetics have been found for all milling regimes tested in both PM and VM, which permits to compare the obtained data using different mills easily (Fig.7). Different milling intensities and temperatures predetermine various rates of reaction (eq.3).

At a rotation speed equal to 683 min^{-1} a change in ball diameter causes a different milling temperature in PM. While the milling intensity is higher for smaller balls than for bigger ones, the milling temperature is somewhat higher for bigger balls. Since the rate of reaction (eq.3) is practically twice as high than in the case of bigger balls it is believed that mainly the milling temperature accelerates the reaction of mechanical alloying. The same tendency is observed for the kinetics of mechanical alloying at a rotation speed of 1237 min^{-1} for different ball diameters, i.e. milling temperature rather than milling intensity accelerates the reaction (eq.3). Thereby, the rate of reaction is almost 10 times higher for a higher rotation speed than for lower one.

When the kinetics of mechanical alloying in VM and PM are compared, the governing role of the milling temperature became apparent. The rate of reaction (eq.3) in VM with W equal to 21 W is only slightly higher than that in PM with W three times lower. Thus, the slightly higher milling temperature in PM is believed to level the rate of reaction (eq.3).

The influence of milling temperature can also be deduced from phase compositions after alloying for 45 min in VM with different milling temperatures and constant milling intensity. It was found, that a higher content of γ-Fe(Mn) and therefore higher rate of reaction (eq.3) corresponded to a higher milling temperature.

Finally, for different milling temperatures the energy input E_i (MJ/mol) can be calculated, which is required for reaction (eq.3) (see Fig.7). The lower the milling temperature, the higher energy is necessary input for the studied reaction.

Thus, the milling intensity is not the only factor affecting the kinetics; and the milling temperature plays a significant role. The increase of both factors can accelerate reactions (eq.3).

This conclusion is not valid for all types of solid state reactions during mechanical alloying. The formation of amorphous phases and supersaturated solid solutions from pure metals has been suggested to be retarded at higher milling temperatures.

Conclusions

Energy intensity and temperature were considered as the most important characteristics of the milling process. These parameters were determined both by computer simulation of the milling process and experimentally. Magnitudes of energy parameters obtained by different methods agree closely with each other.

The results of the energy parameters investigation were applied to the kinetics of phase formation in the $Fe_{50}Mn_{50}$ composition. The rate of formation of γ-Fe(Mn) phase increased with an increase in both milling temperature and milling intensity. The energy input, which is required for γ-Fe(Mn) phase formation depends on milling temperature.

Acknowledgements
This work was supported by RFBR (00-03-32529a).

REFERENCES:

[1] C. Kurt, L. Schultz, J. Appl. Phys. 73 (1993), p. 1975.
[2] L.B. Hong, B. Fultz, ibid. 79 (1996), p. 3946.
[3] I. Börner, J. Eckert, Mater. Sci. Eng. A. 226-228 (1997), p. 541.
[4] A.W. Weeber, W.J. Haag, A.J.H. Wester, H. Bakker. J. Less-Comm. Met. 140 (1988), p. 119.
[5] E. Gaffet, N. Malhouroux, M. Abdellaoui, J. All. Compound 194 (1993), p. 339.
[6] V.V. Boldyrev, S.V. Pavlov, V.A. Poluboyarov, A.V. Dushkin, Inorganic Materials 31 (1995), p. 1128.
[7] L. Liu, S. Casadio, M. Magini, C.A. Nannetti, Y. Qin, K. Zhen, Mater. Sci. Forum 235-238 (1997), p. 163.
[8] L. Liu, M. Magini., J. Mater. Res. 12 (1997), p. 2281.
[9] P.Yu. Butyagin, Izv. SO AN SSSR, ser. khim. nauk 5 (1987), p. 48.
[10] C.C. Koch, D. Pathak, Proc.2 Int. Conf. Str. Appl. Mech. All.-Vancouver (1993), p. 205.
[11] J. Xu, J.H. He, E. Ma, Metall. Mater. Trans. A. 28 (1995), p. 1569.
[12] T. Klassen, U. Herr, R.S. Averback. - Acta Mater. 45 (1997), p. 2921.
[13]. A.N. Streletskii, Proc.2 Int. Conf. Str. Appl. Mech. Al.-Vancouver (1993), p.51.
[14]. K.B. Gerasimov, A.A. Gusev, V.V. Kolpakov, E.Yu. Ivanov, Sib. khim. J. 3 (1991), p. 140.
[15]. A. Calka, D. Wexler, Z.L. Li. - Proc.Int. Conf. RQ-9, Bratislawa, 1996-Elsivier, (1997) p. 191.
[16] Scholl R., Kubsch H., Wegerle R., Fritsch GMBH, In Situ Report 2 (1997), P.42.
[17] N. Burgio, A. Iasonna, M. Magini, Nuovo Cimento, 13D (1991), p. 459.
[18]. P. G. McCormick, H. Huang, M.P. Dallimore, J. Ding, J. Pan. - Proc.2 Int. Conf. Str. Appl. Mech. All.-Vancouver (1993), p. 45.
[19] M.P. Dallimore, P.G. McCormick, Mater. Sci. Forum. 235-238 (1997), p .5.
[20] M. Magini, Mater. Sci. Forum. 88 (1992), p. 121.
[21] M. Abdellaoui, E. Gaffet, J. de Phis. IV 4 (1994), p. 291.
[22] M. Magini, A. Iasonna, F. Padella, Scr. Mater. 34 (1996), p. 13.
[23] T.H. Courtney, Mater. Trans. JIM. 36 (1995), p. 110.
[24] D. Maurice, T.H. Courtney, Metall. Mater. Trans. 25A (1994), p. 147.
[25] D. Maurice, T.H. Courtney, Metall. Mater. Trans. 26A (1995), p. 2431.
[26] D. Maurice, T.H. Courtney, Metall. Mater. Trans. A. 26A (1995), p. 2437.
[27] R.B. Shwarz, C.C. Koch, J.Appl.Phys. 49 (1986), p. 146.
[28] G.B. Shaffer, J.S. Forrester J. Mater. Sci. 32 (1997), p.3157.
[29] E.V. Shelekhov, A.I. Salimon., Aerosol 12 (1997), p. 61.
[30] E.V. Shelekhov, T.A. Sviridiova, Materialovedenie, N10 (1999), p.13.
[31] E.V. Shelekhov, V.V. Tcherdyntsev, L.Yu. Pustov, S.D. Kaloshkin, I.A. Tomilin, Mater. Sci. Forum 343-346 (2000), p.603.
[32] E.V. Shelekhov, V.V.Tcherdyntsev, L.Yu. Pustov, S.D. Kaloshkin, I.A. Tomilin, NATO Science Partnership Sub-series: 3 High Technologes (2000), v. 80, p.139.
[33] V.V. Tcherdyntsev L.Yu.Pustov, S.D. Kaloshkin I.A. Tomilin, E.V. Shelekhov, Materialovedenie, N 2-3 (2000), p.18, p.22.
[34] V.V. Tcherdyntsev, S.D. Kaloshkin, I.A. Tomilin, E.V. Shelekhov and Yu.V. Baldokhin. Z. Metalkde., 90 (1999), p.747.