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Mechanically induced self-propagating combustions: Experimental findings and numerical simulation results

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Mechanically-induced combustion reactions were carried out in a transparent quartz vial. The combustion processes were followed by high-speed video recording and optical pyrometers. Depending on the vial dynamics, the powder particles were seen to gather in a periodic collective motion, behaving like a granular gas characterised by subsequent changes in its density. After ignition, a considerable increase of brightness was observed, due to the extremely rapid propagation of the high-temperature reaction to the whole mass of powder. Experimental observations find a very good correlation if compared to the results of numerical calculations simulating the particle system dynamics. Balls and powder dynamics were reproduced according to a well-known visco-elastic force scheme, while chemical conversion of each powder particle was described by a conventional nucleation-and-growth kinetics. The propagation mechanism of the reaction was studied and related to the dynamic features of the whole system.

1. Introduction

During the past four decades, mechanochemical methodologies based on Ball Milling (BM) have been successfully applied to the preparation of broad classes of innovative materials [1]. The mechanochemical transformations observed are intimately connected with the enhancement of the chemical reactivity induced by impact events [1], when powder particles are repeatedly fractured, cold-welded and deformed. Most of the transformations take place gradually, following simple asymptotic or sigmoidal curves [1–3]. However, a discontinuous chemical behaviour can also occur under milling when highly exothermal chemical systems are processed. In such cases, the gradual conversion is replaced by very fast self-propagating high-temperature combustion-like processes, generally referred to as Mechanically-induced Self-propagating Reactions (MSR) [4]. The occurrence of such reactions as well as the milling times required to ignite the self-propagating combustion depend on several factors such as mixture stoichiometry, milling intensity and powder charge [4].

In recent years, MSRs attracted considerable interest and are currently regarded as an advanced application in powder metallurgy. In the attempt to enlighten the mechanism of ignition and propagation, MSRs have been compared to the conventional Self-propagating High-temperature Synthesis (SHS) processes [4, 5], investigating the effect of the powders pre-activation on the SHS reactions [5–8]. In this work, an experimental procedure is reported for the direct observation and the analysis of the MSRs during the mechanical treatment. In connection, a numerical modelling was developed to simulate the granular flow inside the moving vial. The particulate dynamics experimentally observed is compared to the model predictions in order to point out the basic features of the combustion propagation mechanism.

2. Experimental findings

MSR trials were carried out on a Spex Mixer/Mill mod. 8000, operating at 875 rpm, i.e., at 14.6 Hz of the vial frequency. A quartz cylinder (QSIL-Quarzschmelze Ilmenen GmbH, Germany) was machined on purpose, with the same dimensions of the standard steel vial, 5.8 cm in length and 3.8 cm in diameter. The cylinder we used as a milling reactor was sealed under

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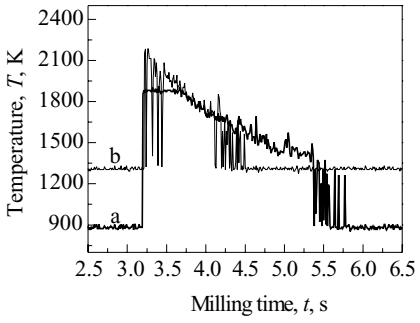

Figure 1 Outputs of the infrared thermometers used to monitor the temperature of the moving vial.

high-purity Ar atmosphere with hardened steel covers and special leak proof o-rings. A single ball with a mass of 7.74 g and a diameter of 12.0 mm was employed with a powder batch of 8 g of the mixture $Ti_{70}C_{30}$. Two high-speed infrared thermometers (Land System 4 Fibroptic-Land Infrared Ltd, England), operating in the ranges 873–1873 K and 1273–2873 K respectively, were employed. Their outputs as registered during the course of the reaction are reported in Fig. 1. It is worth noting that the maximum temperature is around 2183 K, a value relatively close to the adiabatic one $T_{ad} = 1991$ K. This implies that the Ti particles melt during the process. The oscillations in the thermographs are due to the vial motion and the consequent periodic displacement of the burning powders.

High-speed image acquiring systems, the Motionscope 8000 S (Redlake Imaging, Morgan Hill, CA) and the SpeedCam Mod 2000 (Weinberger Deutschland GmbH, Karlsruhe G), were used to record the top and lateral views of the vial during the milling process. Sampled images were analysed with Redlake MotionScope PCI 2 2.20 software. A typical sequence of images, showing the ignition and the propagation of the MSR inside the moving vial, is reported in Fig. 2. After a few hours of mechanical treatment, small, isolated light spots are observed which quickly disappear. The number of light spots—and apparently their life-times—gradually increase until a local

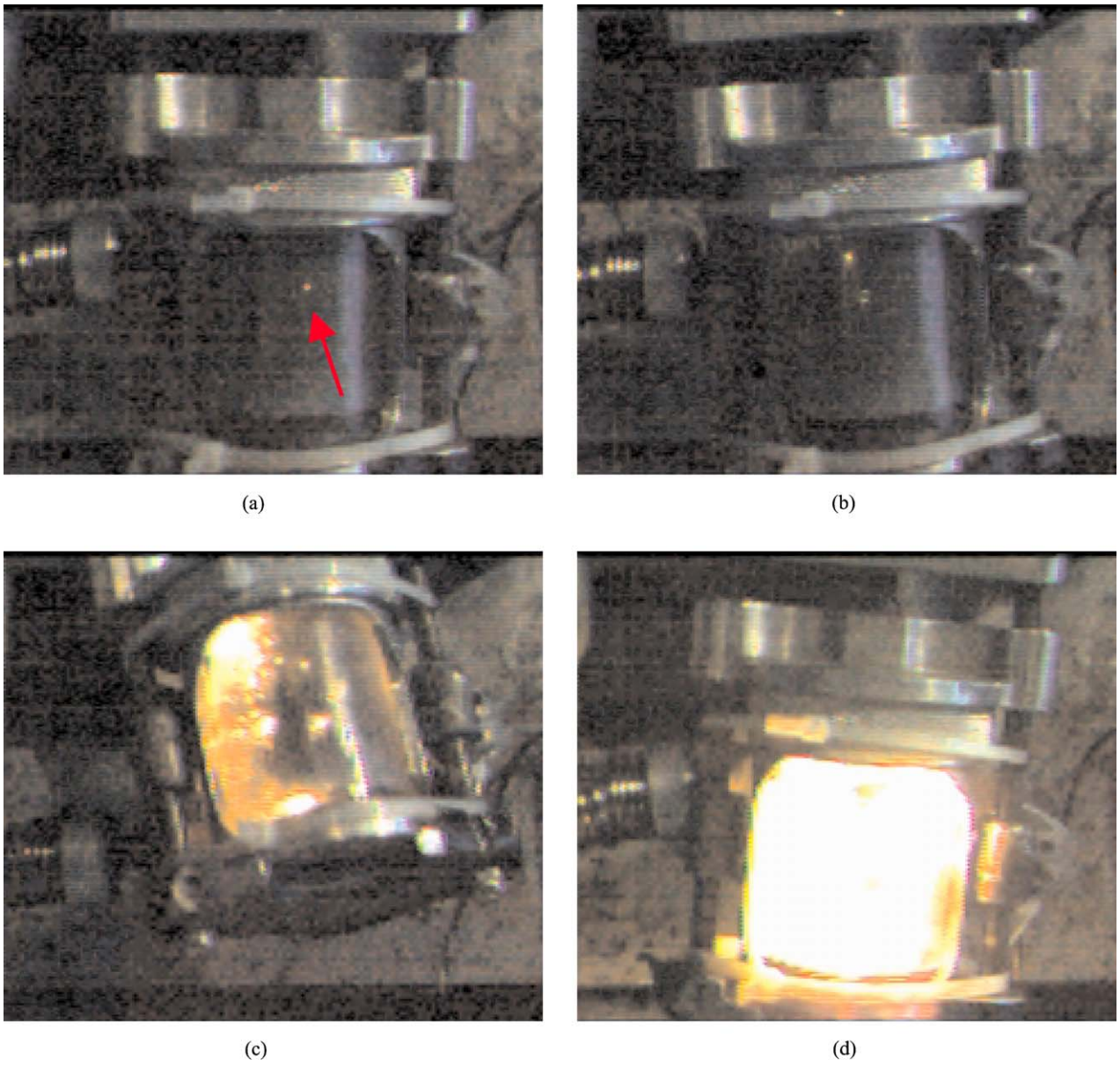

Figure 2 A direct view of the ignition and the propagation of the MSR during the course of the mechanical treatment.

combustion process is ignited. Favoured by the rapid motion of the powders within the vial, the process rapidly propagates to the whole mass of powders and the maximum brightness is achieved after about 355 ms from ignition. The whole combustion process takes approximately 400 ms to reach completion.

The brightness due to the combustion process permits to observe the ball and powder motion inside the cylinder. The particles move *in phase* with the single milling ball and behave like a granular gas undergoing periodic changes in its density due to the reciprocating vial motion. The granular body in its whole follows almost regular trajectories between the opposite vial bases, even if the dynamics of each particle is presumably very complex. The propagation of the combustion reaction seems to be strictly connected with the granular flow observed. The periodic "densification" of the granular gas favours the contacts among particles, thereby increasing the collision probability and so favouring the propagation of the combustion reaction. These experimental observations have been used as a guide for the numerical calculations.

3. Numerical calculations

The system motion is described referring to an inertial Cartesian system, centred on the fulcrum of the mill mechanical arm, and a non-inertial system, moving with the vial and with the origin at the vial centre. The trajectories of ball and powder particles are described in the non-inertial reference system as a function of the 3-dimensional periodic swing of the mechanical arm. Full details are reported elsewhere [9, 10].

In the reconstruction of the system dynamics, the effects of normal and tangential impact forces were simulated by resorting to the so-called Discrete Element Method (DEM) [11]. In this work, tangential forces were neglected for sake of simplicity, resulting smaller than the normal ones. Normal impact forces were expressed according to the following equation:

$$F_{\mathrm{n}} = -k_{\mathrm{n}}\xi - \gamma_{\mathrm{n}}\mathrm{d}\xi/\mathrm{d}t \qquad (1)$$

F_{n} simply represents the force of a damped harmonic oscillator with terms of repulsion and dissipation that allow for modelling inelastic collisions. The constant k_{n} represents the elastic contribution, γ_{n} is a damping coefficient and ξ is the deformation of the colliding surface [11].

We simulated a mono-dispersed system containing 5×10^3 spherical particles, each of mass $m_{\mathrm{p}} = 7 \times 10^{-4}$ g and diameter $d_{\mathrm{p}} = 6 \times 10^{-4}$ m. A single milling ball, with mass $m_{\mathrm{b}} = 8$ g and diameter $d_{\mathrm{b}} = 1.24 \times 10^{-2}$ m, was used. Force parameters are quoted in Table I. A milling frequency $\nu = 14.58$ Hz was employed. Under such conditions, the ball experiences an average impact restitution coefficient $e_{\mathrm{n}} \approx 0.5$. The conventional Verlet algorithm is used to integrate the equations of motion with a time step $\delta t = 5 \times 10^{-6}$ s [12].

Starting from a static equilibrium configuration, we leave the system free to reach a steady dynamic state.

TABLE I Force parameters employed in the numerical simulations. The cases of ball-vial, particle-vial, ball-particle and particle-particle interaction are distinguished

Vial height, h (m)	0.029
Vial base radius, r_{g} (m)	0.019
Ball radius, r_{s} (m)	0.0062
Milling frequency, ν (z)	14.58
Hooke's contant particle-particle, k_{p} (J m^{-2})	3.622×10^{-2}
Damping coefficient particle-particle, γ_{p} (J s m^{-2})	4.85×10^{-3}
Hooke's constant ball-particle, k_{s} (J m^{-2})	5.5452×10^{-1}
Damping coefficient ball-particle, γ_{s} (J s m^{-2})	4.85×10^{-3}
Hooke's constant ball-vial wall, k_{sw} (J m^{-2})	4.14×10^{6}
Damping coefficient ball-vial wall, γ_{sw} (J s m^{-2})	3.622×10^{2}
Rate reaction constant, k (t$^{-\mathrm{n}}$)	6.8645×10^{2}
Avrami exponent, n	1.649
Conversion grade range, α	0.3–0.7
Minimum distance for the propagation, d_{ig} (m)	7×10^{-4}

This occurs in about 1 s. It is stipulated that single particles represents a composite material which reflects the starting mixture composition. Ignition is simulated by imposing that inside a randomly-chosen particle the transformed fraction begins to increase with a given rate. Different mathematical expressions can be used to describe the transformation. We used a conventional Johnson-Mehl-Avrami-Erofeev kinetics

$$\alpha = 1 - \exp(-kt^{\mathrm{n}}) \qquad (2)$$

where α is the conversion grade, $k = 6.86 \times 10^{-2}$ s$^{-1/\mathrm{n}}$ the rate constant, t the time and $n = 1.65$ the Avrami exponent. The values for k and n were estimated from literature data [13]. It is also stipulated that a certain transformed fraction corresponds to a certain increase in the temperature of the single reacting particle under adiabatic conditions. Then, two simple conditions rule the propagation of the reaction from reacting to non-reacting particles: (i) the distance between a reacting and a non-reacting particle must be smaller than $d_{\mathrm{ig}} = 7 \times 10^{-4}$ m and (ii) the reacted fraction α of the igniting particle must ensure a burning temperature above the ignition temperature T_{ig}. In this work, we chose a $T_{\mathrm{ig}} = 1993$ K. The two rules undoubtedly oversimplify the propagation mechanism and introduce a certain degree of arbitrariness. However, even such a simplified model seems to be able to satisfactorily represent the basic features of the reaction propagation during the mechanical treatment.

At the beginning of the simulation, a rather confuse and irregular dynamics is observed. Such a regime rapidly disappears to be replaced by a relatively ordered flow of particles travelling between the opposite vial bases. After a relaxation time of about 1 s, the granular gas reaches a steady state, characterised by a high degree of periodicity and regularity, comparable to the one experimentally observed. This is clearly shown by the statistical distributions of the powder particles positions along the vial axis reported in Fig. 3 together with the corresponding vial positions. It is possible to appreciate the elongation of the granular gas when the particles move freely from one base to the other and the compression when they collide with the accelerating vial. In spite of that, the motion of each powder

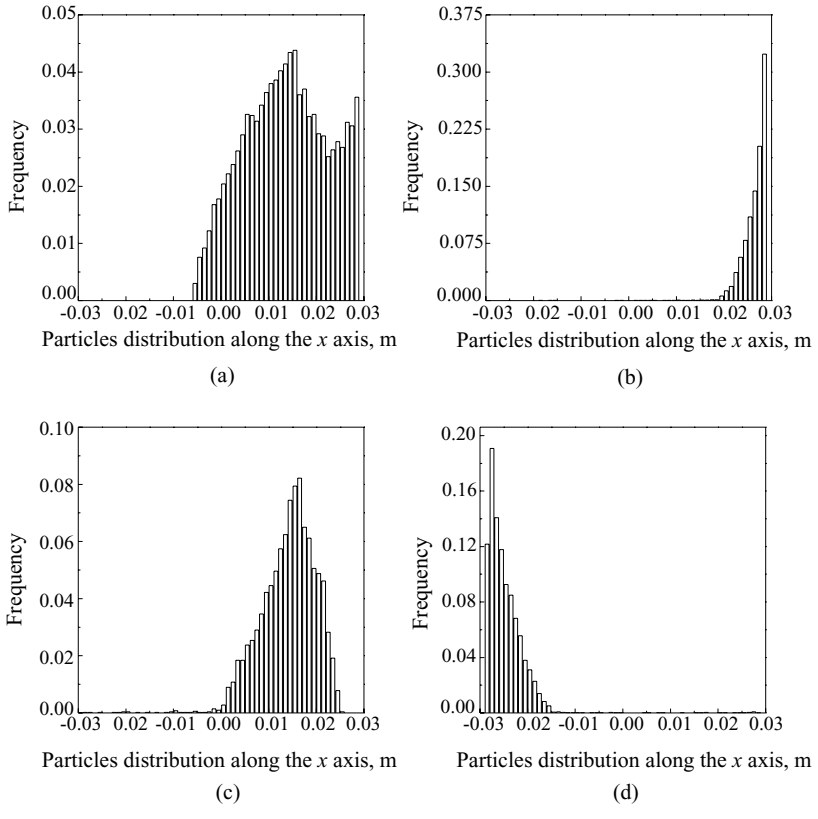

Figure 3 Statistical distributions of powder particles along the vial axis at four different moments of the vial cycle.

particle is complex and its dynamics has been proven to be chaotic [14].

The reaction propagation can be easily followed by evaluating the number of particles ignited at each integration step. One or two vial cycles are necessary for the reaction to propagate and, on average, about the 95% of the powder particles is ignited within 0.083 s, as it can be seen in Fig. 4 where the number of reacting particles is reported versus the elapsed time. Notice the times at which the vial reverses its course. It appears that particle ignition preferentially occurs when the granular gas is compressed against one of the bases, i.e., after the inversion of the vial motion. This is proven by the occurrence of peaks in the number of ignited particles timed with the vial frequency. The sequence of images reported in Fig. 5 offers a direct view of the process to be compared with the experimental one in Fig. 2. These images were taken from one of the several animations produced in order to clearly visualize the granular gas dynamics.

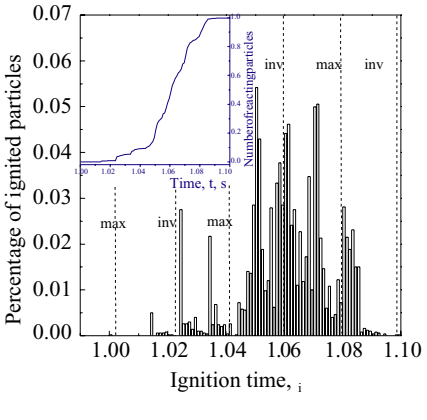

Figure 4 Ignition times and number of reacting particles during the mechanical treatment.

4. Concluding remarks

The experimental and numerical investigations performed reveal novel and appealing aspects of the dynamics of the particulate during the mechanical treatment carried out in milling machines. Contrary to the previously developed "sweeping" model approach [15], powder grains do not behave as a "particle gas". The collective motion of powder particles gives rise, instead, to a highly organised granular flow undergoing a dynamics entirely determined by the vial accelerations. Except for short-lived transient phenomena, the granular flow dynamics attains a steady state characterised by an ordered and periodic motion of the particulate between the opposite vial bases.

Numerical simulations are able to qualitatively reproduce the main features of the ball and powder dynamics. With regards to the ball dynamics, an average impact velocity of about 4.9 m s^{-1} is obtained, with a difference between experimental and predicted values of about 15%. The predicted ball trajectory along the cylindrical reactor wall is also in a good agreement with the direct experimental observation.

The propagation of the combustion reaction appears to be strictly related to the milling dynamics. The numerical simulations, even if performed under oversimplified conditions, reproduce the main features of the combustion process experimentally observed. The reaction times predicted by numerical simulation are relatively comparable with the ones

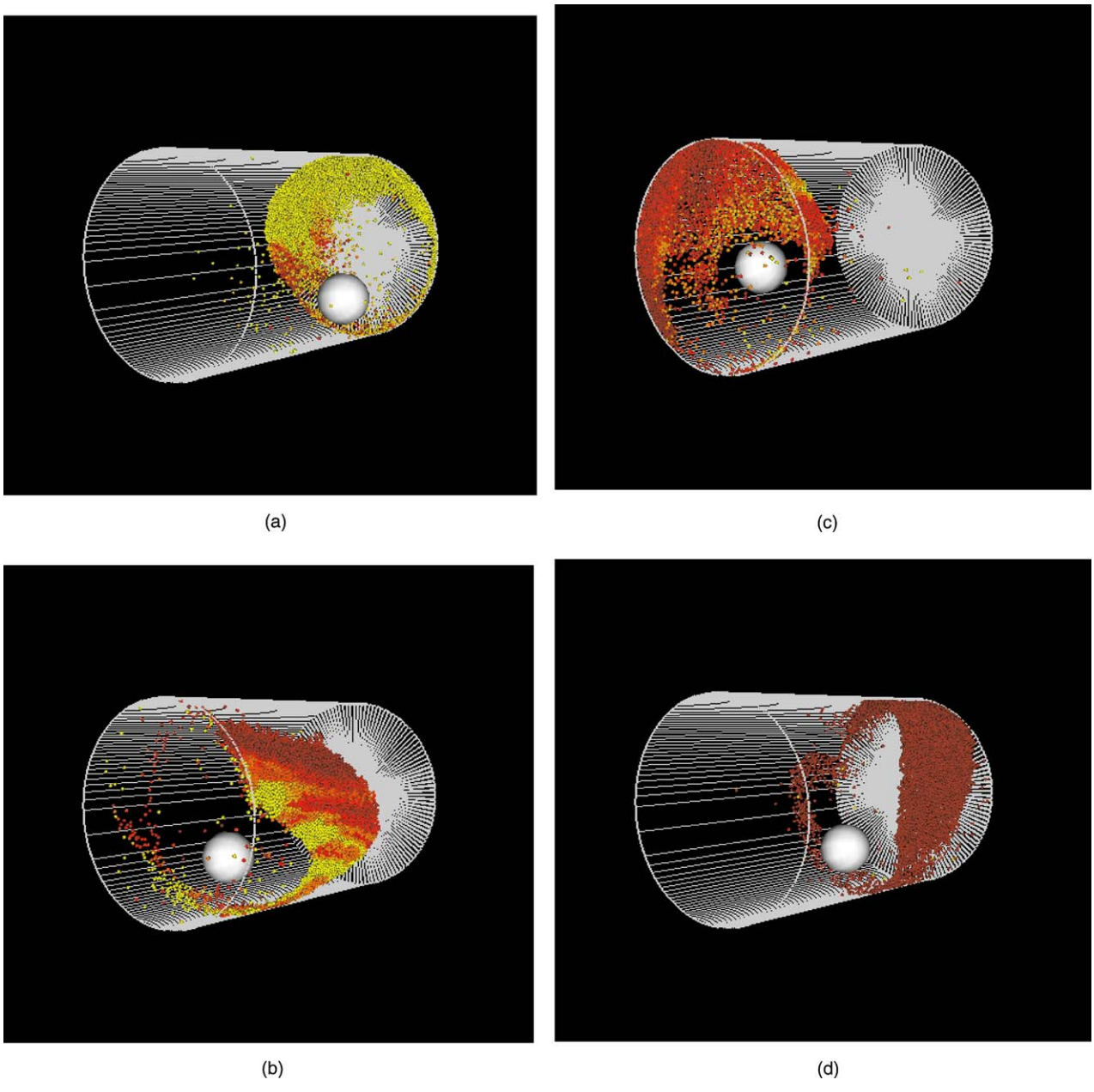

Figure 5 The granular flow inside the moving vial.

experimentally observed. In the experimental case the reaction is completed in about 400 ms, while in the numerical case a reaction time of about 100 ms was found.

Percolation scenarios are most likely to be invoked in order to understand the intimate aspects of the propagation mechanism. The results discussed in this brief report are preliminary and need to be extended in order to improve the comprehension of milling dynamics and approach a higher level of understanding. In particular, poly-dispersed systems should be considered and temperature fields taken into account.

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