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POWER MEASUREMENTS DURING MECHANICAL MILLING—II. THE CASE OF "SINGLE PATH CUMULATIVE" SOLID STATE REACTION

M. MAGINI, C. COLELLA, A. IASONNA and F. PADELLA

ENEA-INN-NUMA, C.R. Casaccia, Via Anguillarese, Rome, Italy

Abstract—The electrical power consumptions during the milling process of a planetary mill have been measured. The results of the experiments, carried out with a suitable chosen system, are perfectly in line with previous milling experiments. The dependence of the power consumption during milling from the third power of the rotation speed and the effect of the filling of the milling device on the energy transfer and power consumption have been clearly established and confirmed. The relevance of *in situ* data acquisition during milling, that can disclose a deeper understanding of the mechanical alloying process, has been discussed within the frame of present and previous results. © 1998 Acta Metallurgica Inc.

1. INTRODUCTION

Since the middle of the 1980s when a renewed nterest arose around the Mechanical Alloying (MA) process, attempts at modelling the process itself have been done investigating the role that parameters such as the number and diameter of balls, the rotation speed or vibration frequency have on the energy transfer and hence on the milling efficiency. Within this frame, modeling has been used to develop various kinds of "Milling Maps" having predictive capability in order to obtain a given product for a given set of milling parameters. The temporary sequence of some of the most relevant papers on modelling are reported in Refs [1–12].

However, while there certainly are in literature both theoretical models of the MA process as well as experimental approaches aimed to clarify the MA mechanisms, very few attempts have been done as far as the direct *in situ* data acquisition of relevant parameters during milling are concerned. In previous works the temperature increase during milling has been indirectly inferred from powder microstructures after the milling action and the whole subject has been reviewed by Koch [13]. Chen *et al.* [5] and Cocco *et al.* [14] measured the frequency and amplitude of specially developed vibrating devices and correlated these parameters to the efficiency of the milling action. Kimura and Kimura attempted to estimate the energies involved in the milling process by measuring the torque applied on the rotating shaft of a suitable home made attritor [15]. In general, until now, no systematic efforts have been undertaken in order to obtain a direct data acquisition during milling of parameter(s) that could be relevant for a unified in-

terpretation of milling results coming from very different milling devices.

In a previous paper, hereafter referred to as Part I, we described an experimental way to measure the power consumption involved in the MA process during milling [16]. It has been shown that such a power consumption, due to the milling action, can be revealed by suitable electrical or mechanical power absorption measurements performed during milling. It has also been shown that the power measurements were perfectly in line with those theoretically evaluated through the collision model [3, 10, 11, 16]. The investigation was done on a planetary mill but, in principle, can be extended to any milling device and the power consumption data could be the basis for a unified interpretation of the experimental results coming from different apparatus.

Briefly summarising, if it is assumed that the collision is the primary transfer event by which some energy is transferred from the milling tools of a planetary mill (balls and vials) to the powder under processing the power involved in the milling process is given by the product of an *intensive factor*, ΔE (kinetic energy released in a single collision event), and an *extensive factor*, v_t (total number of events per unit of time), i.e.

$$P_{mod} = \Delta E v_t \qquad (1)$$

being P_{mod} the power consumption during milling predicted by the collision model. The energy released in a single event and the total number of events (collision frequency of one ball multiplied by the total number of balls) can be evaluated by the collision model [3, 10, 11] and equation (1) takes the
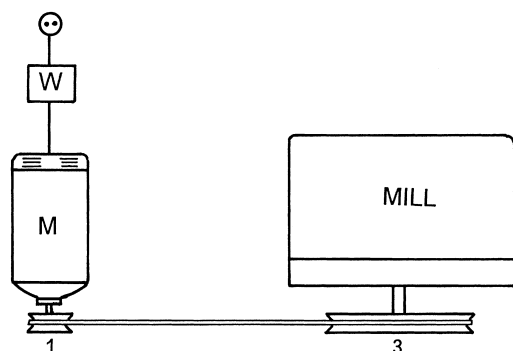
Fig. 1. Scheme of the electrical power measurements during milling. The powers are measured by the power meter indicated by W in the figure. M is the electric motor.

form:

$$P_{\mathrm{mod}} = P^* \frac{1}{2} m_{\mathrm{b}} w_{\mathrm{p}}^3 R_{\mathrm{p}}^2 n_{\mathrm{b}} \qquad (2)$$

where m_{b} and n_{b} are the mass and number of balls used in a given experiment; w_{p} and R_{p} the speed and the radius of the planetary mill disk. P^* is a dimensional coefficient depending on the geometry of mill and on the elasticity of collisions [3, 10] as long as the reciprocal hindering of the balls is negligible (see Section 3).

The obtained results [16] did not only allow a confirmation of the collision model predictions but also gave practical indications in order to set up the suitable milling conditions in order to obtain the wanted end product. Namely, it has been shown that some kinds of reactions, previously called "threshold" reactions [16], are governed by the energy collision ΔE. Aim of the present work is to show that other kinds of reactions, presently called "cumulative" (as better explained in the following: see Section 3), are governed by the total power consumption that is experimentally accessible and that can be expressed by a relation like equation (2).

2. POWER MEASUREMENTS, MILLING EXPERIMENTS AND DATA HANDLING

2.1. Electrical power absorption measurements during milling

It was demonstrated in Part I the feasibility of both electrical and mechanical power absorption measurements during the milling action of a planetary ball mill. The information coming from both kinds of measurements has been proved to be equivalent and since mechanical measurements of the applied torque are much longer and delicate than electrical ones, in the present paper we will only deal with electrical power absorption as indicated in the scheme of Fig. 1.

In a given milling experiment, the power absorptions with filled, P'_{e}, and two equal empty vials, $P_{\mathrm{e}}^{\mathrm{o}}$, were *successively* measured at intervals as a function
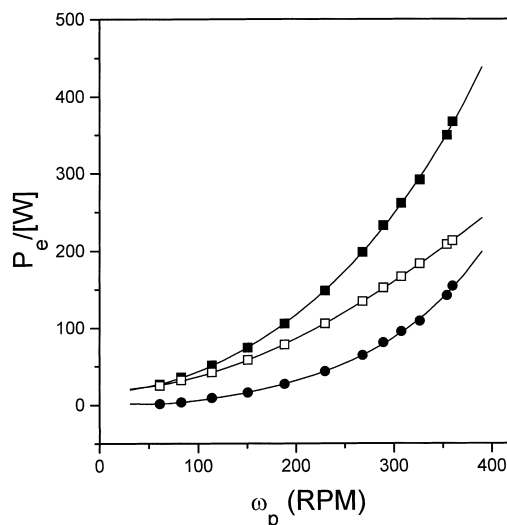

Fig. 2. The gross electrical power absorption measured with two $250\,\mathrm{cm}^3$ stainless steel vials filled with balls and powder is represented by full squares and the power absorption with the two empty vials by open squares. Full dots give the net power differences $P_{\mathrm{e}} = P'_{\mathrm{e}} - P_{\mathrm{e}}^{\mathrm{o}}$. The powers are reported vs the rotation speed of the planetary mill disk plate expressed in rpm (rounds per minute). The continuous lines are the best fits through the experimental points. Note that the symbols' thickness roughly includes the average error in power measurements (y scale).

of the rotation speed of the planetary mill. As an illustration, Fig. 2 gives typical electrical absorption values recorded during one milling experiment.

2.2. The model system to investigate a single path solid state reaction

The nickel and copper oxide displacement reaction:

$$\mathrm{Ni} + \mathrm{CuO} \Rightarrow \mathrm{NiO} + \mathrm{Cu}$$
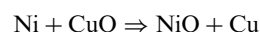
has already been chosen for modelling experiments due to the fact that Ni is the only ferromagnetic phase and the reaction progress can be followed by saturation magnetisation measurements [6]. The reaction enthalpy is $\Delta H = -84\,\mathrm{KJ/mole}$ and the reaction products are thermodynamically strongly favoured. As soon as the mechanical action is able to start up the reaction, only a single path is allowed: namely, the formation of nickel oxide and copper.

Preliminary milling experiment indicated that a milling time of about 8 h was enough to complete the reaction in a given range of investigated milling conditions. The progress of the reaction as a function of the milling time has been followed by recording X-ray diffraction patterns in suitable angular ranges. At a qualitative level, a wide angular range has been explored. Quantitative X-ray analysis has been performed carrying out high statistic measurements in a selected angular range suitable to follow the reaction products (see Section
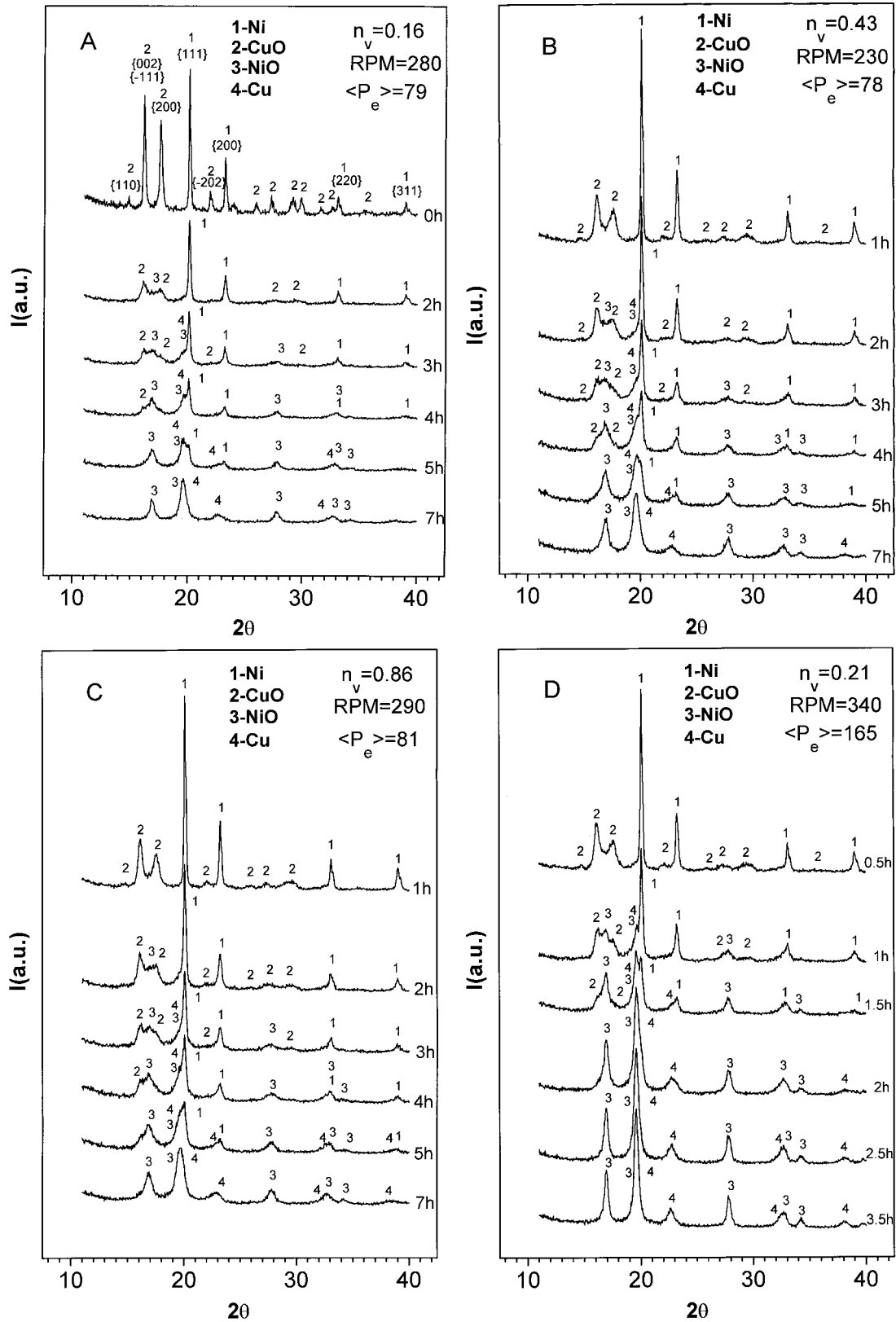
Fig. 3. Qualitative X-ray patterns for the composition Ni: CuO = 1:1 at various representative milling times starting from pure elemental powders in four different milling conditions (A, B, C, D). The labels 1–4 indicate peak lines of starting (Ni, CuO) and end products (NiO, Cu). The experimental milling conditions are given by the filling of the vials, n_v, and the rotation speed in rpm. $\langle P_e \rangle$ is the average electric power consumption during milling (see text). In Fig. 3(A), a zero milling time X-ray pattern is reported for comparison with all the subsequent milling times in any milling condition.
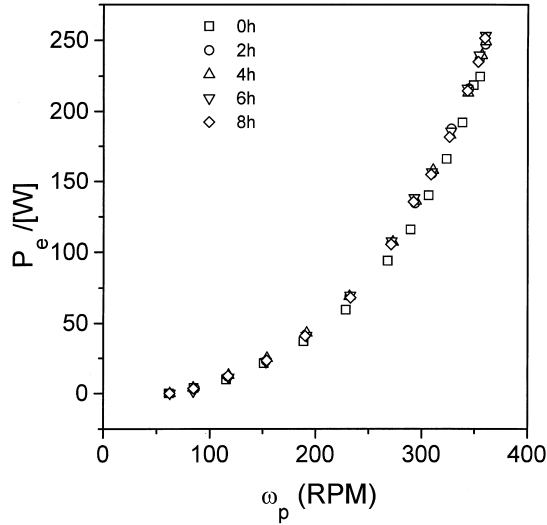
Fig. 4. Example of the net power absorption recorded after 0, 2, 4, 6 and 8 h of milling for the Ni + CuO ⇒ NiO + Cu reaction in a typical milling experiment. Note the overlapping of the symbols at the different times indicating the time independence of the power measurements for the system under investigation.

2.5). Figure 3 shows the typical trends of the reaction progress at a qualitative level for the milling conditions explained in the next section.

2.3. Milling experiments

All milling experiments have been carried out by mounting two equally charged stainless steel vials of 250 cm^3 on a "pulverisette P5" planetary mill (Fritsch). A fixed amount (18 g) of one to one stoichiometric mixture of Ni (purity 99.9%, Koch Chemicals) and CuO (purity greater than 99%, Carlo Erba) was milled in any of the milling conditions chosen. To minimise the average overall temperature increase, milling was carried out by alternating 15 min of milling and 15 min of rest. To avoid oxidation, the vials were sealed and operated under pure argon. However, since sampling was done in air every hour of milling, this resulted in an oxygen contamination, fairly constant in all the samples, of about 4% by weight after about 8 h of milling. After the same milling time, iron contami-

nation was less than 0.5% by weight. The Cu/Ni ratio was checked in some samples and was equal to one indicating that no preferential sticking of the powder components on the surfaces of the milling tools was occurring.

In any experiment, two different parameters were examined and kept constant throughout the integral time of milling: the rotation speed of the mill disk and the filling of the vials, n_v, defined as

$$n_v = \frac{N_b}{N_{b,tot}} \qquad (3)$$

where N_b is the number of balls (in each vial) used in the experiment and $N_{b,tot}$ is the total number of balls, of that diameter, necessary to completely fill up the vial so that no ball movement at all is possible. Stainless steel balls of 10 mm were used for all the experiments and the total number of used balls, n_b, was, $n_b = N_v, N_b = 2N_b$ since N_v (number of vials) was always equal to two.

At the beginning of a milling experiment and after every 2 h; i.e. at 0, 2, 4, 6 and 8 h, the gross, P'_e, and empty, P^o_e, power absorptions were recorded as a function of the rotation speed. Through the difference $P_e = P'_e - P^o_e$, as shown in Fig. 2, the net power absorption curve was derived. The time necessary to collect the (w_p, P'_e) curve is about 10 min and this time was not considered in the integral of the milling time.

It is important to outline that the behaviour of the powder system is such that the net absorption curve (w_p, P_e) remains substantially unaltered after the different milling times as can be seen from Fig. 4. This means that the *power absorbed by the system does not depend on the previous history of the system itself*. This behaviour cannot be *a priori* expected for the system under investigation. We will come back to this point in the Section 3. The milling experiments carried out are summarised in Table 1.

2.4. Data handling of the power absorption curves

The sets of experimental data (w_p, P_e) were least squares fitted to an empirical equation of the type:

Table 1. Experimental milling conditions are given by n_V, degree of filling of the vials, n_b total number of balls used in each experiment, RPB, balls to powder weight ratio and RPM, rotation speed in rounds per minute. The α values of equation (4) have been derived from electrical powers (see text). Columns 7 and 8 give the power efficiency, $\langle P^* \rangle$, and the hindering factor ϕ_b. Last column gives the reaction progress expressed in $A\%$ and $R\%$ (see Section 2.5)

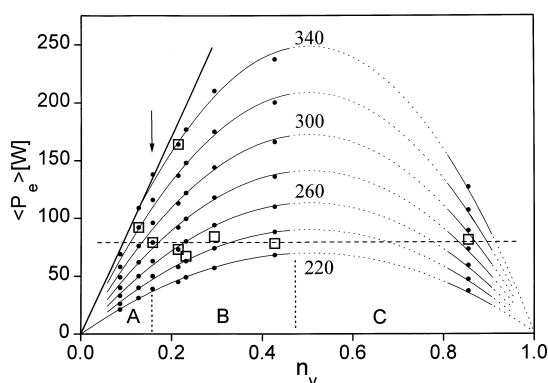| n_v	n_b	rpb	rpm	$\langle P_e \rangle$ (W)	$\langle \alpha \rangle$	$\langle P^* \rangle$	ϕ_b	Reaction at 3 h $A\%$	$R\%$
0.086	25	5.7	360		2.78	1.10	0.99		
0.127	37	8.4	320	92	2.90	1.11	1.00	59	30
0.158	46	10.4	280	79	2.93	1.13	1.01	50	24
0.214	62	14.0	260	73	3.02	0.94	0.85		
0.214	62	14.0	340	165	2.98	0.94	0.85	100	100
0.231	67	15.1	245	67	3.00	0.96	0.86	36	16
0.293	85	19.2	250	84	3.00	0.90	0.81	63	34
0.427	124	28.0	230	78	2.86	0.72	0.65	53	26
0.855	248	56.0	290	81	2.85	0.20	0.18	46	22

Fig. 5. Milling map showing the average power absorption during milling, $\langle P_e \rangle$, as a function of the degree of filling, n_V, and of typical planetary mill rotation speeds from 220 up to 340 rpm. (●) The average power values giving the power absorption map (see text) and the parabolic like curves are the best fits connecting them. (□) Indicate the average power consumption kept constant for the integral time of a given milling experiment (see text). A, B and C indicate three different efficiency regions (see text). The horizontal line identifies an equi-power working condition (see text).

$$P_{calc} = K w_p^{\alpha} \qquad (4)$$

Since in a given experiment the filling parameter n_v (and hence n_b) is fixed, in equation (2) all parameters but one, w_p, are constant and equation (4) is nothing else than the direct derivation of the collision model equation. The K and α parameters have been determined by least squares minimisation of the error sum:

$$U = \Sigma w_i (P_{calc} - P_{exp})^2 \qquad (5)$$

where P_{exp} is the measured power consumption and w_i the weight given to each experimental point [16].

The α values obtained are given in Table 1 as a function of the filling parameter n_V. We outline that for each milling experiment five (w_p, P_e) curves have been recorded at 0, 2, 4, 6 and 8 h of milling. Each (w_p, P_e) curve was analysed by equation (4) and the average of the α obtained values have been reported on Table 1. Figure 5 shows the power absorption during milling as a function of the filling of the vial and of the rotation speeds of the planetary mill. The power values on the vertical axis indicated by dots are the values, calculated for typical rotation speeds in round figures [from the α and K values obtained through equation (4)], averaged over the five least squares fitted (w_p, P_e) absorption curves.

2.5. The reaction progress monitoring

X-ray diffraction analysis has been employed to monitor the milling process (automatic Seifert PAD VI diffractometer equipped with a Mo tube and a monochromator after the sample has been used). It is clear from Fig. 3 that the reaction progress is easily followed, at semiquantitative level, through
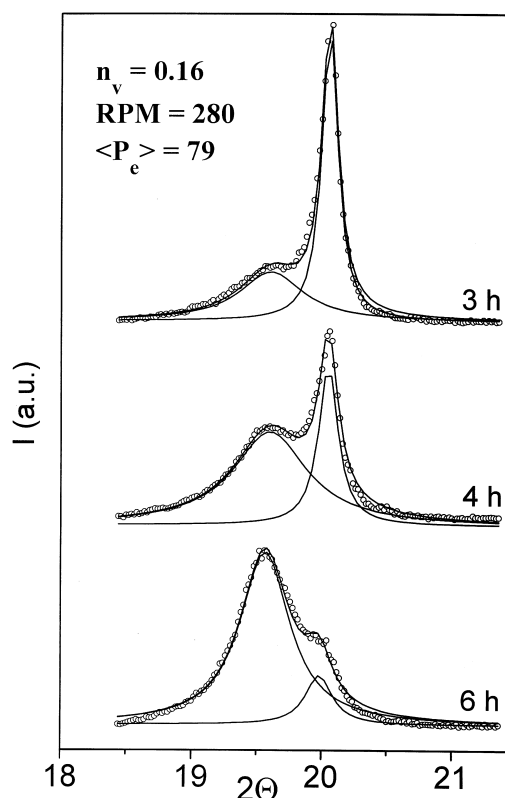

Fig. 6. High statistics X-ray diffraction patterns, recorded in the $18 < 2\theta < 21$ region, are reported for three of the milling times shown in Fig. 3(A). Each area beneath the region has been resolved by two Lorentzian components centred at about 19.6 (sum of Cu and NiO) and about 20.1 (Ni). The area of the first peak with respect to the total area is proportional to the reaction products.

the appearance and disappearance of the main X-ray lines of the end and of the starting products, respectively. The peak lines of the starting Ni and CuO reactants are reported for comparison in Fig. 3(A). After 1 h of milling [see patterns in Fig. 3(B) and (C)] the main noticed effect is a pronounced broadening of the zero time peak lines due to the strain and to the grain size refinement of the starting materials. The only indication of an already started reaction after 1 h of milling comes from the rising of the bottom included between the {002}, {−111} ($2\theta = 16.1°$) and {200} ($2\theta = 17.6°$) peaks of copper oxide (JCPDS No 41-254) which is due to the initial appearance of the { 003 } nickel oxide peak, falling just in between ($2\theta = 16.9$; JCPDS No 22-1189).

In all the examined cases of Table 1 (with one exception at $\langle P_e \rangle = 165$ W), a clear indication of the reaction progress after 2 h of milling [see patterns in Fig. 3(A), (B) and (C)] comes from the shoulder appearing on the left hand side of the main {111} Ni peaks ($2\theta = 20,08°$; JCPDS No 4-850). The shoulder is due to the growth of both NiO {012} and Cu {111} (JCPDS No 4-836) diffraction peaks falling exactly at the same angular value
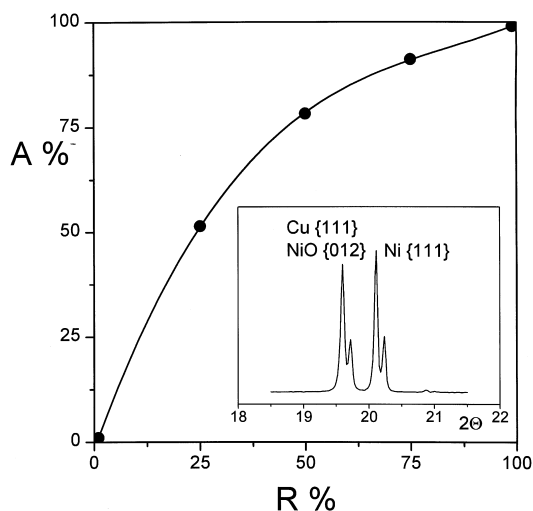
Fig. 7. Calibration curve to transform the area percent ($A\%$), evaluated by the procedure of Fig. 6, in reaction progress ($R\%$). The calibration curve has been obtained by "simulating" a reaction progress of 25, 50 and 75% (see text). The onset shows the X-ray response for a 25% simulated reaction progress.
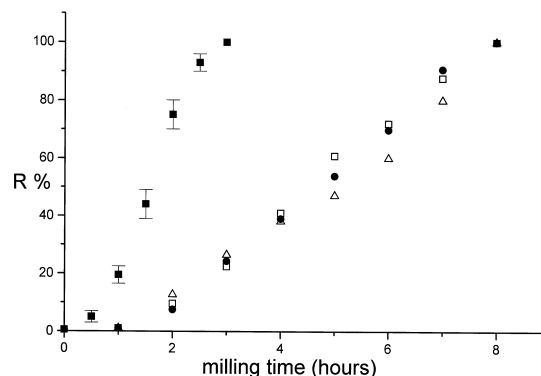

Fig. 8. Reaction progress as a function of the milling time for the milling experiments of Fig. 3 (A) (●), (B) (□), (C) (△) and (D) (■) following the procedure of Fig. 6 and using the calibration curve of Fig. 7. The spread on the results of curves (A), (B) and (C) (equi-power condition) accounts for both uncertainty on the $R\%$ evaluation [shown on curve (D)] and integral reproducibility of the milling experiments.

($2\theta = 19.558°$). By increasing the milling time, the shoulder grows and becomes the dominant peak after 5 h [see patterns in Fig. 3 (A), (B) and (C)]. Concurrently, the starting peak lines vanish and new Cu and NiO lines clearly appear. After 7–8 h of milling the reaction is practically achieved for all the investigated milling conditions.

The decrease of Ni {111} and the increase of the sum of Cu {111}, NiO {012} can be followed at a quantitative level. The $18° < 2\theta < 21°$ region, in fact, is free from any other concurrent peak line and, due to the coincidence of the reaction products peaks, is suitable for a quantitative analysis as shown in the example of Fig. 6. The figure reports high statistic X-ray patterns for three different milling times and for the milling experiment corresponding to Fig. 3(A). The profile of the integral area beneath the complex peak, subtracted from the α_2 component, has been fitted by two Lorentzian components. The first component is due to the increasing sum of the Cu, NiO reaction products while the second one gives the decreasing Ni reactant. The progress of the reaction can be followed by the increase of the percentage of the area of the products, with respect to the integral area of the peak, as a function of the milling time. As an example, column 9 of Table 1 gives the area percent of the end products after 3 h of milling for the different milling conditions. The area percent is only proportional to the effective percentage of the end products because: (i) the peaks overlapping are such that two end products are monitored while only the Ni reactant is followed; (ii) the absolute intensity of the three overlapping peaks is different and (iii) the reciprocal masking effect, due to the different absorption coefficients, will influence the

individual response. However, it is not difficult to obtain the real percentage of the end products by a suitable calibration curve. Such a calibration curve (see Fig. 7) has been obtained by properly accurately mixing the pure Ni, CuO, Cu and NiO powders so as to *simulate* a reaction progress of 25, 50 and 75% and measuring the resulting area percent in the obtained diffraction patterns (see onset of Fig. 7). The calibration curve is then used to transform any area percent, evaluated through the procedure of Fig. 6, into the corresponding reaction progress (last column of Table 1). On Fig. 8 the reaction progress vs the milling time is shown for the milling experiments of Fig. 3(A), (B), (C) and (D).

3. DISCUSSION

3.1. The third power law and the energy transfer

The present results, carried out in different milling conditions with powder and balls, substantially confirm the results of Part I where the experiments have been generally carried out without powder. The electrical power measurements, indeed, can be fitted by equation (4) with an α exponent for the rotation speed very near to the value of 3 predicted by equation (2), that is, *predicted on the basis of a collision model*. This is true for any filling of the vials; that is the power dependence on the third power of the rotation speed is not affected by the degree of filling as shown by the values reported on Table 1. This evidence confirms the hypothesis that even when the vials filling is high, and hence attrition and sliding mechanisms are certainly effective, still collision can be regarded as the main energy transfer event able to explain the experimental behaviour. Further comments on this point have been well reported in Part I.
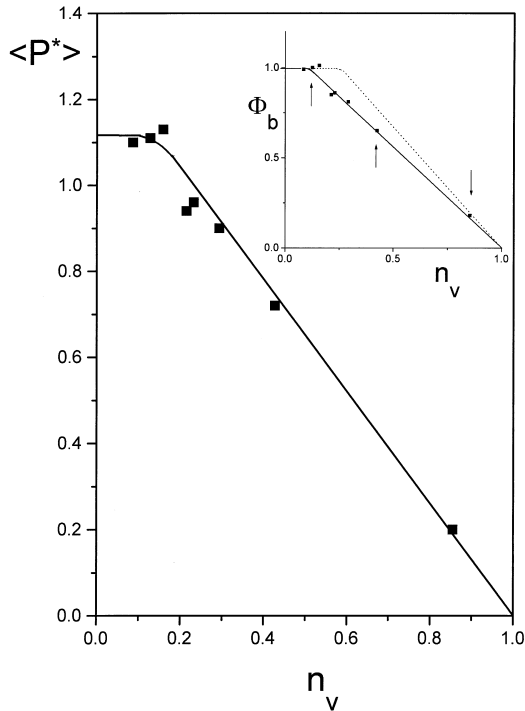
Fig. 9. Power efficiency factor, $\langle P^* \rangle$, as a function of the degree of filling n_V. Region up to $n_V \leqslant 0.2$ identifies the *non-hindering* filling zone (see text). The solid line is the best fit through the experimental points. The solid line of the inset shows the hindering factor, ϕ_b, obtained normalising to one the $\langle P^* \rangle$ values. The dotted line gives the ϕ_b values obtained in Part I without powder. Three experiments, reported in Table 2, with different ϕ_b are indicated (see text).

The milling map of Fig. 5 gives the power consumption due to the milling action at any level of filling and for any rotation speed. We outline that the power consumption is due to the energy transferred from the milling tools to the powder under processing and represents the answer, at macroscopic level, to the sum of the microscopic events occurring during the milling process. It can be seen from Fig. 5 that the existence of three different efficiency regions, previously detected, has been verified here. In the first region (A in the figure) the power consumption, at each w_p, *increases linearly* with the number of balls up to about $n_V \leqslant 0.18$ (see arrow of Fig. 5). In this region we have really *no reciprocal hindering* of the balls and the prediction of equation (2) about a linear dependence of the power consumption with the number of balls is perfectly fulfilled. In Part I, region A extended up to about $n_V \leqslant 0.28$. The lower value found in the present investigation can certainly be ascribed to the presence of powder making more effective the reciprocal hindering of the balls.

The deviation from linearity, region B, means that above a given level of filling, the balls hinder each other with the consequence that the energy transfer process becomes less effective than expected. In Part I, a factor ϕ_b, able to explain the hindering effect, has been evaluated by normalising the map of Fig. 5 with respect to the different w_p, i.e. by deriving the P^* values by means of equation (2):

$$P_i^* = P_{\text{calc},i} \Big/ \left[\frac{1}{2} n_b m_b w_{p,i}^3 R_p^2 \right] \tag{6}$$

where the exponent of the rotation speed has been kept constant to the theoretical value of 3. Averaging over the N values of w_p we obtain the $\langle P^* \rangle = \Sigma P_i^* / N$ values that can be regarded as *power efficiency factors* (see Table 1, column 7) and are plotted in Fig. 9. The onset of the figure gives the hindering factor, ϕ_b, obtained by normalising to the value of one the asymptotic $\langle P^* \rangle$ value. The ϕ_b factor corresponds, ultimately, to the $\langle P_e \rangle$ values, i.e. it represents *normalised power efficiency*. Now, following equation (1), the power depends on the product of ΔE (intensive factor) and v_t (extensive factor). The fact that filling the vial, beyond a certain value, decreases the power efficiency, means that both ΔE and v_t are affected. However, as verified by aimed experiment [10], the collision model can be still assumed just by introducing a suitable hindering factor so that the energy released per collision simply becomes:

$$\Delta E^* = \phi_b \Delta E \tag{7}$$

We will further discuss this point in the next section.

Above the plateau of Fig. 5, the power consumption decreases in absolute value, region C, and tends towards zero. It should be stressed that with completely filled up vials, the power data closely approach the values of empty vials further confirming that it is not the weight to determine the power consumption but exactly the sum of the occurring microscopic events.

3.2. The "govern" of the reactions: the case of "single path cumulative" reaction

Any reaction is characterised by an activation energy that must be overcome in order for the reaction to proceed. Now, in a practical case, we can deal with different systems exhibiting small or high activation energy with respect to the range of input energies normally provided by a mill. In Part I the case of Pd–Si reaction that can be considered a typical example of a *threshold* reaction has been examined extensively. The threshold consisted on the fact that, depending on the milling conditions, two different paths could be followed: namely, the formation of an intermetallic or of an amorphous phase working above or below a given level of input energy. It has been demonstrated that in the case of a threshold reaction the factor governing the end product is not the power consumption but rather the kinetic energy released in the collision

Table 2. Milling experiments having equi-power consumption (column 3) and different energy transfer (column 6)

n_v	rpm	$\langle P_e \rangle$ (W)	ϕ_b	$\Delta E \cdot 10^3$ (J/hit)	$\Delta E \phi_b \cdot 10^3$ (J/hit)
0.158	280	79	1.00	21	21
0.427	230	78	0.65	14	9.5
0.855	290	81	0.18	23	4

event, i.e. the intensive factor ΔE, in the non-hindering region, or $\Delta E \, \phi_b$ in the hindering region. If the threshold is not reached, prolonging the milling time is ineffective and will never result in the formation of the high energy input phase.

Consider the system presently investigated. First of all it should be remembered that in the various milling conditions investigated the number of balls was varied while the weight of the starting powder was kept constant. It is known from experiments that the powder tends to cover the balls and vial walls during milling and that, at the minimum, is just this powder that is trapped in between the colliding tools during a collision event and therefore processed [10]. The surface density of such covering powder can be measured and is of importance as far as elasticity of the collisions [4] and setting up of milling maps [10] are concerned. It has therefore been verified, for the actual series of experiments, that even at the largest balls to powder ratio which has been experienced (see Table 1), the powder weight was always enough to ensure a right covering of the milling tools' surfaces. In other words, it has been assured that in all cases the work done during the collision events was done on powder.

The investigated system has been labelled as "single path" in the obvious sense that, provided that the input energy is high enough to promote the reaction, the system can only go in one direction. We have also labelled the reaction as "cumulative" in the sense that the more one mills, in a given condition, the more the reaction proceeds or, in other words, the system can "cumulate" the work and its temporary state only depends on the integral work done on it up to that moment. Indeed, the invariance of the absorption curves (see Fig. 4) with milling time indicates that the system, at the different milling stages, is always equally prone to the mechanical input so that the effect of the milling action is constant throughout the whole time of a given experiment. This is due to the fact that the powders of both starting and end products show a gentle adhesion on the surfaces of the milling tools *not depending on the milling time*. This behaviour cannot be generally expected. Indeed, often, when dealing with metallic systems and in the early milling stages, the surfaces of both balls and vial walls are coated with a highly adhering powder layers that subsequently, by further milling, fall down from the surfaces. As a consequence, the elasticity of the collisions greatly vary during the process and this finally results in a largely different
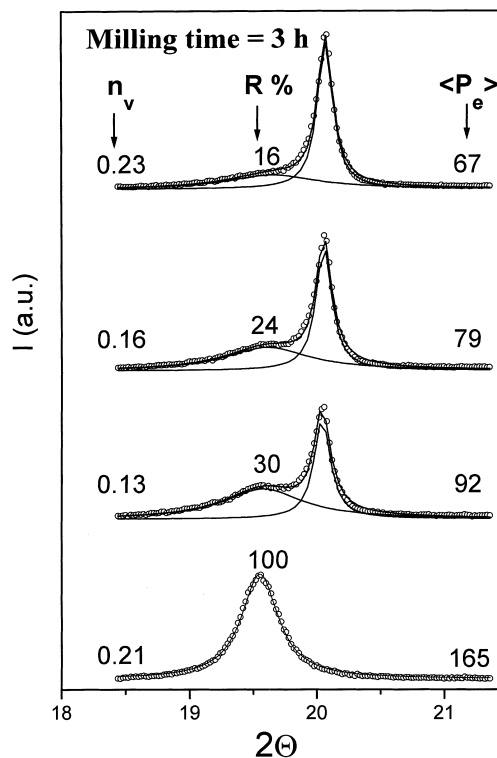

Fig. 10. The progress of the reaction, after 3 h of milling, is shown in correspondence of four $\langle P_e \rangle$ values.

power consumption during milling. This fact, indeed, has been verified with several metallic systems and the argument has extensively been discussed in [4].

Having clarified the meaning of "single path cumulative" reaction, it would be expected that in such a case the only parameter governing the end product should be the *integral work* done on the powder, i.e. the product of the power consumption and the time of milling. Indeed, referring to a milling map like the one of Fig. 5, it is predicted that: "... *one would expect that milling at constant power consumption, for any different* n_v *and* w_p, *one should obtain the same end product for the same milling time*." [16]. This is exactly what has been verified by the milling experiments carried out in the present work. All the milling experiments, with one exception, have been conceived so as to work approximately at equi-power (equi-P) conditions (see Table 1 and horizontal line of Fig. 5) independently from the filling of the vials and of the rotation speed of the planetary mill. The experiments nearest to the equi-P condition are given on Table 2 and it is emphasised the great variation of both vial filling and rotation speed for the reported experiments. As a consequence, the energy transfer does greatly vary as indicated by the last column of Table 2. Nevertheless, due to the constant power absorption, it can be seen that the patterns reported in Fig. 3 (A), (B) and (C) are indistinguishable and

that the reaction progress is coincident within the experimental uncertainty (see Fig. 8 and last column of Table 1).

By increasing the level of power consumption at about twice the equi-P value, the reaction proceeds much faster and is completed in less than half the time [see Fig. 3(D)]. Figure 10 shows the reaction progress after 3 h of milling in correspondence of four different $\langle P_e \rangle$ values. For values not differing much from the equi-P conditions, the reaction progress lies between 15 and 30% (see Fig. 10 and Table 1). At twice the power value the reaction progress at the same time is completed. The analysis of the reaction kinetics, however, is beyond the scope of the present work and could be examined in the future.

Most of the reactions that can be carried out by mechanical alloying or mechanosynthesis [17] certainly fall into one of the two categories recalled before. The "threshold" systems are those that can proceed in different ways depending the level of the energy transfer realised by the milling conditions. Of course, since only one is the stable thermodynamic state predicted for any composition at given P and T, there must be associated the possibility of a kinetically achievable metastable state. In these cases, the factor governing the process is the energy transfer that can be evaluated through the collision model and that can be made effective by experimentally setting up suitable milling conditions.

On the other hand, the systems that can only go in one direction, i.e. the thermodynamically stable state, can behave as "cumulative", in the sense explained in the present investigation, or not, like in the cases of self propagating "explosive" reactions just starting and ending after a suitable "ignition" time (see, e.g. Ref. [18]). For the "cumulative" reactions, the factor governing the process is the power consumption that can be measured and hence assumed as a criterion for the choice of the operative milling conditions

In both cases, threshold or cumulative reactions, a predictive capability for the milling process has been nowadays realised and the possibility of planning a given wanted end product as a function of the milling conditions substantially achieved.

3.3. *Future perspective of* in situ *measurements*

The present and previous work [16] have revealed how important the direct measurements of power consumption during milling can be. However, it cannot be requested to the majority of people working in the mechanical alloying field to acquire such data, notwithstanding their relevance, because the commercially milling apparatus actually available is not conceived for that purpose. Ultimately, Fig. 5 is nothing else than a milling map giving the *net* absorption consumption (measured through a difference procedure at some time intervals) corresponding to the rotation speed, the parameter actu-

ally measured. As a matter of fact, the construction of such a map has required a long and skillful experimental work that could have been avoided by suitable instruments able to *directly* provide the "net absorption power" in any working condition. Such information, once easily achievable, could then be normally acquired in any MA investigation and could be the basis for a deeper and unified interpretation of the milling process.

In other words, we feel that in order to increase our knowledge on the MA process today, we do not need more theoretical approaches, already largely developed, but, rather, we need more sophisticated milling devices able to provide direct *in situ* measurements during milling like those illustrated in the present paper. This is the line that we intend to pursue in the near future.

4. CONCLUSIONS

The main conclusions that can be drawn from the present investigation can be summarised as follows:

1. It has been confirmed in experiments with powder that the power consumption due to the milling action can be revealed by suitable electrical power measurements that fit quite well with equations derived from a collision model. The experiments have been carried out with a planetary mill but the principle can be extended to any milling device.
2. For a "single path cumulative" reaction the only factor governing the progress of the reaction is the power consumption during milling. Even allowing for a large variation of the milling parameters, if we operate in equi-power absorption conditions the progress of the reaction is the same.

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