# Theoretical treatment of a self-sustained, ball milling induced, mechanochemical reaction in the $Fe_2O_3$–Al system

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## Abstract

A theoretical approach to self-sustained reactions (SSR) is established based on self-propagating high temperature synthesis. The corresponding heat conduction equation has been solved numerically and conclusions about the occurrence of the reaction through the whole sample have been obtained from the relationship between the dissipation mechanisms. These results strongly suggest that radiation heat flux plays a dominant role in the propagation of the reaction in reactive ball milling processes. The influence of different parameters on the occurrence of the SSR or its development were studied. Data for the formation of iron–alumina composites by reducing hematite with aluminum were used, in order to obtain realistic values. However the results are sufficiently generic to extrapolate the conclusions to other high enthalpy reactions.

*Keywords:* Ball milling; Theoretical analysis; Nanostructured materials; Numerical calculation; Displacement reactions

## 1. Introduction

To describe the details of a ball milling induced chemical reaction is a difficult task, due to the complex combination of interrelated processes: compression, mixing, surface reactions, interdiffusion, heating and cooling; to mention just a few. To achieve a comprehension of the process as a whole it is necessary to know how each one of these processes develops [1].

Under this point of view it is reasonable to take advantage of the knowledge about individual processes from other research areas. The self-propagating high temperature synthesis (SHS), whose modern development began in 1967, makes use of the ability of highly exothermic reactions to be self-sustaining [2]. In the combustion synthesis reaction of the SHS type, the process is initiated at one point of the sample and proceeds through the reactant mixture in the form of a propagating combustion wave. This wave is driven by heat generated towards un-reacted powder in adjacent layers. It is clear that once the reaction is initiated at some point, there is no need for additional external heat supply [2].

Diffusion through the layer of the formed product limits the reaction rate in a solid-state reaction. Mechanical milling, due to attrition and mixing, increases the interfaces between the reactant particles without product barriers (between un-reacted layers). The continuous agitation of the reactive mass enhance the reaction rate due to the possibility that fresh surfaces being repeatedly brought into intimate contact [3]. There are many types of mechanical milling processes and we are concerned here with those involving solid-state reactions in systems with a high reaction enthalpy [4]. In these cases and under certain conditions, the reaction could proceed in a non-gradual way. This means that there is none or little chemical change in the system until a critical condition is reached at the ignition time ($t_{ig}$), and then the system evolves in a violent way: a combustion front is generated and the reaction is completed in a short period of time [5]. This kind of process is called a self-sustained reaction (SSR). Experimental evidence of local melting, even vaporization, in some milled systems has been found, indicating the high local temperatures rise during these processes [4].

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In this work we focus on a theoretical explanation whose basic idea has been taken from the SHS pioneer works, but adapted to the very special conditions of ball milling, not only in the ignition considerations but also in the sample dimensions and the boundary conditions. In such a way we were able to explain some details in the propagation of the combustion wave, once it is generated, and the influence that several parameters have on the occurrence of SSR. Moreover, it was possible to infer how important is the radiation heat flux as a possible route for the instantaneous propagation of the SSR to the whole sample. Data for the formation of iron–alumina composites by reducing hematite with aluminum were used, in order to obtain realistic values. However the results are sufficiently generic to extrapolate the conclusions to other high enthalpy reactions.

## 2. Basic theory and model

### 2.1. Microstructure

During a typical mechanical milling process, a given sample fraction becomes trapped at random between the hard tools (vial and balls) and submitted to a 'micro forging' process accompanied by some local heating [6]. We assume that as a consequence of the repeated impacts the sample consists of a refined powder where the reactants are intimately mixed. This is supported by transmission electron microscopy (TEM) observations, prior to ignition, on our $Fe_2O_3$/Al samples, where a series of energy-dispersive X-ray analysis (EDAX) were made. In these observations, particle sizes around 200 nm were observed. In spite of some dispersion in the measurements, it was always possible to detect the presence of the three constitutive elements (Fe, Al and O) in each analyzed particle, in a random distribution. Experiments to complete the characterization of the mechanically activated pre-ignition state [7,8] are in progress. This fine mixture, when absorbing the energy of a further impact, may react and under certain conditions, initiate a SSR. For exothermic reactions further local heating takes place, and a SSR can be reached if a critical temperature value is exceeded at a nearby interface [1].

### 2.2. Model

The physical process studied here, just involves phenomena associated with ignition, the combustion wave, the conditions under which it propagates and the heat lost from the reaction. All these processes will be studied in a powder layer through which the reaction proceeds. Ball milling has a strong influence on the sample during the preliminary stages, for milling times up to $t_{ig}$, when it prepares the reactants and eventually ignites the mixture. The athermal forced jumps [9] and the enhancement of atomic diffusion (due to point defect formation) that takes place during milling mainly contribute to the refinement and intimate mixing of the powders. As discussed later, milling may also affect the reaction kinetics by decreasing the activation energy as a consequence of the energy stored during mechanical work.

The first assumption to be made, taking into account the maximum expected temperature, is that heat is propagated through the layer mainly by conduction. We further assume that there is not mass transfer in the layer. The Fourier heat conduction equation governs the process:

$$c\rho \frac{\partial T}{\partial t} = k\nabla^2 T + q_s - q_c \tag{1}$$

where $c$ (J kg$^{-1}$ K$^{-1}$), $\rho$ (kg m$^{-3}$) and $k$ (W m$^{-1}$ K$^{-1}$) are, respectively the average heat capacity, density and thermal conductivity of the products, $q_s$ is the source term (W m$^{-3}$) and $q_c$ is the rate of heat energy lost to the environment (W m$^{-3}$).

### 2.3. Sample geometry

Differential equation (Eq. (1)) will be solved in a cylindrical geometry, in which a layer of reactant powder mixture is considered. When a ball hits a point of this layer, kinetic energy is transformed to heat and the reaction could proceed if a minimum temperature is reached. The dimension of this layer will be related to the area affected by the impact (Hertzian radius, $r_H$), and to the total powder mass inside the cylinder. The estimated values of $r_H$, are of the order of 100 μm [10], and the dimensions of the layer ($r$) must be much greater than this value. Considering the dimensions of our vial, a total inner surface of about 3000 mm$^2$ results. Half of this area corresponds to a circle of radius 22 mm, which may be considered as a practical upper limit to the lateral layer dimensions. But such a big sample would result in an unnecessary poor spatial resolution in our calculations given that once the reaction is in the propagation stage the lateral sample extension is not much significant. As a compromise between these extreme values, $r = 1.5$ mm was chosen.

The thickness of the layer ($z$) was given a reasonable value of 100 μm, one order of magnitude bigger than typical thickness of coating layers measured in balls [11], but closer to estimations of the powder quantity trapped between tools [6]. Any temperature variation across this dimension was neglected. Moreover, due to symmetry considerations, the temperature does not depend on the azimuthal angle. This reduces the Laplacian operator in (Eq. (1)) to one variable, namely the radius.

## 2.4. Source and heat dissipation mechanisms

The heat released by the chemical reaction is the only source present, and it could be expressed as:

$$q_s = \Delta H \rho \frac{\partial \eta}{\partial t} \tag{2}$$

where $\eta$ represents the un-reacted fraction and $\Delta H = \Delta H(T, \eta)$ is the enthalpy change (J Kg$^{-1}$). The dependence of the enthalpy change on temperature and un-reacted fraction was considered in order to give account of phase transformations:

$$\Delta H = \Delta H_r - \sum_p H_p^t f_p (1 - \eta) - \sum_r H_r^t f_r \eta \tag{3}$$

where $\Delta H_r$ is the enthalpy change of the reaction, $H_p^t$, $f_p$, $H_r^t$ and $f_r$ are the transition heat and molar fractions of products and reactants, respectively.

The reaction cannot sustain forever, so it is necessary to take into account how the concentration of the reactants depends on time. As a first approach it will be supposed that the rate at which material is 'burned' depends on the un-reacted fraction (first order kinetic):

$$\frac{\partial \eta}{\partial t} = -\chi(T) \eta \tag{4}$$

where $\chi$ is the rate constant ($1/s$). If it is supposed too that Arrhenius equation holds, $\chi$ could be expressed by:

$$\chi = A \exp\left(-\frac{E}{RT}\right) \tag{5}$$

where $A$ is the pre-exponential factor ($1/s$), while $E$ is the activation energy (J Kg$^{-1}$).

Equations described above indicate that a system of two partial differential equations (Eqs. (1) and (4)) must be solved simultaneously, to obtain $T = T(r, t)$ and $\eta = \eta(r, t)$.

In the dissipation term, $q_c$, it will be assumed that heat is dissipated by radiation and free convection.

$$q_c = 2\frac{h}{z}(T - T_e) + \frac{2e\sigma}{z}(T^4 - T_e^4) \tag{6}$$

where $h$ is the heat transfer coefficient (W m$^{-2}$ K$^{-1}$), $z$ is the layer thickness (m), $T_e$ is the environment temperature (K), $\sigma$ is the Stefan-Boltzmann constant and $e = e(\eta)$ is the emissivity. The factor 2 gives account of the fact that heat is evolved at both faces of the layer. The emissivity may be expressed as a function of the un-reacted fraction:

$$e = \sum_p e_p f_p (1 - \eta) + \sum_r e_r f_r \eta \tag{7}$$

where $e_p$ ($e_r$) is the emissivity of the products (reactants).

## 2.5. Boundary and initial conditions

All the heat reaching the boundary surface by conduction is released by convection, giving a boundary condition of the third type in the upper limit:

$$\left[ k\frac{\partial T}{\partial r} + hT \right]_{r = r_{max}} = hT_e \tag{8}$$

whereas at $r = 0$, we establish a symmetry condition:

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0 \tag{9}$$

It is very important to connect the initial conditions $T_0 = T(r, T = 0)$ and $\eta_0 = \eta(r, T = 0)$ with the actual situation in the milling process. Until $t_{ig}$ is reached there are no chemical reactions in the system [12], therefore $\eta_0 = 1$.

There are many ways to induce a SHS reaction and so define $T_0$: laser radiation, radiant flux, resistance-heating coil, spark and chemical oven, etc. [2]. Some of them are very precise in both the amount of energy supplied and the affected area. On the contrary, in a ball milling process the SSR is induced by the energy transferred during one impact, which seems to be much lower than those typically employed for SHS. It is well known that almost 95% of the work done in metalworking operations are manifested in heat evolution [6]. Therefore, the assumption that plastic deformation work is entirely converted into an adiabatic temperature rise ($\Delta T$) of the impacted powder is justified. From this model of mechanical alloying, $\Delta T$ values ranging from 0.2 to 633.6 K has been estimated for various materials and experimental conditions [6]. This temperature increase ($\Delta T$) applies to the bulk of the trapped powder and gives no indication about the certainly higher surface temperatures. Therefore these values represent a lower limit under the situation studied here, because even when the bulk temperature were too low to initiate MSR, the surface temperature achieved during a collision event could be sufficiently high. The existence of these 'hot spots', with temperatures much higher than the average, is a problem shared with the study of the ignition of solid explosives by impact [13]. Therefore a Gaussian temperature profile was supposed for $T_0(r)$, with a maximum $\Delta T = 600$ K and a FWHM equal to 300 μm.

## 2.6. Numerical and experimental considerations

Due to the impossibility to derive a simple exact solution of the Fourier heat conduction equation, with the terms described above, it will be solved numerically. The method of solution is based on the numerical method of lines, where the spatial derivatives are approximated by finite differences. The spatial resolution was selected as 15 μm. As a consequence, there are

200 sections, of 15 μm each, within the studied layer ($\phi = 3$ mm). Moreover, along each section there are, on the average, 75 powder particles as those analyzed by TEM/EDAX (200 nm) and according to these measurements, every particle shows a fine mixture of the constitutive elements.

In this model we made the further assumption that all the physical parameters remain constant, independent of temperature and un-reacted fraction, exception was made of the enthalpy change and emissivity, Eq. (3) and Eq. (7), owing to their relevance in some of the results derived below. The values used in the numerical calculation were selected to describe the reduction of hematite by aluminum according to the following chemical reaction:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 \qquad (10)$$
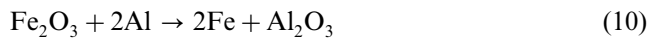
To study this specific reaction allow us to specify not only the constants selected in the first column in Table 1[14], but also the specific functions described in Eq. (3) and Eq. (7). Thermodynamic and radiative properties of materials involved in Eq. (10) were listed in Table 2 and Table 3[14].

The above reaction has been studied by us as well as by other groups, and a comparison between the experimental results obtained has been made in a previous work [12,15,16].

Once the reaction is attained in a microscopic layer, it propagates to the rest of the powder and a macroscopic temperature rise is detected. Fig. 1 shows temperature

Table 2
Thermodynamic properties of materials involved in the reaction: $Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$

| Transformations | Transition temperature (K) | Heat of transition (kcal $g^{-1}$ $mol^{-1}$) |
|---|---|---|
| Al (sol.) | 931.7 | 2.57 |
| Al (liq.) | 2600 | 67.9 |
| Fe($\alpha$) | 1033 | 0.41 |
| Fe($\beta$) | 1180 | 0.217 |
| Fe($\gamma$) | 1673 | 0.15 |
| Fe($\delta$) | 1808 | 3.86 |
| Fe(liq.) | 3008 | 84.62 |
| Al$_2$O$_3$(sol.) | 2300 | 26 |
| Fe$_2$O$_3$($\alpha$) | 950 | 0.16 |
| Fe$_2$O$_3$($\beta$) | 1050 | 0 |

Table 3
Radiative properties of the materials involved in the reaction: $Fe_2O_3 + Al \rightarrow Al_2O_3 + Fe$

| Materials | Emissivity |
|---|---|
| Al | 0.06–0.07 |
| Fe(sol.) | 0.21 |
| Fe(liq.) | 0.29 |
| Al$_2$O$_3$ | 0.2–0.3 |
| Fe$_2$O$_3$ | 0.82–0.89 |

Table 1
Influence of the different parameters on the numerical results of Fourier's heat conduction equation

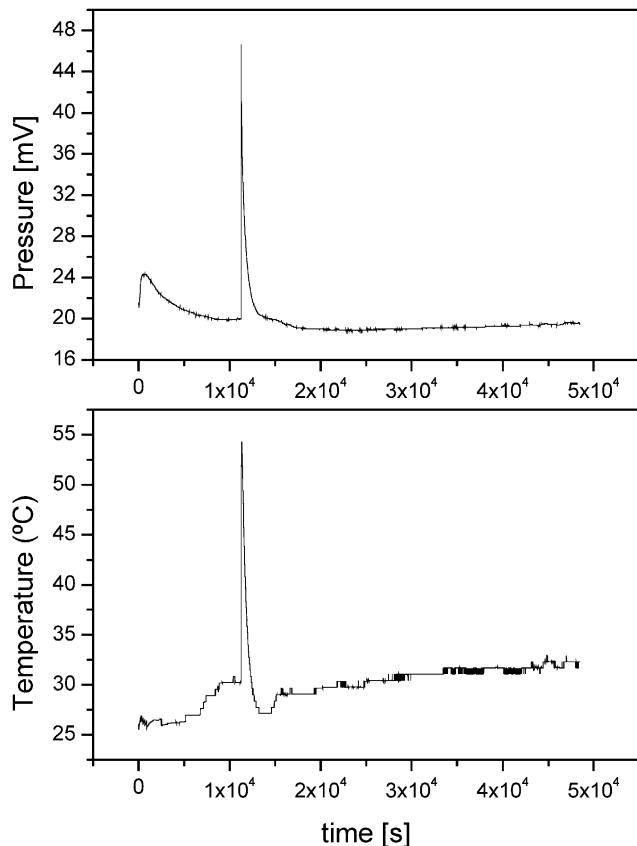| Initial parameter | Modified parameter | Wave front velocity (m s$^{-1}$) | Minimal ignition temperature (K) |
|---|---|---|---|
| $A = 1 \times 10^7$ s$^{-1}$ | $A = 1 \times 10^8$ s$^{-1}$ | 2.75 | 467 |
|  | $A = 1 \times 10^6$ s$^{-1}$ | No explosive | 617 |
| $E = 83.8$ kJ mol$^{-1}$ | $E = 167.6$ kJ mol$^{-1}$ | No explosive | 1159 |
|  | $E = 41.9$ kJ mol$^{-1}$ | – | 244 |
| $k = 53.12$ W m$^{-1}$ K$^{-1}$ | $k = 106.24$ W m$^{-1}$ K$^{-1}$ | 2.66 | 532 |
|  | $k = 26.56$ W m$^{-1}$ K$^{-1}$ | 0.96 | 532 |
| $c = 600$ J kg$^{-1}$ K$^{-1}$ | $c = 1200$ J kg$^{-1}$ K$^{-1}$ | 0.77 | 532 |
|  | $c = 300$ J kg$^{-1}$ K$^{-1}$ | 4.2 | 532 |
| $\Delta H$ | $2\,\Delta H$ | 2.63 | 510 |
|  | $\frac{1}{2}\,\Delta H$ | 1.35 | 555 |
| $h = 200$ W m$^{-2}$ K$^{-1}$ | $h = 400$ W m$^{-2}$ K$^{-1}$ | 1.71 | 554 |
|  | $h = 100$ W m$^{-2}$ K$^{-1}$ | 1.69 | 512 |
| $z = 100$ μm | $z = 200$ μm | 1.67 | 510 |
|  | $z = 50$ μm | 1.69 | 555 |
| $e$ | $e_1$ | 1.65 | 532 |
|  | $e_2$ | 1.71 | 532 |

Fig. 1. Temperature and pressure recorded during the milling of a 1 g sample of a mixture of $Fe_2O_3$ and Al.

($T$) and gas pressure ($P$) recorded as a function of the milling time in a 1 g sample prepared according to the stoichiometric equation in the Al–$Fe_2O_3$ system (experimental details are available in Ref. [12]. The simultaneous jump in both registers determines the ignition time ($t_{ig}$) and so the occurrence of SSR in these samples. If the temperature of the vial is supposed to be equal to the maximum temperature sensed by the $T$ probe, and the maximum $P$ recorded is taken as an indication of the argon gas temperature, a simple calorimetric calculation can be made. Using vial and ball masses of 181 and 7 g, respectively, and 0.11 kJ kg$^{-1}$ K$^{-1}$ for the specific heat of steel [14], a value of $Q \approx 2.6$ kJ is reached. This value compares reasonably well with the heat released by a 1 g sample that fully reacts according to Eq. (10): (3.97 kJ).

## 3. Results and discussion

Fig. 2 shows one successful attempt to attain SSR within the given assumptions and represents the time evolution of un-reacted fraction and temperature in the sample. A combustion front, characterized by a sudden temperature increase, develops and propagates beyond the area where the initial heating took place as a result of the impact. This temperature wave front travels
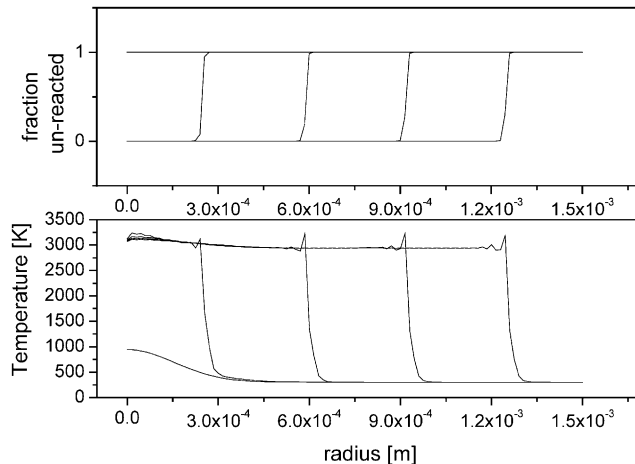


Fig. 2. Time dependence of un-reacted fraction and temperature distribution after the simulated impact (time interval between consecutive fronts = 0.2 ms, front wave velocity = 1.65 m s$^{-1}$).

through the un-reacted material with an approximately constant velocity of 1.65 m s$^{-1}$. After the exothermic process, and when the reactants are exhausted the temperature starts to decrease slowly.

If the layer is subjected to the same conditions, as before, except in $T_0$, which is assumed uniform throughout the sample, the minimal uniform initial temperature, to produce a SSR, is equal to 532 K. Any temperature profile under 532 K, cannot ignite the mixture and the layer just cools down.

The temperature profile, after ignition, conserves its shape during propagation. For a better visualization we plot it as a function of time at a specific point, $r = 3r_H$ as shown in Fig. 3. The above cited wave front velocity ($v_{WF}$) of 1.65 m s$^{-1}$ was calculated from this graphic measuring the time and displacement between consecutive fronts.
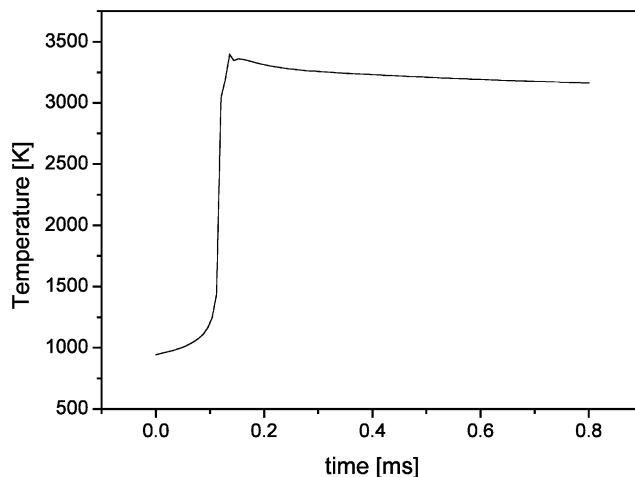


Fig. 3. Time dependence of the temperature distribution after impact in a particular point ($r = 3r_H$), front wave velocity = 1.65 m s$^{-1}$.

The temperature distribution in any reacting mixture is stabilized when the rate of heat loss by conduction or convection from any volume element is equal to that produced by the reaction itself in that volume element. A thermal explosion results when the rate of heat loss cannot compensate for the rate of heat production and the temperature increases exponentially. When the rate of heat production is lower than the rate of heat loss, the system behaves in an unstable way too; cooling down rapidly, and not presenting a SSR. A plot of both terms as a function of $T$ shows, at the crossing point, the minimal uniform ignition temperature ($T_0^{\min}$) (Fig. 4) [17]. Later, this value will serve to characterize the sensitivity of a given system to a change in their parameters, referred to the occurrence of SSR.

In the following we analyze the sensitivity of the system to the variation of each parameter at a time, by two routes. First, we determined the SSR occurrence and the corresponding wave front velocity, always maintaining the same initial condition: a fixed Gaussian temperature profile representing the heating of the mixture as a result of the impact. Second, we determined the minimum uniform temperature needed to ignite the layer ($T_0^{\min}$); this is to investigate what initial condition is favorable in order to reach a SSR. Each meaningful parameter entering the Fourier equation will be investigated under both premises.

The pre-exponential factor, also known as frequency factor ($A$), gives us some idea about how fast a reaction proceeds. This kinetic parameter, as well as the activation energy ($E$, considered bellow), was varied to get either a combustion wave or extinction of the initial reaction [1]. Several values were intended and, as shown in Table 1, any value bellow $10^6$ s$^{-1}$ inhibits combustion as a direct consequence of a too high minimal uniform ignition temperature (Table 1, fourth column). This means that the layer could be ignited only with an
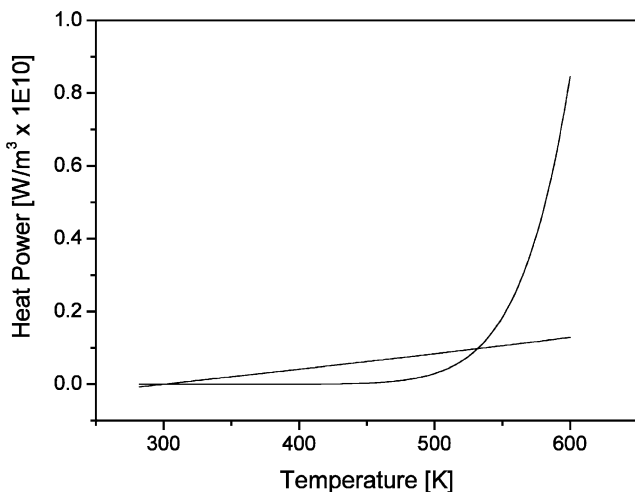
increased collision energy. For further calculations a value $A = 10^7$ s$^{-1}$ was taken. Higher values of $A$ would yield unrealistic wave fronts velocities (Table 1), far away from the range of reported values in SHS reactions [18]. This kind of upper limit for $A$ has been already observed by Ewald et al. when studying the combustion of zirconium in oxygen with a finite difference model [19]. They concluded that a linear relationship between $A$ and the wave front velocity exists.

The activation energy ($E$) is characteristic of the reaction and governs the temperature influence on the reaction rate. Several values of $E$ were intended in order to get a combustion wave. Low values of the activation energy ($E \approx 42$ kJ mol$^{-1}$, i. e.) result in a room temperature explosive reaction, while higher values ($E \geqslant 170$ kJ mol$^{-1}$, i. e.) yield a too high minimal ignition temperature ($T \geqslant 1100$ K) out of the expected range for collision induced heating [6,20]. An intermediate value, $E = 83.8$ kJ mol$^{-1}$, was selected that leads to an ignition temperature of 532 K (Table 1). Forrester and Schaffer, studying the mechanochemical reduction of CuO by Fe (a SSR, less exothermic than the one discussed in this work) reported an important reduction of the activation energy, prior to ignition, by ball milling [21]. This is perhaps the main mechanism for the reported decrease of the ignition temperature with the mechanical activation time [8]. Forrester and Schaffer go a step further using kinetics measurements to identify the rate-controlling step. The observed change in the activation energy implies a change in diffusion mechanism from that of ions in a perfect lattice ($E$ typically equal to 600 kJ mol$^{-1}$) to that of ions down short-circuit paths ($E < 200$ kJ mol$^{-1}$) [21]. An important reduction is then expected, justifying the apparently low selected value (83.8 kJ mol$^{-1}$).

If the thermal conductivity diminishes to half the initial value (53.12 W m$^{-1}$ K$^{-1}$), the reaction proceeds with a decrement in the velocity of propagation of the combustion front. A higher thermal conductivity (twice the initial value) results in a faster reaction front (Table 1). However a further increment of the thermal conductivity results in the suppression of the reaction. Obviously this is a direct consequence of the faster dissipation of the deposited energy. On the contrary, $T_i^{\min}$ does not reveal any change at all (Table 1), as expected from the fact that neither $q_s$ nor $q_c$ depends on $k$.

One way to decrease the ignition probability is by means of the addition of an inert additive. Many experiments have been reported on this subject [22]. This behavior is comprehensible because the total specific heat of the system rises while the reaction enthalpy remains the same and therefore the adiabatic temperature decreases [1]. Thereby it is important to know how much the reaction is affected by a change in $c$. The specific heat of the system was obtained as a mass



Fig. 4. Dissipated (lineal function) and generated (exponential function) specific power versus temperature.

weighted average of the reaction products; a value of 600 J kg$^{-1}$ K$^{-1}$ was used. When it was modified by a factor of two, $T_i^{min}$ did not present any change, consistent with the fact that it appears in both terms ($q_s$, $q_c$) as a scale factor. On the contrary, the exothermicity of the reaction changed (maximum temperature achieved), being increased or decreased in an inverse relation to the specific heat, according to the above discussion. Higher specific heats slows down the reaction (low wave front velocities) whereas lower ones raise it (Table 1).

The reaction enthalpy $\Delta H$, is an important parameter, due to its presence in the heat source term. Moreover it has been postulated that an adiabatic temperature higher than 1300 K is required for a SSR as opposed to a gradual reaction [5]. A change in this parameter affects the exothermicity in a direct manner. $T_0^{min}$ decreases when $\Delta H$ increases (fourth column, Table 1). This is an expected behavior that can be explained in terms of the adiabatic temperature. There is a direct relationship between the reaction enthalpy and the wave front velocity: a higher (lower) reaction enthalpy induces a higher (lower) wave front velocity (third column, Table 1). One of the consequences of ball milling is that the enthalpy stored ($\Delta H_{BM}$) in the lattice defects should be added to the reaction enthalpy $\Delta H$. Eckert et al. demonstrated that, in the specific case of fcc metals, this stored enthalpy could be as high as 50% of the heat of fusion [23]. Nevertheless, in the present case of a highly exothermic reaction, the stored enthalpy is negligible when compared to the reaction enthalpy ($\Delta H_{BM}/\Delta H = 0.66\%$).

An estimation of the heat transfer coefficient is difficult to obtain. A layer entirely surrounded by Ar, and without forced convection inside the cylinder would yield a heat transfer coefficient around 10 W m$^{-2}$ K$^{-1}$ [24]. On the other hand under ball milling conditions the layer mainly dissipates heat to the cylinder and milling tools at a faster rate. Therefore, a much higher value, 200 W m$^{-2}$ K$^{-1}$, was assumed. Increasing the dissipation rate results in an increased minimal ignition temperature (Table 1).

The layer thickness was taken as 100 μm. When the layer thickness is augmented the exothermicity increases, and $T_i^{min}$ decreases. The increased reaction exothermicity is a consequence of the decrement in the dissipation of a layer with a lower surface to volume ratio. If the layer thickness is reduced, the exothermicity lowers, but $T_i^{min}$ does not (Table 1).

The high temperature reached in this kind of reactions suggests that radiation plays a fundamental role in the energy dissipation. Taking into account the meaningful differences between product and reactive emissivities and their influence on the radiation term, we have considered a concentration dependent emissivity. Fig. 5 represents the rate at which heat energy is dissipated
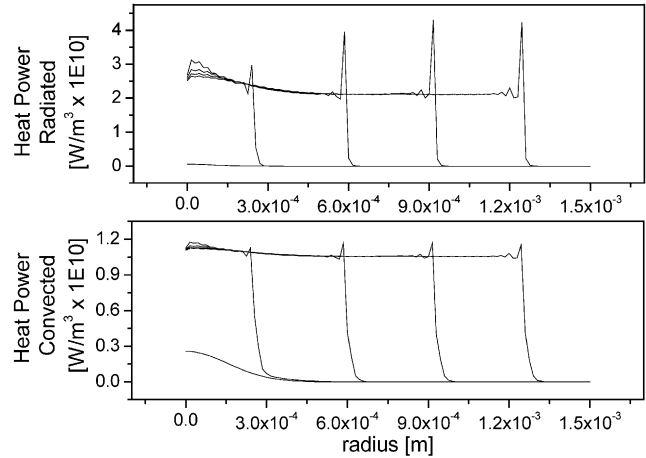


Fig. 5. Power heat dissipated by radiation and convection as a function of position after the simulated impact (time interval between consecutive fronts = 0.2 ms, front wave velocity = 1.65 m s$^{-1}$).

(radiation and convection). When these values are compared, radiation becomes the dominant mechanism. In the same figure, it can be observed that radiation shows a pronounced peak, at the wave front. This behavior is a consequence of the abrupt change in $\Delta H$ from vaporization of Iron, that is the responsible for the temperature peak around 3000 K in the temperature profiles (Fig. 2, i.e.), and the change in emissivity during the reaction, from that of Al+Fe$_2$O$_3$ ($e \approx 0.63$) to that of Fe+Al$_2$O$_3$ ($e \approx 0.25$) (Table 3). This dissipated energy is radiated in all directions in space and all the other particles receive it almost instantaneously. On the other hand, the other possible mechanism by which the rest of the sample could reach SSR is by conduction between particles. This could be a very inefficient way for powder samples due to the fact that a true contact among particles is not assured. Moreover argon, which surrounds the powder inside the chamber, has a very low conductivity (0.01772 W m$^{-1}$ K$^{-1}$). All these facts together seem to indicate that radiation, in an already ignited sample, cannot be neglected as a possible vehicle to propagate to the rest of the sample the needed additional energy to reach SSR. The dependence of ignition temperature and wave front velocity on emissivity was investigated taking the lower (upper) extreme value of emissivity on each material for $e_1$ ($e_2$), according to Table 1. Minimal ignition temperature does not present any change, as radiation is meaningless at low temperatures. However the wave front velocity depends slightly on emissivity (Table 1).

## 4. Conclusions

In this theoretical approach to self-sustained, mechanochemical reactions, induced by ball milling, we have attempted to identify the main parameters that influence

the reaction occurrence and/or its development as well as its relationship with the experimental conditions.

The kinetic parameters ($A$, $E$) exert a strong influence in the process (Table 1). A little variation (specially in the activation energy) can bring the system from the cooling down regime to the SSR condition, where collision induce heating makes possible ignition.

The minimal ignition temperature does not depend on thermal conductivity and specific heat. However both of them exerts a strong influence on the reaction front velocity.

The reaction enthalpy and its discontinuities (i.e. phase transformations) influences both the wave front velocity and the minimal ignition temperature.

The wave front velocity slightly depends on the heat transfer coefficient as well as on the emissivity. Nevertheless the former has a strong influence on the minimal ignition temperature as opposed to emissivity.

There is a slight dependence on the wave front velocity with the thickness of the layer. However a variation in this parameter has a bigger influence on the minimal ignition temperature.

It has been concluded that radiation heat flux could be a relevant mechanism for the propagation of the SSR in the ball milling process. This establishes an important difference between SHS and mechanochemical processes perhaps not sufficiently emphasized. Additional calculations about this fact as well as the contribution of the $T$ and $\eta$ dependence of $k$, $c$, $e$ and $\rho$, are in progress.

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