EFFECT OF CHEMISTRY AND PARTICLE SIZE ON THE PERFORMANCE OF CALCIUM DISILICIDE PRIMERS
PART I – SYNTHESIS OF CALCIUM SILICIDE (CaSi$_2$) BY ROTARY ATOMIZATION

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14. ABSTRACT
Rotary atomization was used to synthesize spheres of four calcium silicide (CaSi$_2$)-based compositions in order to understand issues relative to primer performance for military applications. Elemental silicon and calcium were used to synthesize the line compound CaSi$_2$ or the eutectic composition between CaSi$_2$ and silicon (Si). Iron (Fe) was added to form FeSi$_2$ as a secondary phase in selected compositions. In one composition, it was shown that a commercially available CaSi$_2$ material, containing FeSi$_2$, could be used as one of the starting compositions. Rietveld analysis was used to show that CaSi$_2$ polytypes in the synthesized materials consisted primarily of 6R, with less 3R and some hexagonal material. As synthesized materials had low surface areas ($\approx$0.1 m^2/g), but short milling times were used to increase the surface area by an order of magnitude. Higher surface areas, as expected, showed faster oxidation. Chemistry and particle size characterization are discussed relative to military specifications for primers. Synthesized and existing current production lot of calcium silicide was mixed in FA874 primer mixtures. Peak pressures, pressure rise time, and ignition voltage showed no differences between the materials, demonstrating a pathway for producing synthetic primer additives.

15. SUBJECT TERMS

Calcium disilicide   Calcium silicide (CaSi$_2$)   Primers   FA874   Rotary atomization

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INTRODUCTION

Calcium disilicide has long been recognized as a compound reactive in oxygen, but stable in air and is a strong reducing agent used as a deoxidizer and desulfurizer in the steel industry (refs. 1 and 2). The military uses calcium silicide ($CaSi_2$) for starter pellets, primers, smoke generators, and tracer compositions (ref. 3). Two types of $CaSi_2$ are specified, with the main differences being the amounts of Ca and iron (Fe) (table 1) and particle size (table 2) (ref. 3). The finer type I particles require a tap density between 1.2 and 1.5 g/cm^3 (ref. 3).

Table 1
Military specification for primer chemistry (ref. 3)

Characteristic	Weight%	
	Type I	Type II
Moisture, maximum	0.1	0.1
Si, minimum	60.0	60.0
Fe, maximum	10.0	3.8
Ca, minimum	20.0	30.0
Total Si, Ca, and Fe, minimum	92.0	----
Metallic Fe, maximum	0.2	----
Alkalinity (as CaO), maximum	2.0	----
Free carbon, maximum	3.0	----
Carbides and phosphides, maximum	1.0	----

Table 2
Military specification for primer particle size (ref. 3)

Characteristic	Type I	Weight% Type II	
	Minimum	Minimum	Maximum
Retained on 150 µm sieve	----	----	1
Passing 150 µm sieve	99.9	----	----
Retained on 106 µm sieve	----	----	1
Retained on 75 µm sieve	----	6	12
Passing 63 µm sieve	65.0	----	----
Retained on 45 µm sieve	----	25	50
Passing 45 µm sieve	----	40	65

The Fe, calcium oxide (CaO), carbon (C), and carbide contents are maximum values with no minimums given, and the Ca and Si are minimum values. As shown in figure 1, $CaSi_2$ is a line compound with a peritectic decomposition temperature of 1030°C (ref. 4). The weight% Ca in $CaSi_2$ is 41.6, which means that the military specifies free Si. The eutectic between $CaSi_2$ and Si occurs at 72 at.% Si (64.3 wt.% Si) at 1020°C, which is within the composition specified for both types of material. The theoretical density of $CaSi_2$ g/cm^3 is 2.17 g/cm^3, which is slightly less than Si (2.33 g/cm^3). Iron would increase the density, so it is unclear why there is a tap density specification rather than a shape description. Spherical particles generally pack in the 60 to 74% range, which would still make them eligible for both types of particles.

There are many ways to synthesize $CaSi_2$, including reacting elemental Ca and Si (refs. 5 and 6); CaO and Si (refs. 2 and 7); calcium carbonate ($CaCO_3$), Silica (SiO_2), and carbon (C) (refs. 8 and 9); electrolysis (refs. 10 and 11); calcium hydride (CaH_2) and Si (ref. 12); SiC and CaO (ref. 13); and combustion synthesis (ref. 14). Calcium disilicide is presently prepared for military applications by the carbothermal reduction of $CaCo_3$ and SiO_2, but compositions prepared are outside the military specifications and require a variance for acceptance.
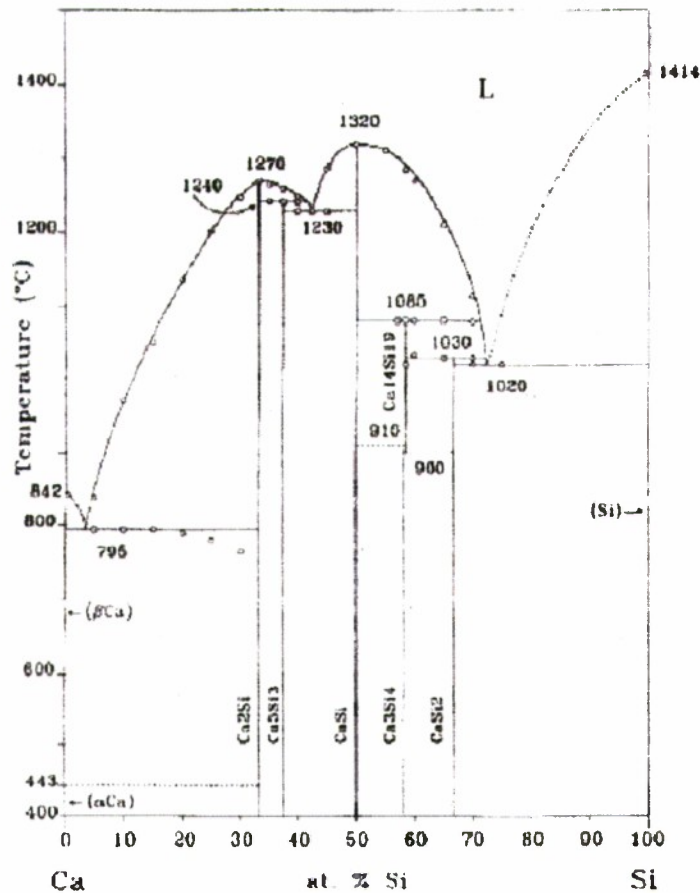
Figure 1
CaSi$_2$ phase diagram (ref. 4)

In order to understand primer performance for military applications, this study was initiated using rotary atomization as a method for controlling the chemistry. Rotary atomization uses induction melting to produce a homogeneous fluid, which is quenched as spheres are cooled in an inert atmosphere. While more expensive than carbothermal reduction, rotary atomization is capable of precise chemistry control, but lacks the ability to make fine particles, such as those typically produced by gas atomization processes. The purpose of this work was to show that rotary atomization could be used to produce military quality CaSi$_2$, but more importantly, to understand the role of free Si and FeSi$_2$, in calcium disilicide primers. The primer performance of the materials described in this study will be investigated and reported at a later date. The four CaSi$_2$ compositions chosen for this investigation were: CaSi$_2$ line compound, CaSi$_2$-Si eutectic composition, CaSi$_2$-Si eutectic composition with 3 wt.% Fe as F3Si$_2$, and CaSi$_2$-Si eutectic composition with 6 wt.% Fe as FeSi$_2$. Two of the four compositions are knowingly outside the military specifications for type II primer grade calcium disilicide in order to look at the effects of Si and FeSi$_2$ on primer performance. The surface area of all materials was controlled by milling time.

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EXPERIMENTAL PROCEDURES

Rotary Atomization

Commercially available Ca (grade 0.-0260, Hummel-Croton, South Plainfield, New Jersey) with a purity of 98.8% [with impurities as analyzed by the manufacturer of 0.5 wt% magnesium (Mg), 0.5 wt.% aluminum (Al), 0.02 wt.% Fe, and 0.04 wt.% manganese (Mn)]; Si (Veritas Alloy, Canberry Township, Pennsylvania) with a purity of 99.3% (impurities of Fe = 0.33 wt.% and Ca = 0.26 wt.%); Fe (Allied Metals, Troy, Michigan) with purity of 99.8% [impurities of 0.07 wt.% Mn, 0.01 wt.% chrominum (Cr), and 0.01 wt% nickel (Ni)]; and $CaSi_2$ (Veritas Alloy, Cranberry Township, Pennsylvania) with chemistry of Si = 59.55 wt%, Ca = 31.78 Wt.%, Fe = 5.48 wt.%, Al = 0.86 wt.%, and C = 0.6 wt.%) were batched according to table 3.

Table 3
Compositions batched at Ervin Industries

Description	Ca (wt.%)	Si (wt.%)	Fe (wt.%)	$CaSi_2$ (wt.%)
1st run - stoichiometric $CaSi_2$	41.6	58.4	0.0	0.0
2nd run - eutectic composition	35.7	64.3	0.0	0.0
3rd run - eutectic with 3 wt% Fe	34.6	62.4	3.0	0.0
4th run - eutectic with 6 wt.% Fe	33.5	60.5	6.0	0.0
5th run - eutectic with 3 wt.% Fe	19.6	33.6	0.0	46.7

Atomization took place in a helium (He) atmosphere after pumping down the chamber in vacuum. Twenty kilogram charges were inductively melted inside a commercial rotary atomizer (Ervin Technologies, Tecumseh, Michigan) and melted at tap temperatures given in table 4. The average speed of the rotary atomizer for each run is also given in table 4 along with the time required to complete the atomization once the liquid was discharged. The distance from the cup to the wall of the chamber was approximately 2 m, allowing time for the molten spheres to solidify prior to hitting the wall. Figure 2 shows how the molten fluid is atomized as it contacts the spinning rotary atomizer.

Table 4
Batching and atomization parameters

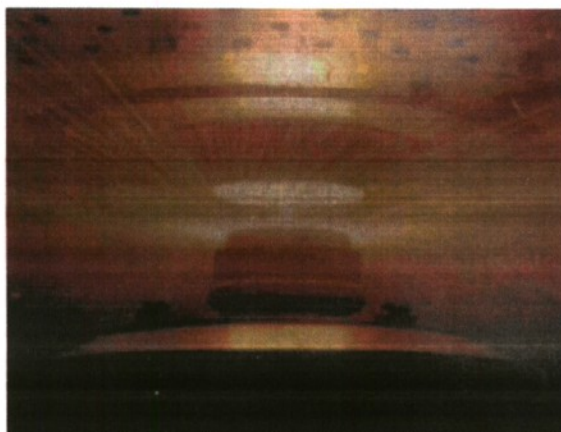| Run number	Batching (kg)				Atomization parameters		
	Si	Ca	Fe	$CaSi_2$	RPM	Tap temperature (°C)	Time (min)
1	13.2	9.5	0.0	0.0	29,900	1327	3.6
2	14.6	8.1	0.0	0.0	31,600	1225	2.0
3	14.1	7.9	0.7	0.0	31,300	1227	2.0
3R*	14.1	7.9	0.7	0.0	30,300	1221	2.0
4	13.7	7.6	1.4	0.0	16,800	1224	10.5
5	7.7	4.5	0.0	10.6	30,600	1243	1.9

Figure 2
Rotary atomization in an Ervin reactor showing vertical molten feed stream impinging on disk
and spherical particles being ejected horizontally from the rotating disk

Particle Size Reduction

Powders were milled in 1.5 L of n-hexane using 7 kg of 9.5-mm hardened steel media inside a stainless steel mill containing 1.5 kg of calcium disilicide powder. The 150-mm inner diameter mill rotated at a speed of 75 rpm for 5 hrs.

Powder was classified using stainless United States mesh screens in accordance with MIL-C-324C. Larger batches were classified by screening 500 to 800 g of powder for 30 min using 200-mm screens containing 400 g hardened steel media. A sieve-shaker (RoTap model RX-29, W.S. Tyler, Mentor, Ohio) was used for all screening.

Low surface area type II distributions were made by adding 100 g of -140/+200 mesh as-received rotary atomized powder, 440 g of -230/+325 mesh as-atomized powder, and 560 g of -325 mesh as-atomized powder and mixing the powders for 1 hr to homogenize. Higher surface area type II distributions were made by adding 100 g -140/+200 mesh as-atomized powder, 340 g of -230/+325 mesh as-atomized powder, and 660 g of -325 mesh milled powder and mixing the powders for 1 hr to homogenize. The milled powders were also prepared at type I particle size distributions.

Characterization

Thermal gravimetric analysis (TGA)/differential thermal analysis (DTA) was performed (Netzsch model STA 409) by heating 70 to 300 mg powder in air to 1400°C at a rate of 5°C/min. Surface area was measured using a multipoint BET analyzer (Micromeretics model Tristar). About 0.1 g of powder was dispersed in 25 mL of deionized water using 1 mL of a commercial dispersant (Rhodaline 102, Rhodia) with an ultrasonic horn for 5 min before using light scattering (Beckman model LS 230) to determine the particle size distribution.

X-ray diffraction (XRD) patterns were obtained using a goiniometer (Phillips Model PW 3040, Phillips, Eindhoven, the Netherlands) using copper (Cu) K_α radiation (λ - 1.54183 Å) with a graphite monochromator at generator settings of 45 kV and 35 mA. The diffractometer data were collected over a 2Θ range of 15 to 75 deg with a step of 0.02 deg and a counting time of 1 sec/step. A commercially available software package (X'Pert, Phillips) was used for Rietveld fitting (refs. 15 and 16).

A scanning electron microscope (SEM) (model JSM-500/LV JEOL) was used for imaging particles. Inductively coupled plasma (ICP) elemental analysis was obtained from a commercial vendor (Constellation Technology Corporation, Largo, Florida).

Primer Characterization

FA74 primer mixtures (40.0% lead styphnate, 44.3% barium nitrate, 14.0% calcium disilicide, 0.5% gum arabic, and 1.2% acetylene black) were prepared by hand using identical ingredients with the exception of calcium discilicide. A PCB model P119B12 piezoelectric pressure sensor was used to measure pressures as part of the signal conditioning and data acquisition system. The PCB models 402M186 in-line amplifier and 482A22 signal conditioner were used in the signal conditioning part of the system and a LeCroy 6050A digital storage oscilloscope recorded the pressure signals. The sample fixture well was filled with the primer composition to 35 ± 0.5 mg, then assembled and placed in an explosive chamber. The power supply leads were attached to a nichrome heater wire and a 6 V push button used to heat the wire and ignite the material. The pressure rise time was defined as beginning at 10% and ending at 90% of peak pressure in pound per square inch kPa.

RESULTS AND DISCUSSION

Rotary atomization produced spherical, crystalline powder of the desired chemistry (fig. 3) for all six runs. Run 4 also experienced freeze off issues due to insufficient heating of the tundish, but this was not related to composition. The yield for this run was only 67%, but yields were generally above 80%. Using a larger charge in the rotary atomizer should allow yields to be greater than 95%. The main advantage of rotary atomization as compared to carbothermal reduction is in the control of chemistry. For example, the uncertainties from ICP analysis for run 3 were Si = 62.4 ± 1.0 wt.% (target was 62 wt.%), Ca = 34.8 ± 0.9 wt.% (target was 35 wt.%), and Fe = 2.8 ± 0.05 wt.% (target was 3 wt.%).
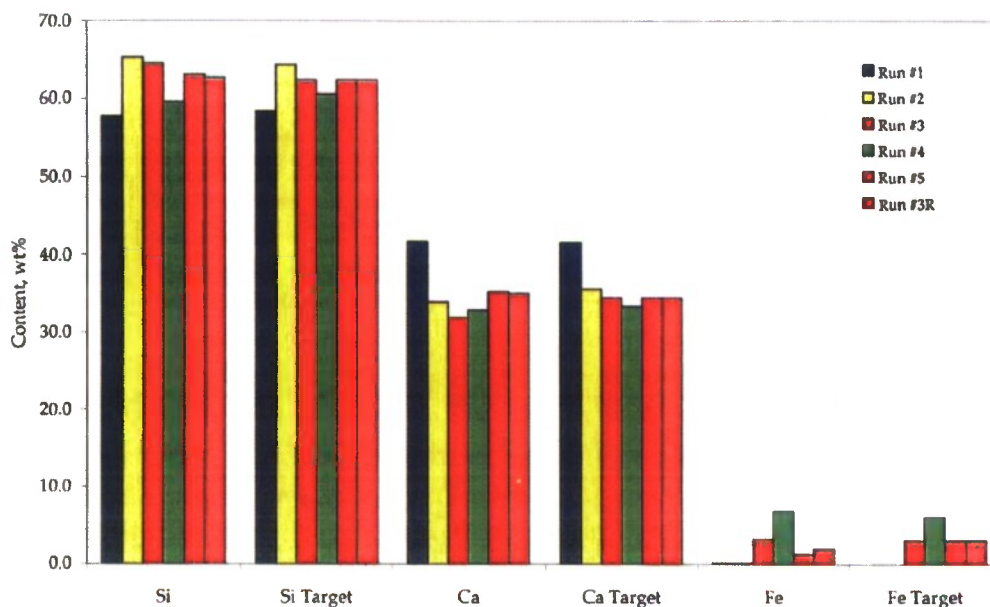

Figure 3
Chemistry as measured by inductively coupled plasma

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Selected samples were analyzed in air using TGA/DTA. While the synthesis of $CaSi_2$ from the elements is mildly exothermic, the oxidation of $CaSi_2$ in air is very exothermic. For the reaction

$$Ca + 2Si \rightarrow CaSi_2 \tag{1}$$

ΔH_f and ΔG_f at 1,000 K are -153.5 kJ/mol and -122.0 kJ/mol, respectively. The expected oxidation products upon heating calcium disilicide in air are wollastanite (or pseudowollastanite) and SiO_2 such that

$$CaSi_2 + 2.5\, O_2 \rightarrow CaSiO_3 + SiO_2 \tag{2}$$

Where ΔH_f and ΔG_f at 1,000 K are -2,381.6 kJ/mol and -1,960.4 kJ/mol, respectively. The heat of formation at this temperature per gram of product is -1.6 kJ/mol-g and -13.5 kJ/mol-g for reactions 1 and 2, respectively. A general rule of thumb for thermite reactions is that when the heat of formation per gram of product is lower than -1.6 kJ/mol-g, it is possible to separate products and it is too violent to use with a filler material when it is below -4.6 kJ/mol-g.

The powders after rotary atomization could be exposed to air at room temperature without oxidation due to their low surface area. Thermal gravimetric analysis data (fig. 4) demonstrates that milling increased the activity of the particles for oxidation, as expected, but still results in materials that can be handled in air. When $CaSi_2$ is fully oxidized to wollstanite and SiO_2 (reaction 2), it is 183% of its initial mass. None of the powders was reactive enough to be fully oxidized. Differential thermal analysis did not show any large exotherms, consistent with a passive SiO_2 layer that requires activation.
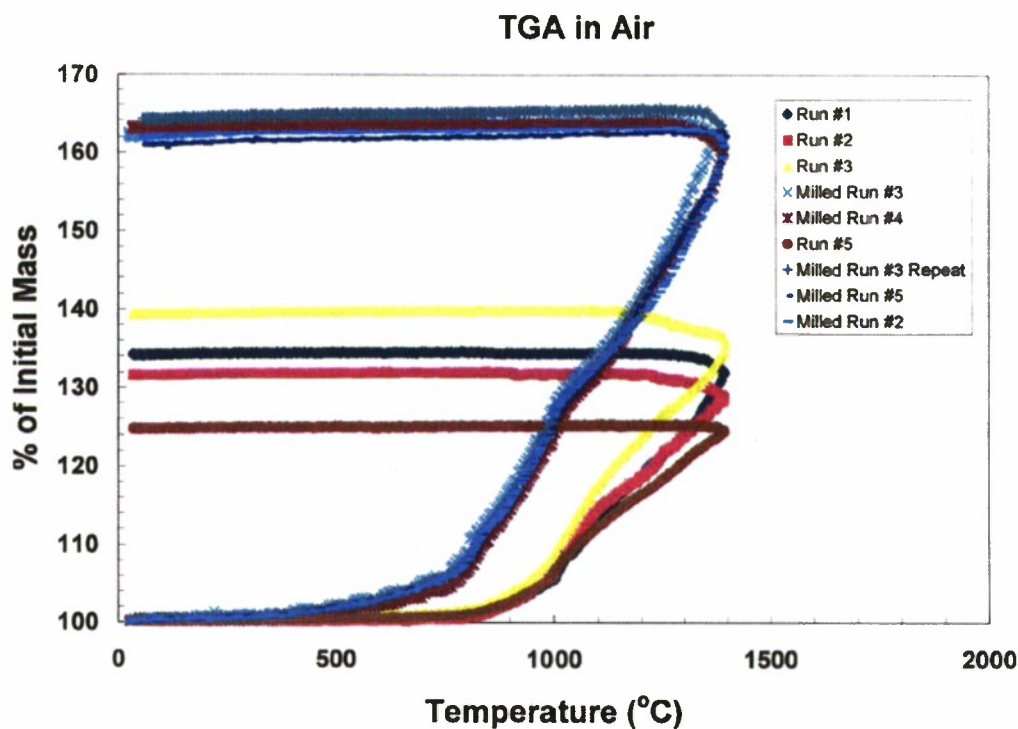

Figure 4
Thermal gravimetric analysis of selected atomized and milled powders

Calcium silicide has been characterized as having either a rhombohedral or hexagonal (refs. 17 and 19) crystal structure. Using a rhomobohedral to hexagonal transformation, it is possible to index $CaSi_2$ using lattice parameters characteristics of hexagonal unit cells (refs. 17). The a lattice parameter from the different polytypes is approximately 3.5 Å, but the c lattice parameter varies with the number of repeat units. The repeat units for rhomohedral structures are reported to be three or six layers (ref. 17) and are noted by the Ramsdell notation of 3R (ref. 18) or 6R (ref. 19). For this study, the hexagonal single layer structure (ref. 17) is given in 1H notation. Table 5 lists the amounts of each of the polytypes present either after atomization or milling. The $CaSi_2$ prepared by rotary atomization is primarily 6R with the hexagonal polytype present in greater amounts than the 3R. An XRD pattern with a Rietveld fit is shown in figure 5. Milling did little to change the distribution of polytypes. The goodness-of-fit values from the Rietveld analysis were low and allow the analysis of phases present by XRD to confirm the validity of the ICP results. X-ray diffraction analysis confirms that rotary atomization results in the expected chemistries.

Table 5
Rietveld data

Run	Description	Rietveld analysis (wt.%)			Si	FeSi$_2$	GOF[a]
		CaSi$_2$					
As-received		1H (ref. 17)	3R (ref. 18)	6R (ref. 19)			
1	Line compound	1.2	0.4	97.3	1.0	0.1	15.6
2	Eutectic composition	8.2	0.3	75.7	15.7	0.2	8.3
3	Eutectic + 3 wt.% Fe	11.7	0.6	68.6	12.8	6.2	7.2
3R	Eutectic + 3 wt.% Fe	8.0	0.5	73.8	11.3	6.5	6.4
4	Eutectic + 6 wt.% Fe	1.0	0.3	79.7	6.6	12.5	5.8
5	Eutectic + 3 wt.% Fe[b]	9.3	0.6	71.4	13.1	5.6	6.1
Milled							
1	Line compound	0.6	0.5	96.1	2.6	0.2	17.6
2	Eutectic composition	3.5	1.0	81.1	14.5	0.0	14.6
3	Eutectic + 3 wt.% Fe	7.5	0.6	71.9	13.3	6.7	6.9
3R	Eutectic + 3 wt.% Fe	7.6	0.6	72.5	12.1	7.2	7.6
4	Eutectic + 6 wt.% Fe	0.8	0.6	78.2	7.1	13.2	9.3
5	Eutectic + 3 wt.% Fe[b]	8.7	0.8	70.5	13.8	6.2	7.1

[a]Goodness-of-fit. Lower value means better fit.

[b]Made with $CaSi_2$ as the source of Fe rather than from the elements.
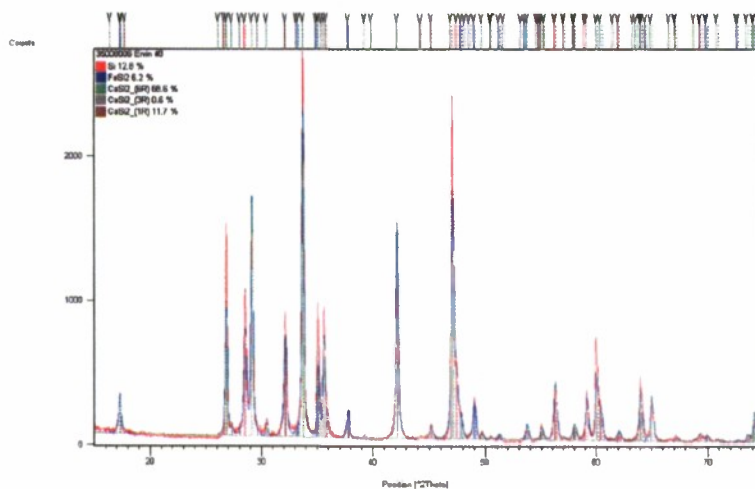

Figure 5
XRD pattern with Rietveld fit for run 3 chemistry

Table 6 lists surface area and particle size data for the atomized and milled powders, respectively. Due to the brittle nature of $CaSi_2$, the milling resulted in an order of magnitude increased in surface area. Type II $CaSi_2$ presently used in primers ranging in surface area between 0.5 and 0.8 m^2/g when measured by the same equipment. Figure 6 compares the microstructures of the atomized, milled, and carbothermally produced material currently used in primers. The atomized powder is distinctive due to its spherical particles, whereas the milled powders are more similar to the material used. One might expect that higher surface area could aid in primer performance, but actual data are needed in order to support that hypothesis. The electrical conductivity of the primer materials are likely to be more influenced by contact resistance than the electrical conductivity of $CaSi_2$, which is reported to be 1.7 x 10^4 S/cm (ref. 20), due to considerations of particle shape and the fact that the silicide is a minor ingredient in the primers. Results of primer performance will be reported in a separate publication once such data are obtained. It is clear that type I and II powders can be prepared using rotary atomization. To illustrate this, the atomized powder was classified by sieve-shaking and the size fractions required to type II powders were prepared as low surface are and medium surface area using the approach discussed in the procedures section. Type I material was prepared using the milled powders. Thirty-six kilograms (2 kg of 18 different powders) were prepared by making low (0.13 ± 0.01 m^2/g), medium surface area (0.69 ± 0.04 m^2/g), and high surface area (1.15 ± 0.09 m^2/g) variations for each of the six runs.

Table 6
Surface area and particle size data

Run	Surface area (m^2/g)	d_{10}	d_{50}	d_{90}	Mean	Minimum	Maximum
As-received				Particle size (µm)			
1	0.0736±0.0004	9.5	5.3	102.7	54.7	≈0.1	≈220
2	0.1135±0.0010	2.0	15.9	63.8	23.5	≈0.04	≈130
3	0.1230±0.0009	4.4	19.7	74.1	30.7	≈0.05	≈115
3R	0.1141±0.0010	1.3	9.3	70.0	19.4	≈0.05	≈115
4	0.0552±0.0004	10.5	81.0	148.2	78.9	≈0.1	≈220
5	0.1068±0.0009	6.0	45.5	116.4	57.6	≈0.05	≈250
Milled							
1	1.1128±0.0113	0.4	5.0	19.9	7.8	≈0.04	50
2	1.2799±0.0123	0.2	4.2	17.7	6.6	≈0.04	40
3	1.3147±0.0113	0.5	6.9	18.9	8.6	≈0.05	45
3R	1.0956±0.0117	0.7	7.3	19.3	8.9	≈0.05	45
4	1.0280±0.0108	0.3	4.7	17.0	6.9	≈0.04	45
5	1.1597±0.0114	0.3	4.3	16.5	6.5	≈0.04	40

It was possible to prepare different chemistries in order to look at the effect of free Si, the effect and mount of $FeSi_2$, and surface area on primer performance. The repeat of run 3 resulted in similar chemistry, surface area, and particle size distributions, suggesting that this method is a good way to prepare primer materials if chemistry control is important. While preparation of calcium disilicide by rotary atomization is more expensive than commercially available $CaSi_2$ prepared by carbothermal reduction, it is advantageous for two reasons: (1) it is easy to control the exact purity required since high-purity Ca and Si are readily available and (2) spherical particles are produced, which are easily handled in air due to their low surface area. Rotary atomization should be used to understand what is important for making calcium disilicide primers. It appears to be an excellent method for producing calcium disilicide in quantities presently needed for primer production.
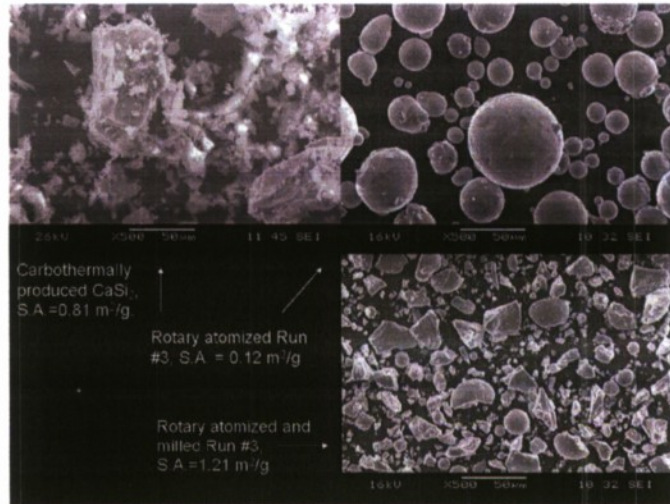
Figure 6
SEM images of atomized and milled run 3 powders compared to primer grade CaSi$_2$ currently used

As a screening test, the calcium disilicide run that most resembled the current production lots was chosen for initial testing. This was run 3R medium surface area (MSA) that contained 3% Fe. The current military standard calcium disilicide used was obtained directly from the vendor. Five shots of each material were performed. The data are depicted in figure 7 (C is commercial while RA is rotary atomized, run 3R medium surface area) with the means diamonds showing the 95% confidence interval, the horizontal middle line crossing the mean value, and the upper and lower horizontal lines being the overlap marks. This data set shows statistical similarity between the two lots of primer (table 7). While only a limited data set, the results encourage further analysis in primer testing of all batches of calcium disilicide in attempt order to resolve the additional factors such as Fe content, surface area, free Si content, and possibly other confounding factors. The primer performance of these additional synthetic powders will be given in a follow-on technical report within the year. The report will include safety and closed bomb performance data of production scale primer mixes.
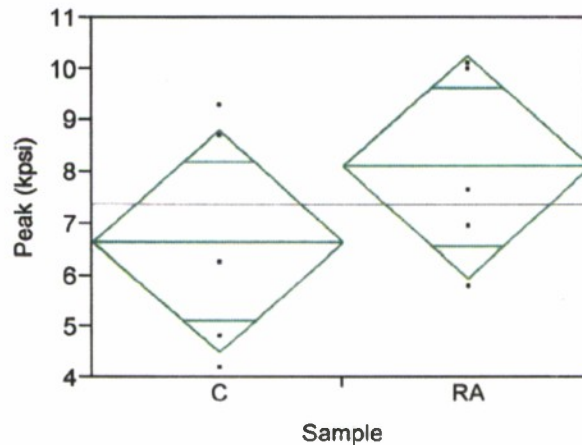

Figure 7
Graphical data of peak pressure in primer testing

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Table 7 show accompanying data for firing voltage and pressure rise time and subsequent t-test results.

Table 7
Mean, standard deviation, and t-test p values at 95% confidence interval of data from primer screening tests

FA 784 mix	Peak voltage (mV)	Peak pressure (kpsi)	Rise time (μs)
Commercial	286 ± 98	6.65 ± 2.28	15.9 ± 2.0
Rotary atomized synthetic	349 ± 82	8.10 ± 1.90	16.6 ± 2.1
p-value	0.3	0.3	0.6

CONCLUSIONS

It was demonstrated that calcium silicide ($CaSi_2$) could be produced by rotary atomization. Yields for 20 kg batch sizes were generally between 80 and 85%, but are expected to be well over 90% when batch size increases above 200 kg. The primary $CaSi_2$ polytype was 6R regardless of the composition synthesized.

The desired chemistries were produced, which should allow the effect of free silicon, iron silicon ($FeSi_2$), and surface area to be evaluated once primer mixes are prepared.

Thirty-six kilograms (2 kg of 18 different powders) were prepared by making low (0.13 ± 0.01 m^2/g), medium surface area (0.69 ± 0.04 m^2/g), and high surface area (1.15 ± 0.09 m^2/g) variations for each of the six runs. It was possible to make a similar surface area when a given composition and processing condition were duplicated.

Primer testing showed that a medium-surface area $CiSi_2$ powder containing $FeSi_2$ had similar performance to commercially available material. Additional testing will allow the effects of surface area and chemistry to be evaluated.

REFERENCES

1. Moissan, H. and Dilthey, W., "Calcium Silicide, CaSi$_2$," J. Chem. Soc., Abstr. 82, II, 320, 1902.

2. Goldschmidt, H., "New Thermite Reactions, Iron Age, 82, 232, 1908.

3. MIL-C-324, "Calcium Silicide," August 1986.

4. Manfrinetti, P., Fornasini, M. L., and Palenzona, A., "The Phase Diagram of the Ca-Si System," Intermetallics, 8, 223, 2000.

5. Wohler, L. and Muller, F., "Calcium Silicides," Z. Allgem. Chem., 120, 49, 1932.

6. Janzon, K. H., Schaefer, H., and Weiss, A., "Alkaline Earth Disilicides," Zeitschrift Anorg. Allgem. Chem., 372, 87, 1970.

7. Wohler, L. and Schuff, W., "TheSilicides of the Alkaline Earths," Z. Allgem. Chem., 209, 33, 1932.

8. Aravamuthan, V. and Sundaram, M., "Factors Influencing the Production of Calcium Silicide," Chem. Age India, 20, 316, 1969.

9. Kuzmenko, A. G., Yu, F., Kekanov, O. V., and Kornev, V. N., "Ore-Roasting Equipment for the Production of Calcium Carbide and Calcium Silicon, Metallurgist, 45, 267, 2001.

10. Dodero, M. "Electrolytic Preparation of Calcium Silicide," Compt. Rend., 198, 1593, 1934.

11. Dodero, M. "Electrolysis of Molten Alkali and Alkaline Earth Silicates," Bull. Soc. Chim., 6, 206, 1939.

12. Louis, V. and Franck, H. H., "Silicide of Calcium," Z. Anorg. Allgem. Chem., 242, 117, 1939.

13. Yamaguchi, Y. and Hayakawa, Y., "The Preparation of Calcium Silicide by Reacting Solid Silicon Carbide and Calcium Oxide," Nippon Kaguku Kaishi, 62, 758, 1941.

14. Cudzilo, S., Huczko, A., and Kicinski, W., "Combustion Synthesis of Carbon and Ceramic Materials and Study of Their Properties," Biul. Wojs. Aka. Tech., 52, 145, 2003.

15. Rietveld, H. M., "A Profile Refinement Method in Neutron and Magnetic Structures," J. Appl. Crystallogr., 2, 65, 1969.

16. Bish, D. L. and Howard, S. A., "Quantitative Phase Analysis Using the Rietveld Method," J. Appl., Crystallogr., 21, 86, 1988.

17. Nakano, H., Yamanaka, S., and Hattori, M., "Reactivity of RF Magnetron Sputtered CaSi$_2$ Film," Solid State Ionics, 53-56, 635, 1992.

18. Dick, S. and Ohlinger, G., "Crystal Structure of Calcium Disilicide, 3R-CaSi$_2$," Zeitshrift fur Kristallographie-New Crystal Structures, 213, 232, 1998.

19. Evers, J. "Transformation of Three-Connected Silicon Nets in CaSi$_2$," J. Solid State Chem., 28, 369, 1979.

20. Hirano, T., J. Less Common Met., 167, 329, 1991.

SYMBOLS AND ABBREVIATIONS

1H	Hexagonal crystal structure with one layer repeat unit
3R	Rhombohedral crystal structure with 3-layer repeat unit
6R	Rhombohedral crystal structure with 6-layer repeat unit
λ	Wavelength of radiation used for XRD
ΔG_f	Change in Gibb's free energy of formation
ΔH_f	Change in enthalpy of formation
2Θ	Diffraction angle
Cu K_α	Radiation used for XRD
d_{10}	Size where 10% of the particles are smaller than this value
d_{50}	Size where 50% of the particles are smaller than this value
d_{90}	Size where 90% of the particles are smaller than this value
DTA	Differential thermal analysis
GOF	Goodness-of-fit
ICP	Inductively coupled plasma
S	Siemens, which is a reciprocal ohm
S.A.	Surface area in units of m^2/g
SEM	Scanning electron microscope
RPM	Revolutions per minute
TGA	Thermal gravimetric analysis
XRD	X-ray diffraction

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