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## Combustion Performance of Mechanically Activated Silicon/Polytetrafluoroethylene

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Mechanical activation (MA) of Al-based reactives has proven advantageous in modifying combustion behavior; however applying the same approach to Si-based reactives has been more challenging. In this work, we present a two-step mechanical activation process to prepare an activated silicon (Si)/polytetrafluoroethylene (PTFE) composite reactive powder. The two-step mechanical activation process consisted of first cryogenic milling, followed by high intensity milling at room temperature. This process resulted in particle refinement of the hard, brittle silicon particles and dispersion within the more ductile PTFE matrix. The resulting reactive powder was characterized for particle size distribution, morphology, powder X-ray diffraction (XRD), specific surface area (SSA), and combustion enthalpy. For the MA composite powder, no intermediate crystalline phases were detected by powder XRD. However, the measured combustion enthalpy was  $15.6 \pm 0.4$  kJ/g, which is 15.9% lower than the predicted heat of combustion of 18.6 kJ/g. The MA composite powder has a flake-like morphology with a bimodal particle size distribution (peaks at 79  $\mu\text{m}$  and 479  $\mu\text{m}$ ). Surface area was found to be moderate at  $1.75 \pm 0.06$  m<sup>2</sup>/g. The ductile nature of the resulting composite particles allowed for near full density pellets to be realized (98.5% theoretical maximum density) without additional binder. Combustion experiments showed that burning rates (from videography) ranged from 1.6 to 2.1 mm/s and combustion temperatures (from visual and infrared spectroscopy) ranged from 1708 to 1889 K. It was shown that these values had comparable performance to mixtures prepared with nanoscale and nanoporous silicon powders.

### 1. Introduction

Silicon has a long history as a reactive fuel in pyrotechnic applications, such as delay and primer compositions, near infrared illuminants, and smoke formulations [11]. While there has historically been significant efforts to study micron sized silicon powders in energetic compositions [8, 16], recent work has primarily focused on the performance enhancement that nanoscale and nanoporous silicon powders and wafers may provide [5, 15, 19, 20]. Increasing the surface area of reactive constituents by either particle size reduction or by chemical processing may increase reactivity, lower melting and ignition temperatures, and increase the intimacy of mixing [7, 23]. 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 and aging of high SSA materials [23]. Recent studies have indicated that mechanical activation provides an efficient, yet cost-effective, means for altering reactivity of particles (such as aluminum), while still maintaining a micron scale morphology [7, 17, 18].

Mechanical activation (MA) is the process of refining materials into a reactive nanocomposite material [7]. While this process is similar to mechanical alloying, MA differs in that the process is interrupted prior to the constituents reacting. This process often yields 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 [7, 17]. While MA often occurs at room temperature, it has been reported by Umbrajkar *et al.* [21] that altering the milling temperature can have a substantial effect on resulting powder properties. By this same premise, milling at cryogenic temperatures (cryomilling) has been investigated as a means to produce microstructural refinement [4, 22], form nanopowders [10], and produce nanocomposite materials (both structural [12, 13] and energetic [2, 24]).

In the case of very hard, brittle materials, such as silicon (ultimate tensile strength of silicon is ~7 GPa), standard high-energy (HE) milling processes cannot readily induce plastic flow (lamellar microstructures), but instead refines the brittle material through fracturing [1, 6]. 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 materials within the ductile matrix [6]. However, in some cases the ductile material may act as a process control agent, hindering the fracturing of the brittle material. Milling at cryogenic temperatures may alleviate this problem by altering the relative ductility of the materials [10]. Chung *et al.* [4] found that the inclusion of hard particles during cryomilling will 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 HE milling at ambient temperature may result in large nanostructured composite particles comprised of adequately refined constituents that are subsequently cold welded together by the more ductile matrix.

The objectives of this study were two-fold: i.) to investigate a two-step cryomilling and HE milling mechanical activation processes for preparation of a reactive Si/polytetrafluoroethylene (PTFE or Teflon<sup>TM</sup>) composite material and ii.) to characterize and compare resulting combustion performance to equivalent nanoscale Si/PTFE/FC-2175 (SiTV) mixtures.

## 2. Methods

### Mechanical Activation and Powder Characterization

The materials used for mechanical activation of Si/PTFE included: Si (Sigma-Aldrich, -325 mesh, 99% trace metals), PTFE (Sigma-Aldrich, 12  $\mu$ m). A constant mixture ratio of 44/51 Si/PTFE (46.32/53.68 wt.% Si/PTFE) was used. One gram of material was placed into a 25 mL polycarbonate tube with hermetically sealed steel end caps and a single steel 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. The mill was programmed to pre-cool the sample for 10 minutes and then mill the powder for 6 cycles. Each cycle had a duty cycle of 1 minute ON and 1 minute OFF. Following the 6 milling cycles, the milling container was removed, allowed to warm up to room temperature, and then the reactive mixture was extracted in an argon-filled glove box.

Constituents were then placed into a 30 mL high density polyethylene (HDPE) container (Cole Parmer EW-62201-01) and milled according to the HE milling procedures outlined by Sippel *et al.* [18]. A charge ratio of 24 was used (5 large media, stainless steel, 9.5 mm diameter, 3.48 g/media; and 15 small media, stainless steel, 4.8 mm diameter, 0.44 g/media). The container was then purged, filled with argon (99.997%), and placed into a HE mill (SPEX, 8000M shaker/mill). A total of 20 cycles (each cycle had a duty cycle of 1 minute ON and 1 minute OFF) was used and the container was cooled during milling using a fan. Following the HE milling procedure, material was extracted in an argon filled glove box and then stored for further characterization.

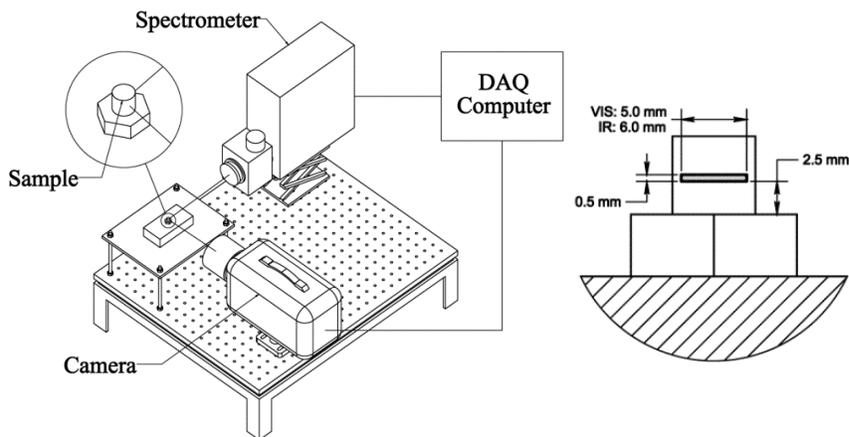
Powder characterization was performed on all MA Si/PTFE mixtures using standard techniques. Flame experiments were performed on a vented burn plate using a butane torch as the ignition source. The particle size distribution of the milled materials was determined by laser diffraction (Malvern Mastersizer Hydro 2000 $\mu$ P) 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 hours. Imaging of the milled material was performed by optical microscopy (Hirox KH-8700). Phase composition of the milled materials was accomplished by X-ray diffraction (XRD) analysis (Bruker D8-Focus) using a scan rate of 8.97 deg./min. The heat of combustion of the milled material was determined by oxygen calorimetry (Parr 1281) using a custom-made alumina-silicate crucible [18]. All heats of combustion were compared to theoretical values as calculated by the Cheetah 6.0 thermal equilibrium code [3].

### SiTV Combustion Experiments

Two reactive materials were prepared for combustion experiments: 44/51 weight ratio Si/PTFE (as prepared from MA) and 44/51/5 wt.% Si/PTFE/FC-2175 (SiTV mixture). It should be noted that both of these mixtures are fuel rich, because their ultimate use would be as ingredients in reactive formulations or for use in aerobic conditions. The SiTV mixture was comprised of 44/51 Si/PTFE (as prepared from MA) and FC-2175 (3M Fluorel<sup>TM</sup> Fluoroelastomer, chemical equivalent to Viton A). FC-2175 is a 60/40 wt.% copolymer of Vinylidene Fluoride and Hexafluoropropylene and was used as a binding agent. SiTV mixtures were prepared and resonant mixed (Resodyn LabRam mixer) according to the mixing procedures outlined by Terry *et al.* [20]. Each reactive material was then pressed to into 6.35 mm diameter pellets. 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<sup>®</sup> High Vacuum Grease) was used as a radial inhibitor.

Spectroscopy and burning rate experiments were performed using spectrometers and videography as shown in Fig. 1. Both a visual (VIS) spectrometer (Spectraline VS100 Imaging Spectrometer, 0.55  $\mu\text{m}$  to 1.02  $\mu\text{m}$ , 0.5 mm x 5.0 mm slit, 12 kHz sampling rate) and an infrared (IR) spectrometer (Spectraline ES100 Imaging Spectrometer, 1.11  $\mu\text{m}$  to 4.75  $\mu\text{m}$ , 0.5 mm x 6.0 mm slit, 1.32 kHz sampling rate) were used to investigate spectral emissions. Videography (Canon XL2 3CCD Digital Video Camcorder at 30 fps, Canon EF 100mm f/2.8 Macro USM Lens) was used to analyze pellet deflagration and measure burning rates. After each pellet was properly aligned and mounted, a Ni/Al ignition increment was placed on top of the pellet ( $18 \pm 3$  mg of loose MA Ni/Al powder, planetary mill, 1:1 molar ratio, dry milled 15 minutes, wet milled in hexanes 15 minutes [14]), and combustion was initiated with a coiled 30 gauge Nichrome wire at 10V.

Assumed grey body emissions from the SiTV combustion experiments were analyzed via coefficient of determination ( $R^2$ ) optimization with Planck's Law [20]. Using that procedure, spectral intensity traces were analyzed and converted into time dependent temperature and effective emissivity profiles. The grey body assumption was assessed by ensuring a minimum  $R^2$  value of 0.95 for any measurement made.



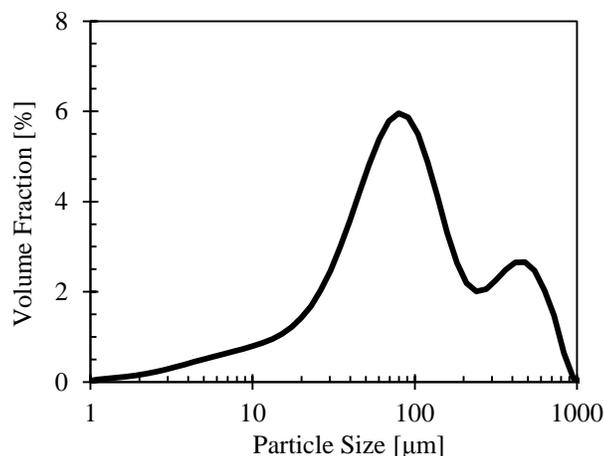
**Figure 1.** A diagram of the experimental setup used for SiTV combustion experiments (Left). A diagram of the spectrometer alignment with a SiTV pellet (Right).

### 3. Results and Discussion

#### Characterization of MA Si/PTFE

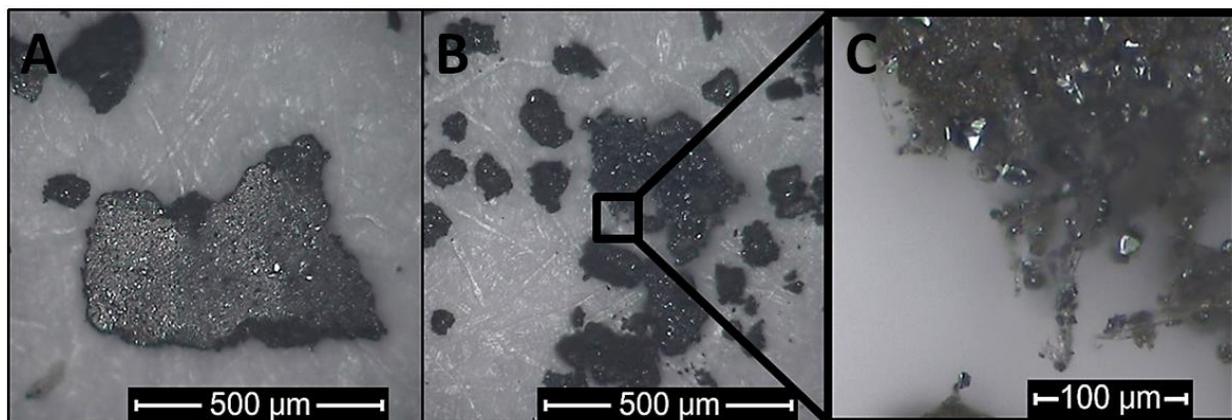
The combined cryomilling/HE milling process was found to yield material that had similar reactivity to equivalent nanoscale mixtures. Flame experiments of the as-milled powders showed that the cryomilled/HE milled 44/51 Si/PTFE mixtures were easily ignited via butane igniter, which cannot be done with a physical mixture of the initial precursors, or from single step ambient milling, but can be observed with nanoscale mixtures. The silicon and PTFE used in this study were micron in size, which results in a large effective diffusion distance between constituents as well as a low fuel SSA. The reactivity of the MA Si/PTFE observed during flame experiments indicates that the fuel morphology and/or mean diffusion path between the silicon and PTFE constituents had been successfully altered.

As shown in a previous study [18], the HE SPEX mill generally produces large particle sizes when milling with PTFE. It can be seen from particle sizing (Fig. 2) that the MA 44/51 Si/PTFE powder is bimodal with peak particle sizes at 79  $\mu\text{m}$  and 479  $\mu\text{m}$ , indicating that the MA powder is much larger than the starting material. Specifically, MA 44/51 Si/PTFE was found to have a mean particle size ( $D_{50}$ ) of 78.2  $\mu\text{m}$ , a surface weighted mean particle size ( $D_{3,2}$ ) of 31.7  $\mu\text{m}$  and a volume weighted mean particle size ( $D_{4,3}$ ) of 142  $\mu\text{m}$ .



**Figure 2.** Particle size distribution of MA 44/51 Si/PTFE material.

This particle size distribution was supported by optical microscopy of the MA 44/51 Si/PTFE powder (Fig. 3), which verified that there is a bimodal distribution of the powder. Both large particle flakes (on the order of 500  $\mu\text{m}$ , Fig. 3A) and smaller particles (on the order of 100  $\mu\text{m}$ , Fig. 3B) were observed. While these particles are large, the surface of the particles were fairly rough and appeared to have a surface consisting of consolidated PTFE fibers and  $\sim 5$   $\mu\text{m}$  silicon particles. It was also observed that the edges of the flake particles had thin ( $\sim 15$   $\mu\text{m}$ ) diameter PTFE fibers that were decorated with smaller  $\sim 5$   $\mu\text{m}$  silicon particles (Fig. 3C). The BET specific surface area of MA 44/51 Si/PTFE was found to be  $1.75 \pm 0.06$   $\text{m}^2/\text{g}$ , which supports the observed surface and particle morphology of the milled Si/PTFE nanocomposite material.



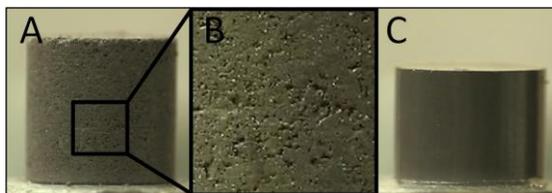
**Figure 3.** Optical microscopy of MA 44/51 Si/PTFE powder showing: the larger  $\sim 500$   $\mu\text{m}$  flake particles (A); smaller  $\sim 100$   $\mu\text{m}$  particles (B); PTFE fibers decorated with  $\sim 5$   $\mu\text{m}$  silicon particles (C).

X-ray diffraction of MA 44/51 Si/PTFE powder (not shown) indicated that no crystalline intermediate species were formed during the two-stage milling process and that no evidence of contamination was observed from the milling media or liquid nitrogen medium. However, bomb calorimetry of the milled material found that MA 44/51 Si/PTFE had a combustion enthalpy of  $15.6 \pm 0.4$   $\text{kJ/g}$ , which is 15.9% lower than the theoretical heat of combustion of 18.6  $\text{kJ/g}$ , as predicted by Cheetah 6.0 [3]. A similar loss in combustion enthalpy when milling Al/PTFE reactives was also observed by Sippel *et al.* [18], which reported that 20 minutes HE milling of 70/30 wt.% Al/PTFE resulted in a roughly 21.7% loss in combustion enthalpy from theoretical values. However, they also reported that physical mixtures of 70/30 wt.% Al/PTFE yielded only a 12.7% reduction in combustion enthalpy. As no intermediate species were observed, it can be assumed that all reductions in combustion enthalpy are from amorphous material ( $\text{SiO}_2$  or intermediate species) or due to incomplete combustion of the milled material. If the loss in combustion enthalpy was due to the presence of amorphous

SiO<sub>2</sub>, then the resulting silicon particles would have an active content of 80%. Combustion enthalpy of a physical mixture of 44/51 Si/PTFE has not been completed yet, therefore it is not known how much of the loss is a result of milling induced amorphous material or a result of incomplete combustion.

#### SiTV Combustion

While preparing MA 44/51 Si/PTFE pellets for combustion experiments, it was found that MA 44/51 SiTV was able to consistently compact to very high TMD values: 98.6±0.2% (with binder) and 98.5±0.3% (without binder). Not only can this material be processed to high TMD values, but no additional binder was necessary. During the pressing process, each MA Si/PTFE particle is able to freely deform due to the ductile matrix of the composite, producing a high compact density. It can be seen in Fig. 4A,B that at 78% TMD (without binder) the produced pellet is visibly porous with high TMD particles visible throughout the compact, reinforcing the hypothesis that MA Si/PTFE is comprised of large, high TMD particles that are being plastically deformed into place during pressing. Figure 4C shows a high density pellet obtained without additional binder being added. The high TMD values measured by MA 44/51 SiTV mixtures are congruent with the hypothesized morphology of the milled particles. As shown in the particle sizing measurements, this powder is characterized by large particles (mean particle size of 78.2 μm). It is hypothesized that these particles are comprised of fractured silicon particles dispersed in a PTFE matrix. During the two-step milling process, cryomilling facilitates fracture and reduction of both materials into a refined homogeneous powder. High energy milling then increases the Si/PTFE particle size by cold welding the PTFE particles together, forming a near full density matrix of PTFE with silicon dispersed. As optical microscopy of MA 44/51 Si/PTFE indicated the presence of PTFE fibers decorated with silicon particles, it can also be hypothesized that the inner particle structure could also be of similar morphology: cold welded PTFE lamellar strands decorated with refined, silicon particles.



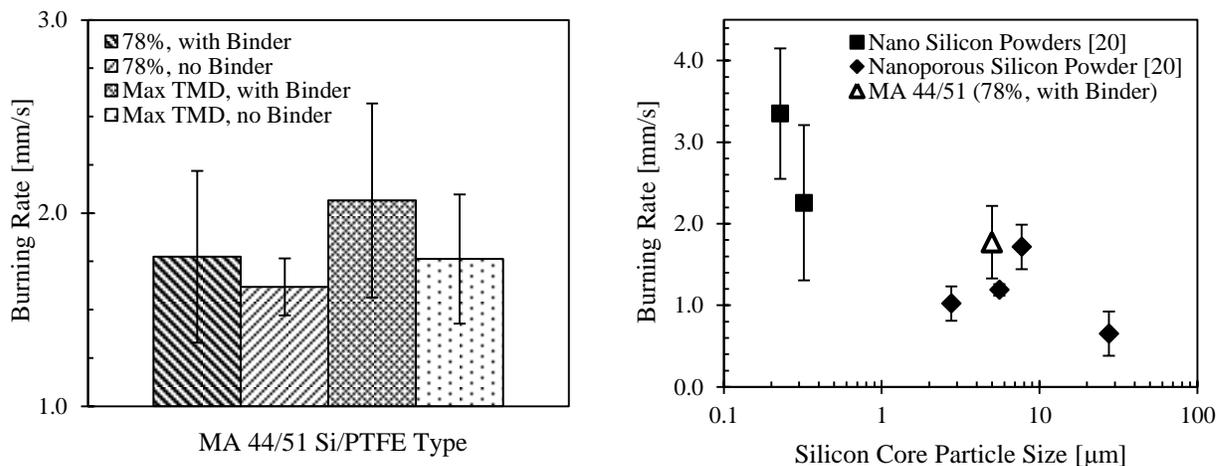
**Figure 4.** Pellets (6.35 mm diameter) of MA 44/51 Si/PTFE pressed to: 78% TMD (A); detail image of surface morphology of the 78% TMD pellet (B); maximum attainable percent TMD – 98.5% (C). These pellets were pressed without the use of FC-2175 binder.

In order to compare the high TMD values for MA 44/51 Si/PTFE with corresponding nanoscale mixtures, three 44/51/5 SiTV mixtures were made and pressed to the maximum attainable percent TMD using the same mixing conditions and materials reported by Terry *et al.* [20]. The following maximum attainable percent TMD values were measured: 87.8% (Vesta Ceramics PSi\_E3, 5 nm pore diameter), 93.7% (US Research Nanomaterials, Inc., nominally 30-50 nm), and 94.2% (CS#1, salt assisted combustion synthesized silicon powder [20]).

Burning rates for all mixtures (both 78% TMD and maximum attainable percent TMD) yielded comparable results (Fig. 5A) with rates ranging from 1.62±0.15 mm/s (78%, no binder) to 2.07±0.50 (max TMD, with binder). While all deflagration rates were of statistical variance of each other, two comments can be made from these results. First, the variance and average magnitude of the burning rates are slower at both 78% TMD and maximum attainable percent TMD when 5% FC-2175 binder is not included in the reactive mixtures. This smaller variance is contrary to expected trends, as binders are generally assumed to increase repeatability (better interfacial contact and reduced void space). Second, the average burning rates and variance of the maximum TMD pellets are of the same magnitude as the 78% TMD samples. This is again counterintuitive as increased pellet density can often lead to lower burning rates [23] and smaller variance. If the mass burning rate of these particles were constant for both densities, then the burning rate of the maximum attainable percent TMD pellets would have decreased by roughly 21%. Instead, the mass burning rates of the pellets increased by 47% for the mixtures with binder (0.308±0.077 g/cm<sup>2</sup>-s → 0.454±0.110 g/cm<sup>2</sup>-s) and increased by 38% for the mixtures without binder (0.285±0.026 g/cm<sup>2</sup>-s → 0.392±0.074 g/cm<sup>2</sup>-s). This increase in mass burning rate suggests that at higher densities, there may be increased contact area between particles, promoting an increased thermal diffusivity that would act to increase burning rate.

From comparison of the MA SiTV burning rate (78% TMD, with binder) with equivalent nanoscale 44/51/5 SiTV (Fig. 5B), it can be seen that the burning rate was comparable, if not statistically higher, than most nanoporous silicon powders used in the study [20]. Additionally, the MA SiTV burning rate was statistically comparable to some

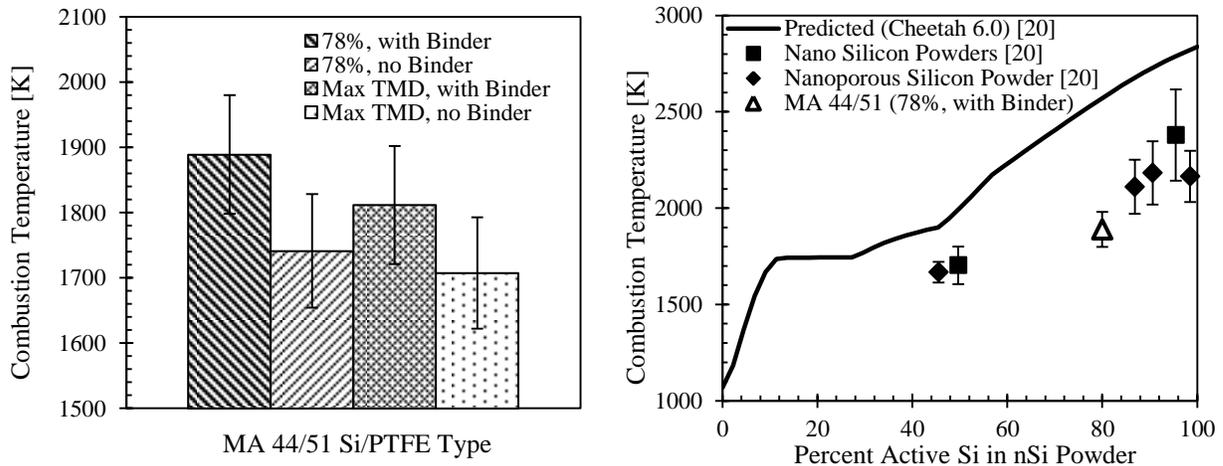
truly nanoscale SiTV compositions (American Elements). As Terry *et al.* [20] indicated that the burning rate of 44/51/5 SiTV follows the shrinking core model [9], it was hypothesized that the silicon core particle size ( $D_{4,3}$ ) is the driving parameter in SiTV burning rate. This trend would suggest that the silicon particle size distribution within the large MA composite particles should be on the order 1-10  $\mu\text{m}$ , which would be much smaller than the initial silicon size of -325 mesh (44  $\mu\text{m}$ ). This is in agreement with the  $\sim 5 \mu\text{m}$  silicon particle size that was observed decorating the MA Si/PTFE particles in microscopic images (Fig. 3). This indicates that the cryomilling process does succeed in refining the large silicon particles into a viable particle size for energetic mixtures without hazardous chemical processing (e.g., use of strong acids).



**Figure 5.** Burning Rates of MA 44/51 SiTV (A, left); Burning rate of 44/51 SiTV (78%, with binder) in comparison to equivalent nanoscale and nanoporous silicon based SiTV mixtures (B, right). All data points represent 5 measurements.

Thermal equilibrium calculations (Cheetah 6.0 [3]) predict that 44/51 SiTV should produce adiabatic combustion temperatures of 2837 K (with binder) and 2867 K (without binder). However, measured average combustion temperatures as determined by assumed grey body emission (Fig. 6A) ranged from  $1708 \pm 80$  K (max TMD, no binder) to  $1889 \pm 91$  K (78%, with binder). While there is some variance in these results, all standard deviations are  $\sim 85$  K, so all temperatures are within statistical variance of each other. However, it is noteworthy that there is an average drop of 126 K in combustion temperature for the compositions without binder (thermal equilibrium predicts an increase of 30 K in adiabatic flame temperature for SiTV without binder), suggesting that the fluoroelastomer binder may play a more significant role in the aerobic combustion of SiTV than thermochemical predictions are able to predict. As the binder was introduced following the cryomilling/HE milling processes, it must be assumed that the incorporation of the binder had a direct correlation with the increased combustion temperatures.

Terry *et al.* [20] showed that percent active content in nanoscale SiTV compositions was the driving powder characteristic for measured combustion temperature, as is shown in Fig. 6B. Mechanically activated 44/51 SiTV (78%, with binder) was initially predicted to have a near 99% active content, as the base silicon powder was of 99% purity (metals basis), and all mixing practices occurred in an argon environment. However, the reduction in combustion temperature suggests that either there are amorphous impurities/oxides in the MA Si/PTFE powder or the material does not burn to complete combustion; combining this result with oxygen bomb calorimetry data indicates that the relative active content of Si may be reduced by as much as 20%. Figure 6B shows that the combustion temperatures of MA 44/51 SiTV are comparable to nanoscale SiTV mixtures if an active silicon content of 80% is assumed.



**Figure 6.** Combustion temperatures of MA 44/51 SiTV (A, left); Combustion temperature of 44/51 SiTV (78%, with binder) in comparison to equivalent nanoscale and nanoporous silicon based SiTV mixtures (B, right). All data points represent 5 measurements.

#### 4. Conclusions

A two-step mechanical activation process was used to produce 44/51 Si/PTFE reactive materials. This process involved cryomilling the constituents at liquid nitrogen temperatures to break up the brittle silicon particles and then subsequently HE milling the material at ambient conditions in order to consolidate and cold weld the refined silicon particles into a ductile PTFE matrix. It was shown that the process produces large, ductile composite particles that are able to freely deform and are able to be pressed to nearly full TMD values (98.5%) without additional binder.

It was observed from combustion experiments that burning rates ranged from 1.6 to 2.1 mm/s and combustion temperatures ranged from 1708 to 1889 K. These results appeared to follow the same trends and were comparable in magnitude to equivalent nanoscale and nanoporous SiTV mixtures, yet would be much less costly and the process does not involve strong acids. These results indicate that a two-step mechanical activation process using both cryomilling and HE milling may be a suitable process for the MA of brittle/ductile systems with a high relative disparity in constituent ductility and should be evaluated in other brittle/ductile systems.

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