



# Altering combustion of silicon/polytetrafluoroethylene with two-step mechanical activation



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## ABSTRACT

Though silicon (Si) has been widely considered as a reactive fuel, the ability to tune its ignition and combustion characteristics remains challenging. One means to accomplish this may be mechanical activation (MA), which has been shown to be effective with aluminum fuels. In this work, a two-step MA process was developed to prepare fuel-rich Si/polytetrafluoroethylene (PTFE) composite reactive powders. The process consisted of cryogenic milling, followed by high intensity milling at room temperature. This resulted in particle refinement of the hard, brittle silicon particles and also dispersion within the more ductile PTFE matrix. Surface area of the as-milled powder was found to be moderate, ranging from  $1.75 \pm 0.06 \text{ m}^2 \text{ g}^{-1}$  (44/51 Si/PTFE) to  $5.37 \pm 0.10 \text{ m}^2 \text{ g}^{-1}$  (90/10 Si/PTFE) and was driven by the fraction of refined Si powder not dispersed in a PTFE matrix. Combustion enthalpies ranged from  $15.6 \pm 0.4 \text{ kJ g}^{-1}$  (44/51 Si/PTFE) to  $21.8 \pm 2.2 \text{ kJ g}^{-1}$  (90/10 Si/PTFE) and were higher than a physical mixture of the precursors. Combustion experiments showed that burning rates ranged from 1.6 to  $2.1 \text{ mm s}^{-1}$  and combustion temperatures (as measured from gray body emission) ranged from 1708 to 1889 K. The combustion performance of MA Si/PTFE was comparable to mixtures prepared with nanoscale and nanoporous silicon powders, indicating that the reactivity of silicon fuel had been successfully altered inexpensively without many of the major drawbacks associated with using high specific surface area powders.

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## 1. Introduction

Silicon (Si) has a long history as a reactive fuel in pyrotechnic applications, such as delay and primer compositions, near infrared illuminants, and smoke formulations [1]. While there has historically been significant efforts to study micron sized silicon powders in energetic compositions [2–7], recent work has primarily focused on the performance enhancement that nanoscale and nanoporous silicon powders and wafers may provide [8–16]. Increasing the surface area of reactive constituents by either particle size reduction or by chemical processing may increase reactivity, lower ignition temperatures, and increase the intimacy of mixing [17–19]. However, major drawbacks to using nanoscale and nanoporous silicon powders include: high cost; difficulty of synthesis (e.g., use of strong acids); processing issues due to the high specific surface area (SSA); and rapid oxidation (aging) of high SSA materials [17]. Recent studies have indicated that mechanical activation

(MA) provides an efficient, yet cost-effective, means for altering reactivity of metal-based reactive composites, while still maintaining a micron scale morphology [18,20–25]. However, MA has not been fully explored for silicon-based reactive composites due to the high hardness and low ductility of silicon (ultimate tensile strength is ca. 7 GPa [26]).

Mechanical activation is the process of refining materials into a reactive composite material [18] using low or high intensity milling. While this process is similar to mechanical alloying, MA differs in that the process is interrupted prior to the constituents reacting. This process can yield micron-sized, nanostructured composite particles that are fully dense, resulting in altered reactivity due to decreased diffusion length scales and increased interfacial contact area between constituents [18,21]. While MA often occurs at room temperature, it has been reported by Umbrajkar et al. [27] that altering the milling temperature can have a substantial effect on material processing. By this same premise, milling at cryogenic temperatures (cryomilling) has been investigated as a means to produce microstructural refinement [28–32], form nanopowders [33,34], and produce nanocomposite materials (both structural [35–37] and energetic [38,39]).

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In the case of very hard, brittle materials, such as silicon, standard high energy ball milling (HEBM) processes cannot readily induce plastic flow (yielding desired lamellar microstructures), but instead refines the brittle material through fracturing [40,41]. When milling a mixed system with very different mechanical properties (i.e., a brittle material with a ductile material), the result is generally a homogeneous dispersion of refined brittle material within the ductile matrix [41]. However, in some cases the ductile material may act as a process control agent (PCA), hindering the fracturing of the brittle material. Milling at cryogenic temperatures may alleviate this problem by altering the relative ductility of the materials [33]. Chung et al. [29] found that the inclusion of hard particles during cryomilling can cause significant particle and grain size reductions to both the brittle material and the ductile material. Therefore, a two-step process consisting of cryomilling followed by HEBM at ambient temperature may result in large micron scaled composite particles with nanostructured intraparticle features comprised of refined constituents that are subsequently cold-welded together by the more ductile matrix. While a two-step milling process (cryogenic and room temperature) has been used to study the grain size evolution of single materials [34,42,43], it has not been investigated as a means to mechanically activate reactive or non-reactive binary brittle/ductile composite systems.

The objectives of this study were twofold: (i) to develop and characterize a two-step cryomilling and HEBM mechanical activation process for preparation of a reactive, fuel-rich Si/polytetrafluoroethylene (PTFE or Teflon™) composite material; and (ii) to determine if mechanically activated Si/PTFE can achieve comparable reactivity to nanoscale Si and PTFE.

## 2. Experimental section

### 2.1. Mechanical activation and powder characterization

A summary of all mixtures evaluated in this study is presented as Table 1. The materials used for mechanical activation of Si/PTFE included: Si (Sigma–Aldrich, –325 mesh, 99% trace metals) and PTFE (Sigma–Aldrich, 12 μm). The reactive mixtures prepared and studied were: 44/51 (46.3/53.7 wt.% Si/PTFE), 60/40, 70/30, 80/20 and 90/10 wt.% Si/PTFE. One gram of reactive mixture was placed into a 25 mL polycarbonate tube (SPEX CertiPrep 6751C4 vial) with hermetically sealed stainless steel end caps (SPEX CertiPrep 6751E plug) and a single stainless steel impactor (SPEX CertiPrep 6751P impactor). The container was then purged, filled with argon (99.997%), and placed into a cryomill (SPEX CertiPrep 6850 Freezer/mill) using liquid nitrogen as the cryogenic medium. After pre-cooling the sample for 10 min, the material was milled for 6 cycles (1 min ON and 1 min OFF). The milling container was then removed and allowed to warm up to room temperature before the reactive mixture was extracted in an argon-filled glove box.

**Table 1**

A summary of all mixtures evaluated in this study.

Material	Silicon (wt.%)	PTFE (wt.%)	FC-2175 (wt.%)
MA 44/51 Si/PTFE	46.32	53.68	0
MA 60/40 Si/PTFE	60	40	0
MA 70/30 Si/PTFE	70	30	0
MA 80/20 Si/PTFE	80	20	0
MA 90/10 Si/PTFE	90	10	0
MA 44/51 Si/PTFE (with Binder)	44	51	5
SiTV (Ref. [11])	44	51	5
44/5 nSi/FC-2175	89.80	0	10.20
44/5 (Cryomilled Si)/FC-2175	89.80	0	10.20

Constituents were then placed into a 30 mL high density polyethylene (HDPE) container (Cole Palmer EW-62201-01) and milled following the HEBM procedures outlined by Sippel et al. [20]. Specifically, a charge ratio of 24 was used (5 large media, stainless steel, 9.5 mm diameter; and 15 small media, stainless steel, 4.8 mm diameter). The container was then purged, filled with argon (99.997%), and placed into a high energy mill (SPEX, 8000 M shaker/mill). The material was milled at room temperature for 20 cycles (1 min ON and 1 min OFF), during which the container was cooled using a fan. Following the HEBM procedure, material was extracted in an argon filled glove box and stored for further characterization.

Powder characterization was performed on all MA Si/PTFE mixtures using standard techniques. The particle size distribution of the milled materials was determined by laser diffraction (Malvern Mastersizer Hydro 2000μP) using de-ionized water as the dispersant medium. The specific surface area was determined by Brunauer, Emmett, and Teller (BET) analysis (Micromeritics Tristar 3000) with nitrogen as the adsorbent gas. All BET samples were degassed at 50 °C for 18 h. Imaging of the milled material was performed by optical microscopy (Hirox KH-8700), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) (FEI Quanta 3D-FEG). Phase composition of the milled materials was accomplished by X-ray diffraction (XRD) analysis (Bruker D8-Focus) using a scan rate of 2.0 deg. min<sup>-1</sup>.

Thermal and reaction characterization was also performed. Simple powder flame experiments were performed on a vented burn plate using a butane torch ignition source in order to make qualitative observations of the reaction. The thermal behavior was determined by simultaneous differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) (TA Instruments Q600) at 10 K min<sup>-1</sup> in ultra-high purity argon (99.999%). The heat of combustion of the milled material was determined by oxygen calorimetry (Parr 1281) using a custom-made alumina-silicate crucible [20]. All heats of combustion were compared to theoretical values as calculated by the Cheetah (version 6.0) thermal equilibrium code [44].

### 2.2. SiTV combustion experiments

Two fuel-rich reactive materials were prepared and pressed into pellets: 44/51 weight ratio Si/PTFE (as prepared from MA) and 44/51/5 wt.% Si/PTFE/FC-2175 (SiTV mixture [11]). The SiTV mixture was comprised of 44/51 Si/PTFE (as prepared from MA) and FC-2175 (3 M Fluorel™ Fluoroelastomer [11,16], chemical equivalent to Viton A). SiTV mixtures were prepared and pressed into 6.35 mm diameter pellets according to the SiTV procedures outlined by Terry et al. [11]. Pellets were either pressed to a stop at 78% theoretical maximum density (TMD) or pressed without a stop to the maximum attainable percent TMD. Vacuum grease (Dow Corning® High Vacuum Grease) was used as an inhibitor to avoid flame spreading down the sides of the pellet.

Spectroscopy and burning rate experiments were performed using spectrometers and videography following the setup and procedures outlined by Terry et al. [11]. Both a visual (VIS) spectrometer (Spectraline VS100 Imaging Spectrometer, 0.55 μm to 1.02 μm, 0.5 mm × 5.0 mm slit, 12 kHz sampling rate) and an infrared (IR) spectrometer (Spectraline ES100 Imaging Spectrometer, 1.11 μm to 4.75 μm, 0.5 mm × 6.0 mm slit, 1.32 kHz sampling rate) were used to investigate spectral emissions. All spectrometers were aligned and calibrated in accordance with Ref. [11]. Videography (Canon XL2 3CCD Digital Video Camcorder at 30 fps, Canon EF 100 mm f/2.8 Macro USM Lens) was used to analyze pellet deflagration and measure burning rates.

Assumed gray body emission from the SiTV combustion experiments were analyzed via coefficient of determination ( $R^2$ )

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