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High temperature reaction behaviour of nanoporous silicon based explosive formulations

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Abstract

Nanoporous silicon based explosive formulations are currently being explored, with an aim of replacing lead based primary explosives. Nanoporous silicon combines with oxidisers to form energetic mixtures. It is known that the reactivity of such explosive formulations is influenced by the amount and type of oxidiser used in combination with porous silicon. Related studies have shown that, on exposure to ambient air, freshly etched porous silicon becomes progressively oxidised. The shelf life of porous silicon based explosive formulations is influenced by various factors including the level of oxidation of the nanoporous silicon. More resent work, on porous silicon explosive formulations, highlights degradation of the thermal sensitivity of such formulations after a prolonged storage. A new test method has been developed which distinguishes the difference in response characteristics between energetic mixtures. In this study, different oxidisers were used to manufacture nanoporous silicon based explosive formulations. Reported results quantify ageing characteristics and also show the influence of density on the reactivity of nano-porous silicon formulations, when subjected to thermal stimuli.

Keywords: *Ageing characteristics, density, explosive, high temperature reaction, nanoporous silicon*

1 Introduction

The use of nanoporous silicon in exploding or detonating compositions only started in 2002 after the accidental discovery of the explosive property of porous silicon [1]. The subsequent development work of nanoporous silicon-based explosive formulations aimed to replace lead-based explosive formulations like lead azide and lead styphnate [2]. Lead-based primary explosives are used in both the military and commercial explosives industry. Porous silicon-based explosive formulations include mixtures of nanoporous silicon with a wide range of oxidizers that includes perchlorates and nitrates. Loni et al. also showed that, on exposure to ambient air, freshly etched porous silicon becomes progressively oxidised [3]. The rate of oxidation increases with the addition of oxidisers. Internal work related to this study have shown that state of oxidation of freshly etched porous silicon influence the reactivity of porous silicon explosive formulations. Quantifying these differences in reactivity remained a challenge. This study introduces a novel method of characterising and quantifying the thermal reactivity of the porous silicon explosive mixtures, when subjected to thermal stimuli. This study further describes the influence of oxidation on the relative reactivity of porous silicon explosive formulations, ageing characteristics and the influence of density on the reactivity of nanoporous silicon formulations

2 Experimental

The test samples were evaluated by exposing them to heat. A modified laboratory hotplate was used as the primary heat source for this set of experiments. The hotplate was modified in such a manner that the temperature could be controlled to be within a tolerance of ± 1.0 degree Celsius (°C). The modified hotplate was calibrated by measuring the temperature inside an aluminium cup in 5 second (s) time intervals (results are not presented in this paper). The temperature of the hotplate was pre-set and allowed to stabilise at 400 °C.
A sample, of the formulation to be evaluated, was put on a specific position of the heat source. A noise meter (decibel meter) was positioned 150 millimetres (mm) horizontally away from the sample and 140 mm up, to be diagonally above the sample. The decibel meter recorded the noise (in decibels (dB)) generated by the reaction. The time taken, for a

reaction to occur, was measured using a standard, calibrated stop watch (aided by standard rate videography). This time is the time measured from the instant the sample was placed on the hotplate until the moment a reaction is obtained. Figure 1 show the test set-up.

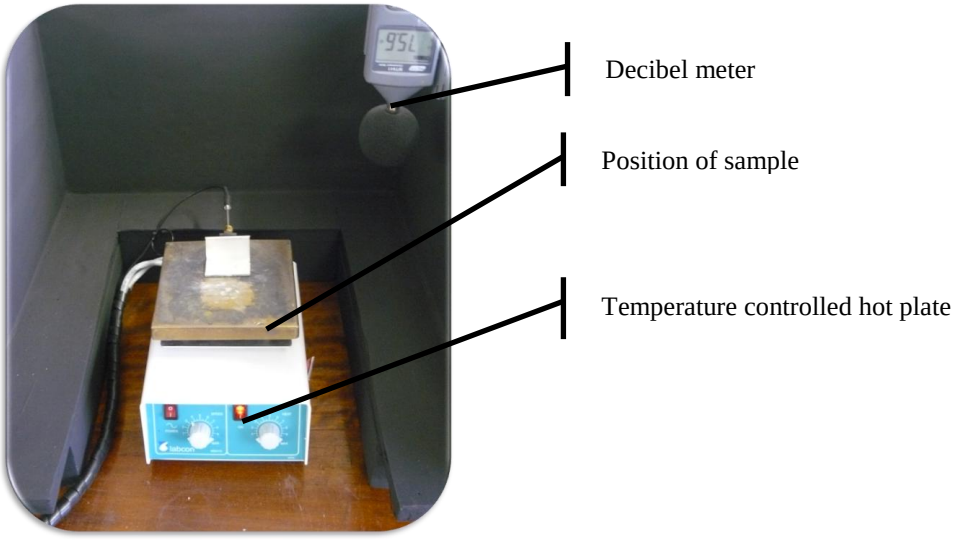

Fig. 1: Generic thermal reactivity test set-up

Variables that could influence the results include sample mass, silicon (Si) to oxidiser ratio and the rate of temperature change. These variables were controlled by; keeping the rate of temperature change as constant as possible, predetermining the Si to oxidiser ratio and keeping this ratio constant. The optimum sample mass, which showed the least effect on the noise reading, was determined to be between 0.030 gram (g) and 0.040 g and was used for all the samples that were tested. Evaluations were conducted to determine the difference in reactivity of nanoporous silicon explosives formulations prepared using aged nanoporous silicon. Relative reactivity evaluations were also conducted on aged nanoporous silicon based explosive formulations. The effect of density on the thermal reactivity of the nano-porous based explosive formulations was also determined. Porous silicon membranes were prepared from 6 inch silicon substrates by electrochemical anodisation using HF-methanol electrolyte. The membranes were subsequently ball-milled in an air environment, using a zirconia grinding medium. This method yielded a particle size distribution where 10 percent (D10) distribution is equal to or less than ($\leq$) 4µm; 50% D50 $\leq$ 24µm and; 90% D90 $\leq$ 86µm. Thermal oxidation of powders was carried out in normal air, using a oven with borosilicate glassware. The temperature and time the nanoporous silicon were exposed to, were varied, in order to obtain nanoporous silicon samples that were at different states of oxidation [4]. The properties of the artificially aged nanoporous silicon are given in Table 1.

Nanoporous silicon explosive formulations were prepared by mixing selective oxidisers with the nanoporous silicon. Sodium perchlorate ($NaClO_4$) and pentaerythritol tetranitrate (PETN) were selected as oxidisers. Saturated solutions of the selected oxidizers were prepared by dissolving the oxidiser in dry, high purity acetone. The Sodium perchlorate were dried under vacuum at 50 ^{0}C for 24 hours to ensure that it was dry before being used to prepare the afore mentioned solution.

Table 1: Properties of oxidised porous silicon powder samples

Sample	Pore volume ml/g	Surface area m^2/g	Wt% O (EDX)
PDSi-A	0.982	305	-
PDSi-B	0.982	305	1.3
PDSi-C	0.918	290	5.9
PDSi-D	0.772	245	23.3

The solvent, containing the oxidizer, was added to the porous silicon in such a manner that the selective mixtures of different oxidiser to fuel ratios could finally be obtained. The mixtures were air dried (through evaporation) whilst being refined simultaneously by hand using a dry, bone spatula. Refining continued until a consistently fine powder was obtained. After refining, the formulations were dried in an oven under vacuum (0.7 mega pascal (MPa)) for 3 hours at 55 ^{0}C.

To determine the reactivity of aged nanoporous silicon explosive formulations two different oxidisers were used to manufacture eight different explosive formulations. These formulations were prepared as described earlier using sodium perchlorate (SP) and nitriminoterazole (Tet) as oxidisers. These formulations were stored in a desiccator for a period of one year and tested at different time intervals. The formulations evaluated are given in table 2.

Table 2: Explosive Formulations used in ageing characterization evaluation

Formulation	Oxidiser	Binder	Tet*	Oxidiser to Porous silicon ratio
T1	Tet	Wax (18 %)	-	3 : 1
T2	Tet	Nitrocellulose (NC) (11%)	-	3 : 1
T3	Tet	-	-	3 : 1
T4	Tet	Wax (5 %)	75 %	3 : 1
N1	SP	Wax (18 %)	-	1.4 : 1
N2	SP	NC (11%)	-	1.4 : 1
N3	SP	-	-	1.4 : 1
N4	SP	Wax (5 %)	75 %	1.4 : 1

*Additional nitriminoterazole was added to the nano-porous silicon based explosive formulation

The effect of density on the thermal reactivity of the nano-porous based explosive formulations were determined using formulation T3 (refer to table 2). The selected amount of explosives was weighed (approximately 0.04 g) and consolidated using a hand-press. Samples of the explosive formulation were consolidated in such a manner that the following densities were obtained: 0.71, 1.99, 2.07, 2.11, 2.22, 2.25, 2.52 and 2.60 gram / cubic centimetre (g/cc).

To better compare the difference in reactivity of the nanoporous silicon based explosive formulations, a relation was developed between the noise generated by the reaction and the measured time to reaction. The postulated relation is shown in equation 1;

$$R_r=\delta\alpha \tag{1}$$

With R_r being the *Relative reactivity*, δ is the *noise* measured in decibels and α is the time to reaction measured in seconds. The term relative reactivity used here refers to a level of reactivity relative to a specific temperature (the initial temperature of the hotplate). Equation one, however, did not provide a distinct discrimination between the results of the different samples evaluated. The postulated argument is based on the understanding that, the higher the noise that has been produced the more brisant the explosive formulation is assumed to be. The heat sensitivity of the formulation is a function of the time it took the formulation to react upon exposure to thermal stimuli. A short time to reaction is indicative of a heat sensitive formulation. The R_r of a formulation that produced high noise and a long time to reaction cannot be higher when it is compared to a formulation that produced high noise and a short time to reaction. This problem was overcome by increasing the difference between the noise and time values in the equation. The noise was increased tenfold, and the inverse of the time measurement was used. This gave equation 2:

$$R_r=\delta^{10}\,(1/\alpha) \tag{2}$$

Equation 2 was used to calculate the relative reactivity using the noise and time data obtained from the evaluations conducted.

3 Results

The R_r results obtained from the evaluation conducted on the nanoporous silicon explosive formulations prepared using the aged nanoporous silicon are given in Table 3.

The different formulations evaluated show discriminating results with respect to noise and time. The level of oxidation of the nanoporous silicon has an effect on the reactivity of the nanoporous silicon-based explosive formulations evaluated. Beckman noted, as early as 1995 that porous silicon films underwent pronounced ‘ageing’ when stored in ambient air for a prolonged period of time [5]. The speed and the extent to which the oxidation of the silicon occurs

depends upon many factors such as intensity of light, level of humidity and level of highly oxidising airborne species [6]. Previous studies have shown that the magnitude of influence on the reactivity of the Si / oxidiser mixtures is not only a function of the level of oxidation of the nanoporous Si, but also by the type of oxidiser used. The difference in noise and time to reaction can primarily be ascribed to ageing (oxidation) of the formulations. The results shown in Table 3 demonstrate the influence of oxidiser used in the explosive formulation as well as the effect of the pre-oxidised nanoporous silicon on the reactivity of the explosives formulation

Table 3: R_r results of nanoporous silicon based explosive formulations prepared from aged silicon

	PETN based nanoporous silicon explosives formulation			SP based nanoporous silicon explosives formulation		
Sample	Time (s)	Noise (dB)	Relative reactivity (R_r) x10^{17}	Time (s)	Noise (dB)	Relative reactivity (R_r) x10^{17}
PDSi-A	3.228	62.00	2.60	11.90	105.60	145.00
PDSi-B	4.488	107.26	449.00	9.19	104.68	172.00
PDSi-C	6.068	62.00	1.38	12.07	107.10	165.00
PDSi-D	9.076	62.00	0.93	-	-	-

- Denotes No Reaction

Results of the R_r results of the Ageing evaluation of nanoporous silicon based explosive formulations are shown table 4 (Nitriminietrazole (Tet) used as oxidizer) and table 5 (SP used as oxidizer).
Formulations T1 to T4 and N1 to N4 were used to show the change in reactivity over time. The R_r results (Table 4) indicate a distinct difference in reactivity when T1 is compared to T2, T3 and T4. Difference in reactivity was also noted when N1 is compared to N2, N3 and N4. Nanoporous silicon based explosives formulations, where SP was used as the oxidiser, show a rapid decline in reactivity (Table 5). Formulations N3 (no binder) were non responsive after 24 days. In an attempt to extend the shelf life of formulations N1 and N2 different binders were used (Nitrocellulose and synthetic wax). The results obtained indicate no significant increase in the shelf life of these formulations (Table 5). Formulation N 4 showed a significant decline in reactivity over 380 days but not a complete deprivation of reactivity.

Table 4: R_r results of nanoporous silicon based explosive formulations

	T1			T2			T3			T4		
Days	Time s	Noise dB	R_r x10^{17}	Time s	Noise dB	R_r x10^{17}	Time s	Noise dB	R_r x10^{17}	Time s	Noise dB	R_r x10^{17}
0	4.71	62.26	1.86	3.65	74.10	13.70	5.19	84.00	33.70	4.6	76.23	14.44
5	4.25	60.00	1.42	2.61	73.10	16.70	2.47	76.70	28.50	4.15	71.50	8.41
24	6.92	61.00	1.03	5.03	65.10	2.72	4.35	78.55	20.60	4.61	67.55	4.30
31	5.24	57.00	0.69	4.47	71.60	7.92	3.47	73.30	12.90	3.63	65.70	4.13
45	4.55	59.40	1.20	3.76	68.20	5.79	2.84	74.35	18.20	4.31	66.76	4.08
75	5.28	49.80	0.18	4.03	63.90	2.82	5.08	72.65	8.06	4.42	62.63	2.10
380	6.35	49.80	0.15	3.98	50.17	0.25	6.05	55.38	0.45	6.67	72.01	5.62

Table 5: R_r results of nanoporous silicon based explosive formulations

	N1			N2			N3			N4		
Days	Time s	Noise dB	R_r x10^{17}	Time s	Noise dB	R_r x10^{17}	Time s	Noise dB	R_r x10^{17}	Time s	Noise dB	R_r x10^{17}
0	18.47	75.70	3.35	12.06	108.23	183.00	15.76	106.90	124.00	7.46	76.33	9.00
5	28.07	70.50	1.08	5.28	106.20	346.00	19.21	104.10	77.80	4.76	74.60	11.20
24	42.15	67.00	0.43	8.05	102.30	156.00	35.00	76.20	1.89	5.37	66.26	3.04
31	45.00	65.20	0.31	12.47	97.60	62.90	-	-	-	4.00	65.10	3.42
45	51.44	67.80	0.40	11.25	75.20	5.14	-	-	-	6.48	68.15	3.34
75	-	-	-	10.85	60.90	0.65	-	-	-	5.28	63.40	1.99
380	-	-	-	-	-	-	-	-	-	7.92	68.26	2.77

- Denotes No Reaction

Nanoporous silicon based explosives formulations where Tet was used as the oxidiser, show a rapid decline in reactivity (Table 4). The same binders were used in a similar attempt to extend the shelf life of formulations T1 and T2 (Table 4). Formulation T 4 showed a significant decline in reactivity after 75 days. The reactivity then steadily increased again over the remainder of the 380 days

The oxidation behaviour, of explosive formulation T3 showed a slower decrease in reactivity than formulation N3. The reactivity behaviour of formulations T4 and N4 can be ascribed to the addition of 75% nitriminotetrazole. Table 4 showed a slower decrease in relative reactivity for the formulations prepared with Tet. Table 5 shows a rapid decrease in relative reactivity for the formulations prepared with SP. The results of the relative reactivity of the density of the nanoporous based explosive formulations are shown in table 6.
Increasing the density of the nanoporous silicon explosive formulation (T1), resulted in an increase in the reactivity of the formulation. This increase in reactivity is seen from a density of 2.1 g/cc. The increase in reactivity is achieved through both a decrease in the reaction time and an increase in the noise level of the reaction obtained from the test (Table 6).

Table 6: R_r with increase in density

Density (g/cc)	Time (s)	Noise (dB)	R_r $x10^{17}$
0.71	8.08	77.70	9.93
1.99	7.04	81.73	18.89
2.07	6.28	75.30	9.32
2.11	6.26	99.45	151.13
2.22	7.86	94.20	69.99
2.25	8.19	116.63	568.37
2.52	4.86	116.93	983.43
2.60	5.47	116.30	827.07

4 Conclusions

The responses obtained were scientifically defined by the following three factors: time to reaction, the sample temperature at the time of reaction and the noise level of the reaction. The time measured, for a reaction to occur, is indicative of the sensitivity of the formulation towards heat. The noise level can be related to sound over-pressure [7]. The sound over-pressure can be related to the over-pressure generated by the reaction. By following the relative reactivity theorem described here, both time and noise can be combined to obtain a quantitative measure that can be used to compare different reaction behaviour of explosive formulations.

From the study conducted the following can be concluded that:

i. The oxidiser used in manufacturing nano-porous silicon based explosive formulations influences the relative reactivity of the formulation,
ii. The shelf life of nano-porous silicon based explosive formulations is influenced by the type of oxidiser used as well as the binder systems incorporated in to the explosive formulation,
iii. Increasing the density of nano-porous silicon based explosive formulation results in a significant increase in the reactivity of the formulation,
iv. The relative reactivity methodology can be used to compare different explosive formulations from thermal and noise measurements,
v. the relative reactivity methodology can be used to compare different explosive characteristics from thermal and noise measurements.

5 Future activities

Continuous development of the relative reactive methodology to include thermal and noise measurements studies related to particle size, influence of additives and other explosives characteristics.

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