Silicon Fuel in High Performance Explosives

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Abstract: In an effort to improve the insensitive munition (IM) response but maintain performance of aluminized formulations, silicon was investigated as a possible replacement for aluminum. An RDX-based silicon explosive was developed in which nearly 90% reaction of silicon to silicon dioxide was realized by 7 volume expansions as measured by the 2.54 cm diameter copper cylinder expansion test. In spite of the low nitramine loading in the formulation (79 wt.-%), the corresponding Gurney constant for the explosive was 2.81 ± 0.02 km s^{-1}, which is superior to Composition A-3 under the same experimental conditions (91% RDX, 2.69 ± 0.02 km s^{-1}). Energy calculations from detonation calorimetry also indicate reaction of the silicon, which was further confirmed by both silicon metal and silicon dioxide in the analyzed residue. The energy release, despite it being equivalent to a highly loaded explosive, was found to lag behind the rate of A-3. This indicates silicon oxidation may occur sometime after lighter gas reactions in the reaction front, but is fast enough to impart work in the copper cylinder test.

Keywords: Silicon · Multiuse explosives · Cylinder test · Gurney

1 Introduction

As early as 1943, the aluminum (Al) in aluminized explosives was recognized as a prime contributor to unacceptable response in bullet impact studies [1]. The investigators replaced Al in Minol with silicon to make "Silicominol". Responses obtained to bullet impact with 50 caliber ball ammunition resulted in nearly zero response in the siliconized version of Minol when compared to more violent reactions with the standard aluminized Minol. This early precedent showed silicon could possibly serve as an Insensitive Munition (IM) enhancing fuel additive when compared to aluminum. In regards to these older tests, it is conjectured performance attributes of silicon were unknown, and investigators most likely did not pursue use of silicon due to its cost at that time. Now, with advances in the semiconductor industry, there is ample supply of silicon powder. In theory, the thermodynamic enthalpy of the oxide formation from elemental silicon vs. aluminum is comparable on a per weight basis (15.2 kJ g^{-1} SiO$_2$ vs. 16.6 kJ g^{-1} Al$_2$O$_3$). In order to obtain this energy, however, the reaction rate must be sufficiently fast to obtain usable energy during expansion of the detonation products at early timeframes. From combustion studies, the silicon oxidation rate was shown to be somewhat less than for aluminum [2,3]. Barring kinetic considerations, preliminary thermodynamic code calculations indicated early reaction of silicon in the detonation could be possible, arising from silicon's unique depressed melt characteristics at high pressures and temperatures [4].

In this research, elemental silicon was formulated in high explosives and its reaction rate studied. The definition of early silicon reaction in this study is oxidation by 7 volume expansions in a 2.54 cm copper cylinder expansion test (cylex). Cylex testing is the preferred embodiment to verify early metal reaction. If the metal reacts exothermically to its oxide within the first 15 µs of expansion (which equates to about 7 volume expansions), acceleration of the copper cylinder wall would be greatly enhanced, and the amount of silicon dioxide formed could be assessed. This is achieved with thermochemical computer codes fit to the copper cylinder expansion wall velocities by Jones-Wilkins-Lee-Baker (JWLB) equations of state. This study presents the successful formulation and testing of a high performance pressed explosive containing a silicon metal fuel in an effort to verify theoretical calculations [4]. It was found in these formulations silicon does oxidize early enough to impart significant mechanical energy to the surroundings. The performance attributes and possible mechanisms of reaction are shared in this paper.

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2 Experimental

2.1 Formulations

Two silicon particle sizes were used, one at $d_{50} = 15 \pm 3$ μm and the other at $d_{50} = 60 \pm 11$ μm as measured by laser diffraction (Micromeritics Saturn Digitizer 5200). The 15 μm material was obtained from American Elements (CA, USA) and used without further purification. The 60 μm powder was obtained from Marietta Minerals (OH, USA). The material was wet sieved and collected under 60 μm for formulations. Formulations were made using a 1 L Holston Slurry still. For a typical 200 g mixture, the binder (a proprietary mixture of cellulosic binder and energetic plasticizer) was gelled in methyl ethyl ketone (MEK). The hexogen (RDX) was dispersed in water (1 L) along with the silicon powder at 40 °C. The lacquer with the binder was slowly added until particles formed, at which time vacuum was applied to draw off solvent while the system was heated to 90 °C. The particles were washed thoroughly with deionized water and dried overnight at 60 °C. The final formulation reported here is shown in Table 1 along with details of comparison formulations and the respective characteristics.

2.2 Small Scale Testing and Analysis

The materials were characterized using Bundesanstalt für Materialprüfung (BAM) Friction, BAM Impact, Explosives Research Laboratory (ERL) impact, and Picatinny Electrostatic Discharge (ESD) instrument. The material thermal stability was tested using a Perkin–Elmer 4000 Differential Scanning Calorimeter (DSC) operated at 5 K min^{-1} in dry nitrogen and Sapphire Thermal Gravimetric Analyzer (TGA) operated at 5 K min^{-1} in dry argon. The residues from detonation calorimetry were analyzed using a Rigaku Miniflex X-ray Diffractometer with a Cu-K_α source and 3 mm slit. All pressing was conducted to obtain densities $> 98\%$ theoretical maximum density (TMD) unless otherwise noted.

2.3 Detonation Testing

All formulations were first detonated in a small scale gap test (SSGT) tube at a diameter of 5.1 mm and zero cards to ensure the critical diameter was below 5.1 mm. For the detonation velocity experiment, a 1.91 cm diameter unconfined charge consisting of five 2.54 cm length pellets were placed in an acrylic tube with a 0.318 cm wall thickness on top of a steel dent plate (3.81 cm thickness by 7.62 cm diameter). Five fiber optic cables were used to collect time of arrival data. The charge was boosted with a 1.70 cm diameter by 1.75 cm long Composition A-3 pellet initiated by an RP-80 detonator. Dent depths were measured and pressures calculated from previously calibrated Chapman-Jouget (CJ) pressures.

The detonation calorimeter setup and operation is described in other publications [5]. In short, a 15 g sample of the test explosive was detonated using a 5.0 g C4 booster with an RP-80 exploding bridgewire (EBW) detonator. Confinement was ensured by bonding the sample with a ceramic adhesive in an alumina crucible having a 0.25 cm thick wall. Upon detonation in argon gas, all heat produced is absorbed by the surrounding water bath. The total change in water bath temperature is proportional to the energy liberated in the detonation. The calculation also corrects for any condensed water within the calorimeter. From knowledge of the theoretical energy output, one can estimate the extent of silicon reaction from the detonation event. Since no oxygen was present in the system, the energy obtained was from silicon reacting with only detonation products (anaerobic). The energies obtained were then compared with thermodynamic calculations using Cheetah 5.0 (exp6.6 library), assuming both reactive silicon (100%) and unreactive silicon (0%) by Equation (1):

$$\frac{(Actual\ Detonation\ energy) - (0\%\ Si\ Reaction\ Detonation\ Energy)_{calc}}{(100\%\ Si\ Reaction\ Detonation\ Energy)_{calc} - (0\%\ Si\ Reaction\ Detonation\ Energy)_{calc}} \times 100 \quad (1)$$

Cylinder expansion was performed on the formulations of Table 1 using a low oxygen content soft copper 2.54 cm inner diameter cylinder. The expansion of the cylinder was recorded with a Cordin 121 streak camera. Wall displacement as a function of time resulted in wall velocities used for energy calculations of the expanding products. Wall thinning effects were taken into consideration for the equation of state (EOS) and Gurney Constant calculations [6]. Details on the fits to JWLB using Jaguar code are found in Ref. [4]. Cylex tests were run on Composition A-3 and PAX-Si-15.

3 Results

3.1 Small Scale Testing and Analysis

Results of small scale hazards testing are shown in Table 2. The silicon formulation showed no enhancement of insensitivity over pure RDX. DSC showed an acceptable decomposition onset associated with RDX. For small scale sensitivity

Table 1. Nominal amounts of mixture ingredients used in this study.

Formulation	RDX [%]	HMX [%]	Binder	Silicon [15 μm]
PAX-Si-15	79		9.0 cellulose acetate/energetic plasticizer	12
Comp A-3	91		9 wax	–
LX-14		95	5 estane	–

Table 2. Small scale sensitivity and DSC results.

Formulation	BAM impact [J]	BAM Friction [N]	Picatinny ESD [J]	ERL impact [cm]	DSC onset [°C]	DSC peak [°C]
PAX-Si-15	6	120	>0.25	26.2	200.0	242.2
RDX CL 1 Type II	3	180	>0.25	29.8	201.2	241.3

testing, the silicon does not yield any improvement. In fact it seems to sensitize the formulations somewhat considering there is nearly 12% less nitramine in the system when compared to the higher loaded system of A-3, at least in the ERL impact. However, in the confined test arrangement of BAM impact, the PAX-Si-15 fares somewhat better than pure RDX. It could be that the test arrangement of the gritty sandpaper in the ERL impact led to lower thresholds of "go's" due to light off, but was not enough for a true full "go" in the confined steel sleeve of the BAM impact instrument.

3.2 Detonation Characterization

The detonation rate and plate dent data is shown in Table 3. The detonation velocities were below that of the high performance formulation LX-14 and Composition A-3 [7].

Cylex results are shown in Figure 1. In this Figure the wall velocity was normalized to composition A-3 at 7 volume expansions and plotted as a function of time. Each grouping of data points represents data from 2 walls of 2 shots. The final silicon formulation wall velocity, despite containing 14% less nitramine, was nearly 1.5 times that of A-3, but took about 2–4 µs longer to obtain the same expansion. Figure 2 shows the wall velocity as a function of how much theoretical silicon reacts to obtain the equation of state (EOS) derived from proprietary Jaguar Thermodynamic Code analysis [4]. The fundamental difference between Jaguar and Cheetah is that Jaguar uses more advanced parametric optimization routines to determine the equilibrium compositions, which result in more accurate expansion energies along the isentrope. Assuming 100% and 0% silicon reaction to silicon dioxide, was assessed the amount of silicon reacting to its oxide. In the case of this formulation, nearly 80% of the silicon reacts according to the JWLB fits.

Characterization using detonation calorimetry is shown in Table 4. Duplicates were run for all formulations. The data shows, not all the silicon reacted in the detonation
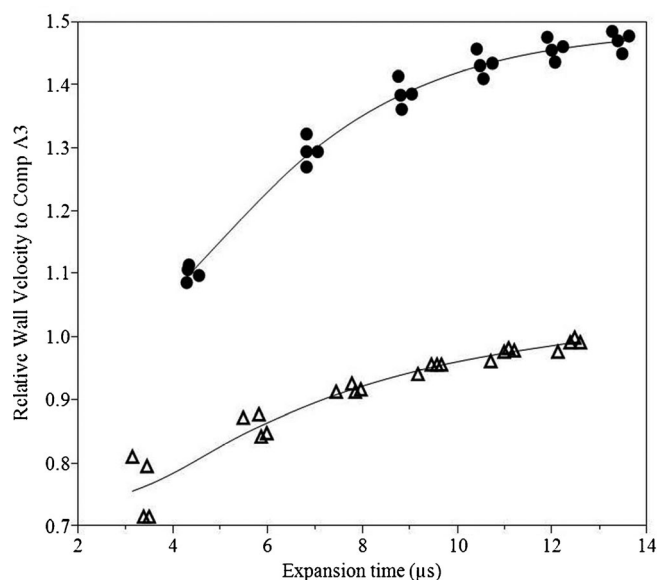

Figure 1. Cylinder wall velocity as a function of time for Composition A-3 (Δ) and PAX-Si-15 (●). The *y* axis wall velocity is normalized to maximum wall velocity of Composition A-3.
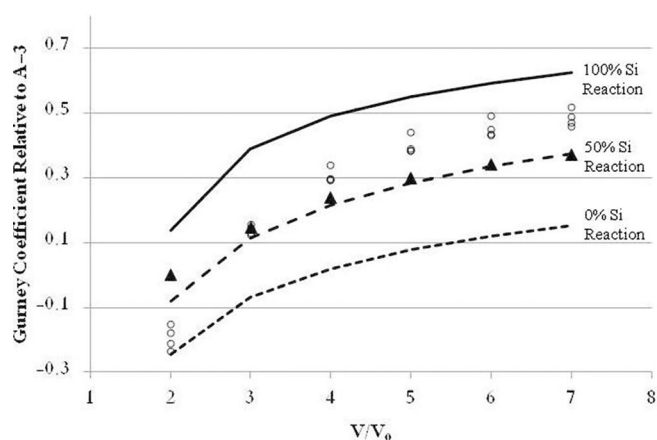

Figure 2. Gurney coefficient as a function of percent of silicon reacted with respect to volume expansion in the copper cylinder test. Composition A-3 data (▲) and PAX-Si-15 (o). Solid line, dashed line, and small dashed line (top to bottom) are respective Gurney coefficients as a function of percent silicon reaction.

Table 3. Dent-rate data for silicon explosive and LX-14. *Data was not available for A-3, so common reference values were used here [6].

Formulation	Unconfined, 1.91 cm diameter	
	Dent [GPa]	Detonation velocity [km s⁻¹]
Composition A-3	29.55*	8.14*
LX-14	29.33 ± 0.42	8.43 ± 0.07
PAX-Si-15	26.63 ± 0.00	7.90 ± 0.05

Table 4. Detonation calorimetry results from silicon shots.

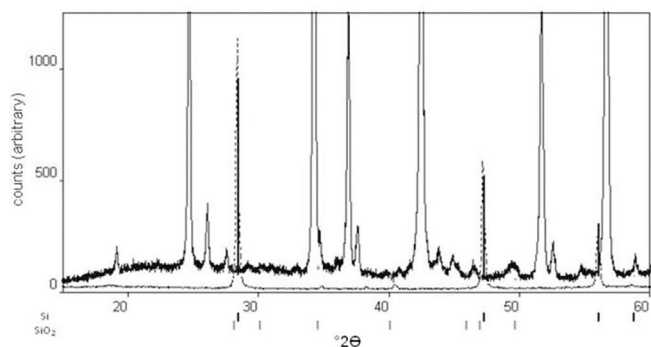| Formulation	Theoretical detonation energy [J g^{-1}] 100% metal reaction*	Theoretical Detonation detonation energy [J g^{-1}] 0% metal	Experimental detonation energy [J g^{-1}]	Estimated % metal reaction
LX-14	–	5916	5703 ± 29	–
PAX-Si-15	6318	4753	6134 ± 29	89
PAX-Si-60	6318	4753	5995 ± 25	79

Figure 3. X-ray diffraction pattern of detonation calorimeter residue (top spectrum, solid line ——) and pure silicon powder (bottom, dotted line ----). Note the peak locations for silicon (Si, black marks) and silicon dioxide (SiO$_2$, grey marks)) shown below the x-axis. The increase in broad background near 20–35° 2θ is also indicative of an amorphous SiO$_2$ presence. Large peaks off-scale are alumina peaks from the mullite ceramic crucible used in the calorimeter.

event according to thermodynamic calculations. This was later confirmed with X-ray diffraction studies of the detonation residue from the PAX-Si shots. While the samples were not pure enough for quantification due to high amounts of calorimeter steel residue and alumina from the crucible, relative primary peak sizes indicated very small amounts of silicon remained while the broad background peaks due to amorphous silicon dioxide were present (Figure 3). Through corroboration of calorimetry energies, cylinder expansion results, and detonation residue analysis, in general about 80% of the silicon reacts in the PAX formulation when 15 micrometer silicon powder was used.

4 Discussion

When compared to higher loaded nitramine explosives without metals, cylex tests of PAX-Si exhibited higher wall velocities with lower nitramine loading. There is no other energy release to account for the wall velocities obtained in Figure 1 and Figure 2. Figure 2 shows that even with the energetic binder, the energy of 0% Silicon reaction is below that of Composition A-3. Therefore, silicon reaction does occur early enough to impart energy on the copper cylinder wall velocity by 7 volume expansions. The JWL of silicon dioxide at detonation conditions was previously con-

structed and now shows good agreement with experimental results [4]. While silicon melts at higher temperatures than aluminum, the silicon melt point is depressed at high pressures [8]. Over the course of this study, it was thought that with a proper particle size, the silicon would melt in sufficient time early in the expansion so oxidation could proceed. Indeed, detonation calorimetry showed there was a concomitant decrease in silicon reaction with an increase in silicon particle size (Table 4). Such an effect in the research of aluminized explosives showed a similar trend. The effect of silicon particle size on the combustion efficiency in this study was not quantified fully, however. From linear fits (main effects) and error analysis, there was a decrease in silicon reaction on the order of 10–20% in the formulation going from 15 to 60 μm as gauged by detonation calorimetry (Table 4).

It is known that a decreasing metal particle size leads to a depressed melting point, otherwise known as the Tammann temperature [9]. It is a reasonable assumption that a calculated detonation temperature of approx. 3800 K and pressures lead to rapid melt and atomization of the silicon which then reacts with oxygen bearing detonation gases. However, it is clear that all silicon does not react in the expansion, and some unreacted silicon is left in the detonation residue (Figure 3). This may be due to the temperature quickly dropping upon adiabatic expansion of gases, resulting in insufficient temperatures and heat flux to fully atomize all silicon. This is in contrast to certain aluminized explosive formulations that do obtain full reaction by 7 volume expansions [10]. These previous studies on aluminized explosives suggest an intimate pre-detonation contact between the Al particles and a surrounding energetic matrix is the key in obtaining early reaction [11,12]. Indeed, when all aluminum reacts early in the volume expansion, the calculated temperatures are hotter by approx. 81 K, even if we are to assume full silicon reaction (Table 5). For this reason, it is likely the silicon does not proceed to a full 100% reaction like aluminum due to quenching at the silicon fusion temperature of approx. 1400 K during expansion. Aluminum, in contrast, is able to maintain a reaction throughout the expansion to approx. 800 K, or its solidification point. With these reasons, as well as small scale sensitivity concerns, silicon does not impart any advantage over aluminum, and in fact may be detrimental to obtaining rapid energy release in a formulation.

At this point, it is interesting to note that use of RDX leads to higher volume expansions at freeze out when

Table 5. Volume expansions of HMX and RDX based silicon formulations. Note decreased time to obtain larger volume expansions before freeze out. Cheetah 6.0 thermodynamic code.

Formulation	CJ temperature [K]	V/V_0 at "freeze out" 1800°K
PAX-Al (15% Al+HMX)	4102	1.99
PAX-Si (12.5% Si+RDX)	4023	1.51
PAX-Si (12.5% Si+HMX)	3921	1.25

compared to HMX (Table 5). Although only a thermodynamic calculation, it suggests there may be further interaction between the explosive gas composition and the ability for the metal to react with oxygen early in the volume expansion. Work is ongoing to understand this relationship further.

In summary, silicon semimetal particles at a size of approx. 15 μm contributed to the high early energy release of a high performance explosive fill. The participation of silicon by 7 volume expansions was determined from analysis of copper cylinder expansion tests and subsequent JWL fits to the wall velocities. Additional testing with detonation calorimetry in an anaerobic environment also indicated substantial consumption of silicon to silicon dioxide based on the energy output of the samples. The substantial gains in early velocities of the cylinder wall are realized by rapid reaction of silicon to silicon dioxide which is highly exothermic. Considerable heat released by the exothermic oxidation leads to sufficient *PdV* work for significant wall velocity. The values were near that of LX-14 and well above that of Composition A-3, which possesses nearly 12% by weight more HMX and RDX, respectively, than this PAX-Si explosive.

Acknowledgments

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