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Oxidation of detonation nanodiamonds in a reactive formulation

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ABSTRACT

Nanodiamonds have been used as reducing agent in energetic compositions. The reactive formulations prepared by mixing detonation nanodiamond (DND) with potassium chlorate (PC) decompose according to two combustion modes, *i.e.* continuous or intermittent, depending on the nanodiamond proportion and pressing level used to shape the pellets. The analysis of a series of experimental results has led to build a predictive prevalence diagram of the combustion mode. In the continuous combustion domain, the reaction rate varies as a power law of the nanodiamond content: $V = V_0[\chi_{DND}]^{-\alpha}$. The pre-exponential factor gives an interesting estimate of the self-sustaining rate of the oxidation of pure nanodiamond loose powder (≈0.8 mm/s). Furthermore, the increase of the nanodiamond ratio in the composition makes the burning more regular, and slows down the combustion rate. The effect of pressing on the morphology of DND/PC compositions was intensively studied and led to the understanding of the combustion mechanisms. The porosity of interstitial DND powder acts as a thermal shield and favours the diffusion of the gaseous species released by the combustion in the fresh composition, leading to a convective propagation. This mechanism accounts for the continuous combustion. The thermal conductivity of DND powder measured experimentally is three orders of magnitude smaller than a typical value for bulk diamond ($\lambda_D = 500\ W \cdot m^{-1} \cdot K^{-1}$). This result is in agreement with the values calculated from Maxwell's model, for spherical DND particles in a continuous fluid (air).

1. Introduction

DNDs have a wide range of applications in various domains of physics, chemistry and biology [1–6]. Amongst the most atypical applications for this material, their use in pyrotechnic compositions has been studied a few years ago [7]. The unconventional pyrotechnic behaviour of the compositions DND/PC was observed for the first time in our laboratory. These reactive formulations were prepared from the DND synthesized and purified according to the process developed by Pichot et al. [8]. The oxidation of DND powder in air occurs when the temperature exceeds 420 °C. In other words DNDs oxidize more readily than bulk diamond, due to the small size of the elementary particles (4–5 nm) and to the surface functional groups that facilitate the activation of the combustion. Interestingly, the DND enclosed in an aramid polymeric coating oxidizes at a higher temperature than pure DND [9] which shows that surface õoxygenated groups have a determining effect on the initiation and the subsequent propagation of the oxidation reaction.

In DND/PC compositions, the reaction can be either continuous or intermittent, and has some similarities with the oscillatory combustions described by Corbel et al. [10]. But contrary to the latter, the intermittent combustion mode in DND-based composition does not self-sustain and needs to be activated permanently, for instance with a continuous wave laser. In this paper, an experimental criterion permitting to predict the combustion mode of DND/PC compositions is proposed taking into account the physical properties of the DND.

The analysis of the continuous combustion has given valuable information on the fast oxidation of DND and has permitted one to determine its autopropagation rate. To the best of our knowledge, the only value of oxidation rate mentioned in the literature is provided by Gaebel et al. [11], who have performed the etching of 50 nm diameter nanodiamonds by a mild oxidation in air at 600 °C. Working in such conditions, these researchers succeed to reduce progressively the size of diamond nanoparticles, without reaching the oxidation runaway. For this reason, the etching speed (≈10.6 nm/h) measured by these authors is eight orders of magnitude slower than the value reported herein (≈0.8 mm/s) which corresponds to the abrupt combustion of DND powder. Despite the kinetics of oxidation of nanodiamond being strongly dependent on the oxidation conditions, we assume that the value which is found in this study is absolute and corresponds to the self propagated and the maximum oxidation rate of nanodiamond.

Pure diamond has a thermal conductivity ranging from 2000 to 2200 $W \cdot m^{-1} \cdot K^{-1}$ at 293 K [12] which makes it one of the most conducting materials. The thermal conductivity of pure DND powder was measured in order to assess whether it could play a role in the very particular reactivity of DND/PC compositions.

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2. Materials and methods

DND powder is prepared at our laboratory by the detonation of a hexolite charge, containing 70 wt.% of trinitrotoluene and 30 wt.% of hexogen. The purification of detonation soot is carried out by the process developed by Pichot et al. [8], involving a chemical treatment by the fluorinated *aqua regia* ($HF/H_2O/HNO_3$) followed by an isothermal oxidation in air. The purified nanodiamonds have a specific BET area of 373 m^2/g and a density of 3.18 g/cm^3 corresponding to a mean particle diameter of 5.05 nm. The elementary analysis of the sample has showed that the contents in carbon, oxygen, hydrogen, nitrogen and mineral ash (TiO_2 and SiO_2) were respectively equal to 80.42, 12.82, 0.74, 2.42 and 3.6 wt.%.

The mixing of potassium chlorate (2–60 μm) with the DND nanopowder (5 nm) was carried out in petroleum ether. The mixture was homogenised by applying simultaneously a magnetic stirring and an ultrasonic treatment for 15 min. Petroleum ether was evaporated at 60 °C under reduced pressure. The DND content of the compositions was varied from 10.2 to 47.5 wt.%, with a theoretical stoichiometry of 15.9 wt.%, corresponding to the reaction balanced with the formation of carbon dioxide.

The specific BET area was measured by nitrogen adsorption, using as SA 3100 Surface Area Analyzer from Beckman Coulter. Prior to measurements, pure DND samples were outgassed by helium flushing at 225 °C for 15 h. The DND/PC compositions, which have a lower thermal stability, were treated under vacuum at 150 °C for 45 min.

The loose DND/PC powders were pressed into 50 mg cylindrical pellets with a diameter of 4 mm, using pressures from 12.3 to 278.5 MPa. In a typical combustion test, the pellet is ignited with a CO_2 laser wave working in continuous mode with a 9 W output power. The combustion modes and rates were determined from high speed videos recorded at 4000 frames per second with a Photron camera.

A thermal conductivity analyser from C-Therm Technologies was used to measure the conductivity and the effusivity of pure DND in powder and in pressed porous discs with a diameter of 18.5 mm and a weight of 0.5 g. The DND loose powder has an apparent density of about 11.7% of the theoretical maximal density (TMD); the porosity can be slightly decreased by pressing the powder from 88.3% to 76.9% (*i.e.* 11.7 to 23.1% of the TMD). When the pelletizing pressure is too low (*e.g.* P = 4 MPa) the discs are brittle and cannot be handled. On the contrary, strongly pressed samples (*e.g.* P = 27 MPa) have a satisfying mechanical resistance, but spalls form on their surface when they are expelled from the compression mould. The surface roughness does not permit one to measure the conductivity accurately, due to the poor contact between the disc and the calorimetric cell. The experiments on the DND/PC compositions, which would require pressing relatively large samples (0.5–1.5 g), cannot be safely carried out, due to the pyrotechnic hazard arising from the high sensitivity to friction of these compositions.

3. Results and discussion

The DND loose powder used for this research had an apparent density of 0.14 g/cm^3. Due to this characteristic, the DND powder totally encloses the micrometric PC particles and fills the interparticle void. Each individual PC particle is initially considered as defect-free, with a density approximating the one of pure PC. The specific area and the porosity ratio of a DND/PC (28/72 wt.%) composition pelletized at different pressing levels linearly decreases with the shaping pressure (Fig. 1). On the other hand, the specific area of pure DND pellets does not vary with their packing density (inset Fig. 1). These results show that DND particles penetrate into large PC particles which disintegrate into smaller particles that fill the interparticle voids of the DND powder, leading to a genuine nanocomposite material.

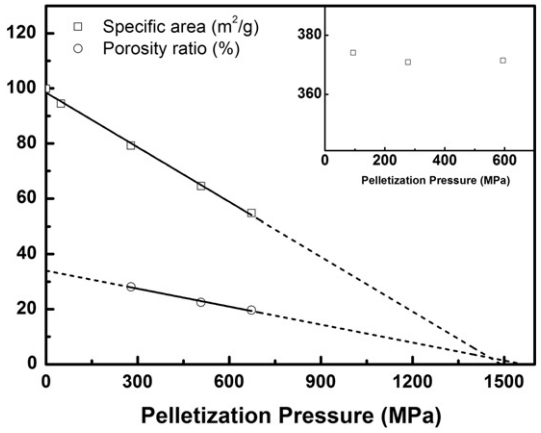

Fig. 1. Evolution of the specific area and porosity ratio of a ND/PC (28/72 wt.%) composition according to the pressure used to form pellets, inset: evolution of the specific area of pure DND.

In the case of loose DND/PC compositions the ratio (Γ_{LP}) between the DND (V_{DND}) and the PC (V_{PC}) volumes, depending on the DND weight proportion (X_{DND}) can be expressed according to Eq. (1):

$$\Gamma_{LP} = \frac{V_{DND}}{V_{PC}} = \frac{\rho_{PC}}{\rho_{DND}} \times \frac{X_{DND}}{1-X_{DND}} \approx 16,6 \times \frac{X_{DND}}{1-X_{DND}} \quad (1)$$

where, ρ_{PC} is the bulk density of potassium chlorate (2.33 g/cm^3) and ρ_{DND} the apparent density of nanodiamond powder (0.14 g/cm^3).

Depending on the composition, the DND volume is 1.9 to 15.0 times higher than the one of PC, which shows that the DND powder really fills the PC interparticle volume in the formulation range studied.

When DND/PC compositions are pressed, the Γ ratio ($<\Gamma_{LP}$) can be calculated from the geometrical features of the cylindrical pellet as follows, making the approximation that the penetration of the DND into the chlorate particle, negligible:

$$\Gamma = \frac{V_{DND}}{V_{PC}} \approx \frac{\pi \Phi_{Pel.}^2 h_{Pel.} \rho_{PC}}{4 m_{Pel.}(1-X_{DND})} - 1 \quad (2)$$

where $\Phi_{Pel.}$, $h_{Pel.}$, $m_{Pel.}$ are respectively the diameter (cm), the height (cm) and the weight (g) of the pellet; and ρ_{PC} is the density of potassium chlorate ($\approx$2.33 g/cm^3).

Moreover, the Γ ratio is a function of two variables, *i.e.* the pressure (P) used to pelletize the composition and its DND content (X). The values of Γ have been calculated for a series of samples, for which the values of P and X were varied in the ranges mentioned in the Section dealing with

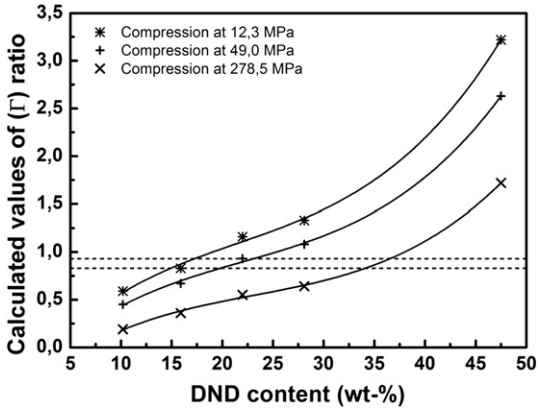

Fig. 2. Curve network representing the evolution of Γ according to the DND content (X) and to the pressure (P) used to prepare the pellets.