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A quantitative approach to mechanochemical processes

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A complex methodology has been developed in order to quantify the conditions of mechanical treatment in laboratory and commercial ball mills. The experimental determination of the collision frequency and the impact energy has been paralleled by an accurate numerical modelling of the balls and powder dynamics. The obtained results have been further confirmed by a direct inspection of the motion of balls and powder inside a transparent quartz reactor by means of high-speed video recording. The temperature of mechanochemical reactors has been also continuously monitored during the course of mechanical treatments. The methodology has been systematically applied to characterise on absolute basis the kinetic behaviour of a large variety of mechanically-induced structural and chemical transformations. In particular, systematic investigations have been performed on the amorphisation of intermetallic and binary systems, on the formation of extended solid solutions in immiscible systems, on the ignition of combustion-like reactions in metal-metalloid mixtures and on the hydrogen storage in nanocrystalline and amorphous multicomponent metallic alloys. Mechanochemical transformations appeared to be basically ruled by two different mechanisms characterised by simple asymptotic trends and sigmoidal curves respectively. An attempt to rationalise the observed mechanisms on a phenomenological basis has been made.

1. Introduction

Mechanochemical effects arise because of the complex interplay between defective structure and enhanced reactivity of excited solid phases [1]. Beyond the chemical aspects, the latter is deeply affected by the spatial arrangement of atomic species [1]. Geometrical factors can be highly perturbed by the action of external forces, for instance by the energy pulses in Ball Milling (BM) processes. Therefore, mechanochemical phenomena also depend on the highly excited, short-lived local states destined to a rapid relaxation, which could become important centres of enhanced reactivity [1, 2]. In this sense, mechanochemical reactions take place under non-equilibrium conditions [3].

An exhaustive approach should be developed to explain mechanochemical phenomenology within a coherent thermodynamic and kinetic framework. Although various sophisticated approaches have been actually developed, difficulties exist to quantitatively measure the excess energy stored by solids in a variety of defects [4]. To some extent, it hinders the exploration of possible links between mechanochemical reactivity and excited thermodynamic states. Along this line, we conceived that useful information could be obtained from an accurate evaluation of the total work done on the system and of the experimental parameters controlling the process [2, 5]. In this paper, we present some qualifying mechanochemical processes connecting the observed reactivity to the milling conditions.

2. The evaluation of the mechanical work

Mechanical processing by BM is based on the repeated occurrence of single impact events at which powder particles are trapped and cold-worked [6]. As detailed elsewhere [5, 7], it has been proven that the accurate experimental evaluation of the impact energy E, i.e. the energy transferred to powders at each impact, and the collision frequency N requires (i) the use of a single milling ball, (ii) the use of a powder amount great enough to ensure the occurrence of inelastic impacts and (iii) the knowledge of the equations of motion of the vial reactor [5]. Under such circumstances, an experimental protocol was developed, based on electronic devices, which permits the measurement of both the collision frequency N and the impact energy E

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[5]. The methodology was supported by the numerical modelling of the milling dynamics [5, 8]. The direct high-speed video recording of the ball and powder motion inside a transparent quartz vial [9] during a Mechanically-induced Self-propagating combustion Reaction (MSR) [10, 11], showed the essential features of the system dynamics as emerged from previous evaluations. The different estimates of N and E obtained sustain each other and also agree with the ones obtained according to the calorimetric method discussed by Butyagin [2].

In the following, the specific milling intensity $I_m = NE/m_p$, defined as the rate of energy transfer per mass unit [2, 5, 7], is used to quantify the milling regime. The transformation kinetics, followed by evaluating the conversion degree according to the procedures described in previous papers [5, 7], is referred to the specific mechanical work $D_m = I_m t$ performed on the system within a given milling time t.

3. Phenomenology of mechanochemical transformations

Mechanochemical transformations generally occur according to three different reactive paths. Two of them imply a gradual phase evolution characterised, respectively, by a continuously decelerating trend or a sigmoidal conversion curve. The third involves, instead, the sudden ignition of self-propagating combustion reactions.

The continuously decelerating kinetic trend has been observed in mechanochemical transformations regarding pure compounds such as intermetallics and oxides. In the first case, the mechanical treatment induces a gradual disordering of the crystalline lattice and the consequent formation of an amorphous structure.

Such a case of transformation kinetics is illustrated in Fig. 1 as a function of the milling time for the $NiTi_2$ [12]. The reported data sets refer to two different milling trials carried out at the specific intensities $I_m = 0.21$ W g^{-1} and $I_m = 0.34$ W g^{-1} respectively. The best-fitting curves are also reported. According to previous work [13], the integrated kinetic equation connecting the conversion degree α with the time of mechanical treatment t is the following one:

$$\alpha = 1 - \exp(-k_t t) \tag{1}$$

where k_t is the rate constant. Quite reasonably, the lowest transformation rate corresponds to the lowest value of the milling intensity. However, the distinction between the curves disappears when the total work done on the powders D_m is taken into account instead of the milling time. Indeed, as shown in the inset in Fig. 1, the two curves superpose displaying a single trend. It is worth noting that such a superposition can be well accounted for by Equation 1, since $k_t t = K_D D_m$, with $k_t = K_D I_m$, as shown in previous works [7, 13].

An analogous behaviour characterises the transition of the ZrO_2 system from the monoclinic to the tetragonal phase. As in the previous case, the conversion degree increases according to a monotonic trend. Data pertaining to trials carried out by employing balls of different mass m_b are reported in Fig. 2 as a function of the time. The transformation rate increases as the ball mass m_b increases.

A different transformation kinetics is observed in the case of binary systems, with the conversion degree following a sigmoidal curve. Such a behaviour has been extensively investigated with reference to the amorphisation of transition metal binary mixtures [7].

As in the case of single phase systems discussed above, the milling intensity determines the rate of the amorphisation process. Fig. 3 shows that the data pertaining to trials performed at different intensities arrange according to different sigmoidal curves when reported as a function of the time, while a single trend is obtained when the milling dose is used as the reference quantity. The best-fitting curves, also quoted in the figure, have the following equation [7]:

$$\alpha = 1 - (1 + k_t t)\exp(-k_t t) \tag{2}$$

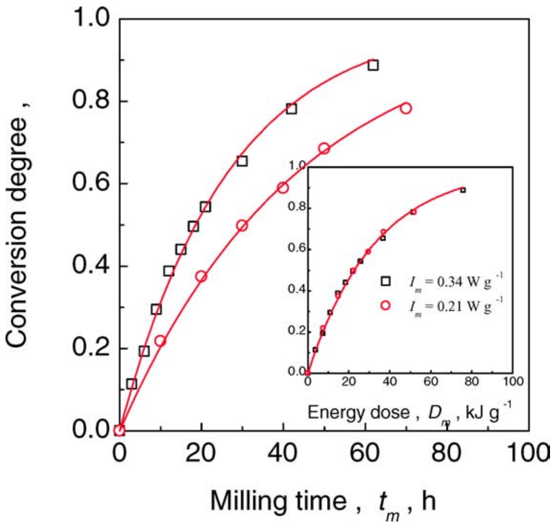

Figure 1 Developing amorphous fractions, α, as a function of the milling time for the intermetallic system $NiTi_2$. The conversion degree is also quoted as a function of the specific milling dose in the inset.

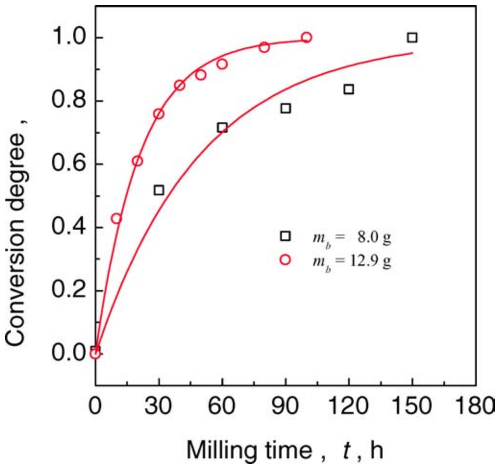

Figure 2 The weight fraction α of the monoclinic ZrO_2 phase as a function of the milling time. The tetragonal-to-monoclinic conversion degree is also quoted as a function of the specific energy dose in the inset.

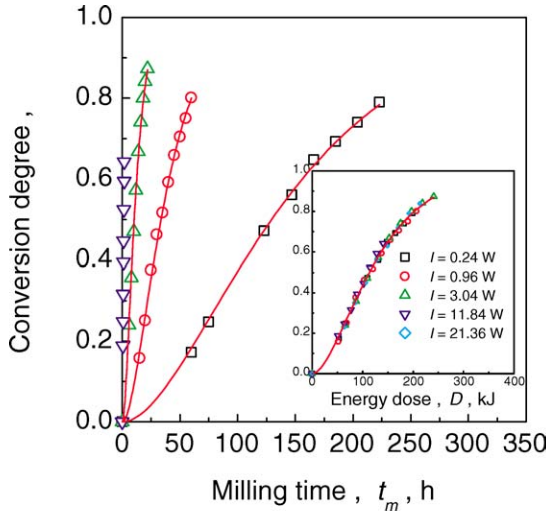

Figure 3 Sigmoidal transformation trends for the $Ni_{40}Ti_{60}$ system as a function of the milling time. In the inset, the data set is reported as a function of the milling dose.

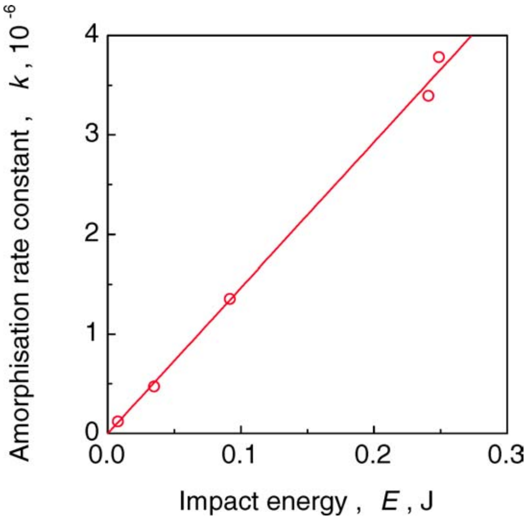

Figure 4 The linear correlation between the rate constants and the impact energy for the $Ni_{40}Ti_{60}$ system.

Taking advantage of the relationship between time and collision frequency, it is possible to refer the curves to the total number of collisions occurred $n = Nt$, in order to obtain a rate constant $k_n = k_t/N$ independent of the collision frequency [13]. Such a constant shows a linear dependence on the impact energy E, as shown in Fig. 4. It then follows that $k_n = \beta E$, where β is a constant characteristic of each chemical system [7, 13].

It is now interesting to note that not all the binary systems display such a linear dependence of the rate constant k_n as a function of E which, as yet, was observed for systems characterised by a negative enthalpy of mixing. In the case of immiscible systems characterised by a positive enthalpy of mixing, a metastable crystalline solid solution is formed instead of an amorphous phase. While the formation of the solid solution follows a sigmoidal kinetics which can be satisfactorily fitted by Equation 2, the linear trend of the rate constant k_n, reported as a function of the impact energy E in Fig. 5, intersects the abscissas axis at a positive E_0 value.

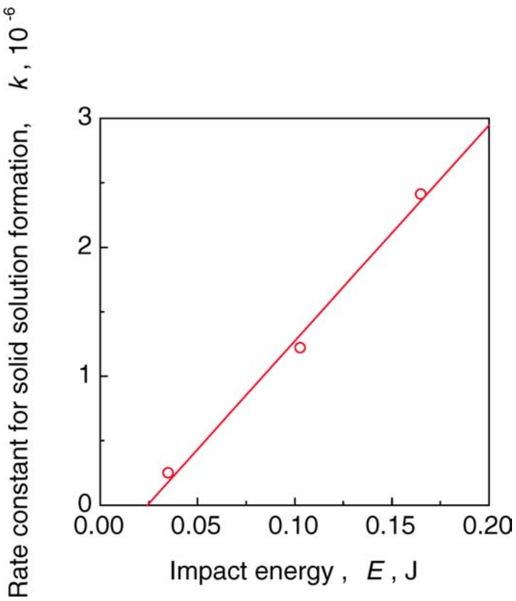

Figure 5 The linear correlation between the rate constants and the impact energy for the $Cu_{50}Ag_{50}$ system. A threshold impact energy $E_0 = 0.024$ J is observed.

Such a value is the threshold impact energy required for the formation of the solid solution. It expresses the mechanochemical activation energy.

This also means that, in this case, $k_n = \beta(E - E_0)$. Consequently, the different kinetic curves obtained at different intensities and reported in Fig. 6 as a function of the time no more superpose when referred to the milling dose $D_m = I_m t = nE/m_p$. As shown in the inset in Fig. 6, they only superpose when the excess energy dose $D^*_m = n(E - E_0)/m_p$ is used.

It is worth noting that an analogous dependence of the kinetics on the impact energy is observed in the case of the Mechanically-induced Self-propagating Reactions (MSR). These reactions are characterised by an abrupt chemical transformation [10]. Indeed, the gradual

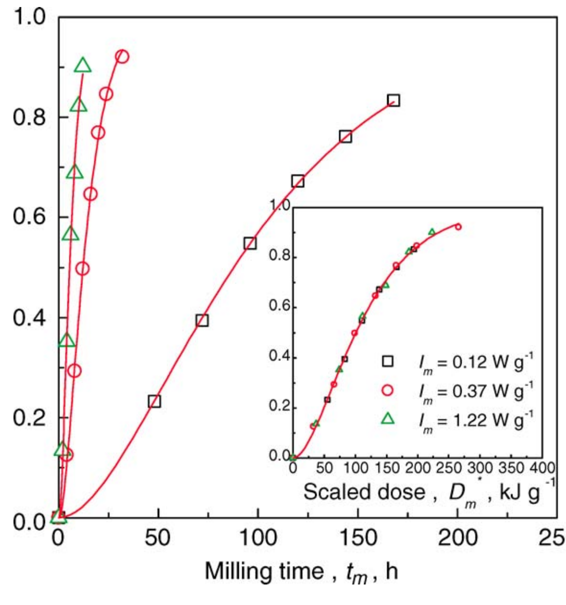

Figure 6 Sigmoidal transformation trends for the $Cu_{50}Ag_{50}$ system as a function of the milling time. In the inset, the data set is reported as a function of the scaled milling dose.

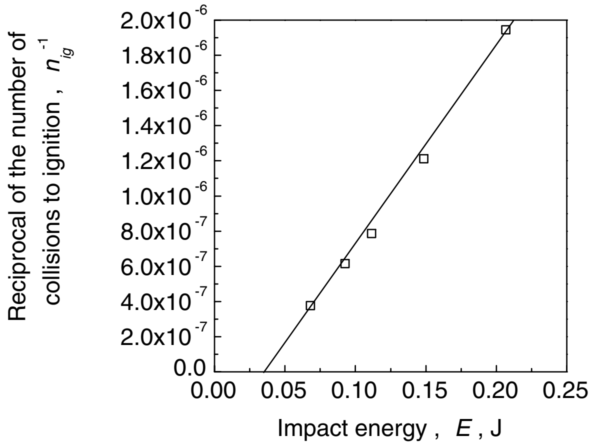

Figure 7 The linear correlation between the reciprocal of the number of collision needed to ignite the combustion process and the impact energy for the $Ti_{70}C_{30}$ system. A threshold impact energy $E_0 = 0.035$ J is observed.

microstructural evolution of the powder mixture during the activation period up to the ignition time, t_{ig}, determines a combustion-like self-propagating reaction which leads to final products in the time scale of ms. Ignition times have been found to depend on a great number of factors such as the mixture stoichiometry and the milling conditions [11, 15]. In particular, the collisions needed to ignite the reaction, n_{ig}, have been shown to hyperbolically depend on the impact energy [14].

Indeed, a linear trend is again observed when the reciprocal of n_{ig} is reported as a function of E as in Fig. 7. As in the previous case, the linear trend indicates the existence of a low impact energy threshold E_0. When such a threshold is properly taken into account according to the above definition of D_m^*, it appears that D_m^* is the invariant quantity instead of D_m [14].

Invariant quantities can be also found in the case of gas adsorption over powder mixtures during the course of the mechanical treatment [15].

4. Conclusions

The mechanochemical reactivity of different classes of pure compounds and binary systems has been discussed. The kinetics of mechanically-induced transformations has been investigated as a function of the main milling parameters. It has been found that conversion degree and conversion rates are basically related to impact energy, collision frequency and powder charge. In particular, the transformed mass fraction depends on the total mechanical work done on the processed powders. According to our findings, this appears to be an invariant, characteristic quantity of each system. On this basis, we hope it could be possible to compare mechanochemical transformations and deepen mechanochemical studies within the necessary reference framework.

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