

Defence Science Journal, Vol 47, No 3, July 1997, pp. 365-371
© 1997, DESIDOC

Role of Silicon in Boron-Potassium Nitrate System

V.S. Bhingarkar, P.P. Sane and R.G. Sarawadekar
High Energy Materials Research Laboratory, Pune-411 021

ABSTRACT

To examine the possibility of improving the ignition characteristics of the commonly used pyrotechnic ignition system based on $B-KNO_3$ -Binder (30:70:10), B was gradually replaced by Si in its composition. The addition of Si was found to reduce the maximum pressure and increase the ignition delay. Maximum dp/dt value was observed with the composition containing 5 per cent Si . The differential thermal analysis results showed single sharp peaks for ignition in the temperature range 500-570 °C. The heat of combustion and burning rate decreased with increase in Si content. Impact sensitivity of the compositions increased with increase in the percentage of Si , whereas no change was observed in the friction sensitivity in comparison with the base composition.

1. INTRODUCTION

Ignition of the rocket motor is an important and vital parameter. For the ignition of solid rocket propellants, wide use of $B-KNO_3$ -based pyrotechnic ignition compositions has been reported. De Yong, *et al*¹ studied the reaction mechanism using the differential scanning calorimeter technique. Heat of explosion and adiabatic flame temperature data were reported by Volk, *et al*². Brassy and coworkers³ studied the thermal diffusivity of $B-KNO_3$ -based pyrotechnic ignition compositions. A series of compositions containing 5-70 per cent B were studied by Charsley, *et al*^{4,5} employing differential thermal analysis (DTA), combustion calorimetry and time-to-ignition techniques.

Laye and Charsley⁶ have reviewed the information available on thermal analysis of pyrotechnics. $Si-KNO_3$ system was studied for temperature profiles. The temperature profile showed a smooth rise to a maximum temperature in the range 1000-1300 °C, except for the

composition with low (< 30 per cent) Si content⁷. From thermal analysis and temperature profile measurements, these workers estimated the kinetic parameters for the processes occurring during controlled heating and combustion of binary Si -fueled pyrotechnic systems⁸.

Studies on the combustion of $Si-KNO_3$ system were extended to examine the behaviour of ternary systems. The effect of substituting calcium silicide ($CaSi_2$) by ferrosilicon ($FeSi_2$) for some or all the Si present in the systems was examined⁹.

$B-KNO_3$ igniter composition was, however, found ineffective for ignition of fuel-rich type propellants which need a prolonged heat flux. Si containing pyrotechnic compositions are known to form slags which could provide the necessary supply of prolonged heat flux. Hence, it was considered of interest to examine the effect of partially substituting B by Si . A composition containing 30 per cent B was chosen as the base composition, to which Si was added gradually in increments of 5 per cent. The effect of adding Si

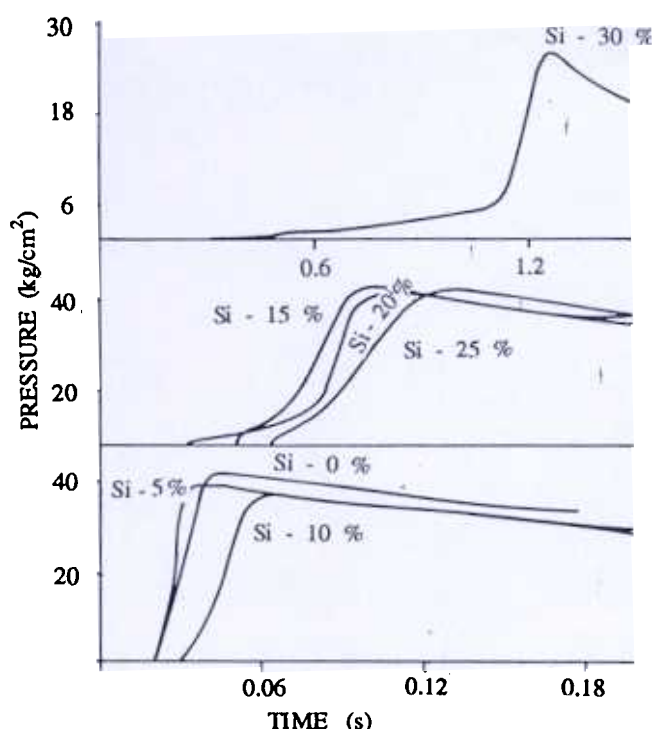


Figure 1. P-T curves for $B/KNO_3/PEC$ system

was studied by DTA, Fourier transform infrared (FTIR), X-ray diffraction (XRD) techniques and by determining the calorific values burning rate and pressure-time (P-T) profiles.

2. EXPERIMENTAL DETAILS

2.1 Materials

The materials used were KNO_3 (laboratory grade, particle size 90μ), B powder (average particle size 0.7μ), Si powder of high purity (average particle size 4μ) and plasticised ethyl cellulose (PEC) (Hercules Co., type N-200).

2.2 Preparation of Composition

KNO_3 was dried at $110^\circ C$ and passed through 90μ sieve. It was then mixed with B and the mixture passed through 600μ sieve three or four times. To this mixture, 10 parts of PEC in distilled toluene was added. This mixture was further granulated using a screen. The granules passing through 600μ sieve and retaining on 300μ sieve were selected for further work. Further, a mixture

was prepared by substituting B by Si , each batch being about 400 g.

2.3 Measurements of Pressure-Time Profiles

Loose granules (7 g) were burnt in a closed combustion chamber of capacity 700 cc. For this experiment, the sample was loaded in a small cotton bag in which a squib was embedded and desired current was passed for ignition. The pressure produced on combustion, and the ignition delay, were measured as a function of time. The signals were transferred to an oscilloscope and the main computer for recording P-T history. The P-T profile gave values of parameters like maximum pressure, burning time for maximum pressure and ignition delay.

DTA curves of these mixtures were recorded on an indigenously-fabricated DTA apparatus using 5 mg sample with $10^\circ C/min$ as the rate of heating. The reaction exothermicities were measured in air at 1 atm by burning these samples in a Julius Peter adiabatic calorimeter bomb. The burning rates of the compositions were determined by the lead tube method.

The combustion products were analysed employing Perkin-Elmer FTIR spectrophotometer model 457 in KBr at room temperature. In addition, X-ray diffraction patterns were recorded on Phillips X-ray diffractometer at room temperature. Sensitivity to impact was measured using a fall hammer apparatus fabricated in the laboratory using a 2-kg drop weight and a sample weight of 20 mg. Bruceton staircase method was used to carry out the test from which the height of 50 per cent explosion was determined.

Sensitivity towards friction was determined using a Julius Peter friction sensitivity apparatus.

3 RESULTS & DISCUSSION

3.1 Combustion Pressure in Closed Vessel

The pyrotechnic compositions were subjected to ignition in a closed vessel at 1 atm. The P-T profiles obtained for all compositions along with that for the base composition ($B:KNO_3:PEC:30:70:10$) are presented in Fig. 1. The values for

Table 1 : Pressure-time data (X % ,Y %, 70 % KNO_3 and 10 parts PEC)

X B (%)	Y Si (%)	P_{max} (MPa)	Ignition delay (ms)	Burning time up to P_{max} (ms)	dp/dt I (kg/cm ² /s)	dp/dt II (kg/cm ² /s)
30	0	4.25	24	21	2017	
25	5	4.15	22	14	3024	
20	10	3.83	32	28	773	1880
15	15	3.76	58	42	363	
10	20	3.59	61	48	122	
5	25	3.49	75	58	306	
0	30	2.55	955	310	5	11

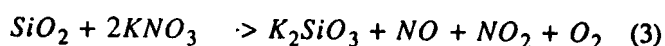
P_{max} ignition delay, dp/dt , etc. are given in Table 1. It is observed that by substituting Si, the maximum pressure decreases with increase in Si content. The base composition and the composition containing 5 per cent Si showed sharp peaks, while the remaining compositions showed two steps in the ignition transient. A composition containing 30 per cent Si gave pressure which is nearly half of the base composition. The composition containing 5 per cent Si was observed to have the least ignition delay value. Beyond 5 per cent, the ignition delay increased with increase in Si content (Fig. 2). The presence of Si particles supports the combustion phenomenon for 5 per cent Si composition in which combustion of B takes place very fast. This is also reflected in the values of burning time to maximum pressure.

The composition having 5 per cent Si has the least burning time (14 ms) to maximum pressure after which the burning time to maximum pressure

goes on increasing with further addition of Si particles. Krishnamohan, *et al*¹⁰ found the compositions containing more than 40 per cent Si to have ignited in lead tube experiments. This indicates that even 30 per cent Si—70 per cent KNO_3 composition ignites in the closed vessel testing.

The dp/dt value of the base composition is 2017.7 kg/cm²/s, while that for 5 per cent Si composition is 3024.3 kg/cm²/s. The latter value of dp/dt shows that the reaction rate of the composition with 5 per cent Si is faster than that of the base composition. The oxidation of Si and B takes place simultaneously and hence it has lower ignition delay and burning time values, leading to higher dp/dt values. The dp/dt values indicate that the first reaction is due to the oxidation of Si and the second one due to the oxidation of B. With increase in Si content in the composition, the reaction is observed to slow down. This can be explained as follows:

The oxidation of Si takes place at 400 °C to give SiO_2 and that of amorphous B takes place at 700 °C to give B_2O_3 ¹¹. These reactions are:



The products obtained from these reactions produce hot slag, which strikes on the propellant

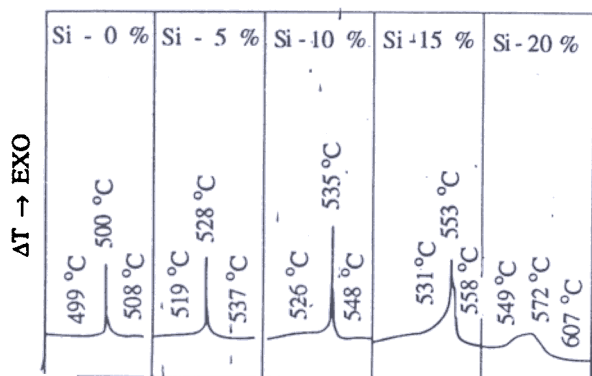

 Figure 2. DTA curves for B/ KNO_3 /PEC system

Table 2. Calorific value, burning rate and sensitivity test (X %, Y %, 70 % KNO_3 and 10 parts PEC)

X B (%)	Y Si (%)	Calorific value (cal/g)	Burning rate (mm/s)	Friction (kg)	Impact (cm)
30	0		7.03	36	122
25	5		6.90	36	84
20	10	1529	5.01	36	93
15	15	1508	3.78	36	90
10	20	1402	.91	36	72
5	25	1382	.73	36	70
0	30	1158	Not ignited	36	63

surface and ignites the propellant even at low temperatures. The pyrotechnic composition containing 5 per cent Si only could ignite a fuel-rich propellant (conditioned at -20°C for 8 hr), while the base composition failed to ignite this fuel-rich propellant.

3.2 Differential Thermal Analysis

The DTA of amorphous B shows a single broad exothermic peak at 697°C , which is attributed to the oxidation of B in air. It always forms stable B_2O_3 . The DTA of KNO_3 shows an endothermic peak at 130°C , which is due to phase transition from orthorhombic to trigonal structure. The second endothermic peak at 334°C is attributed to the melting of KNO_3 . It shows a broad exothermic peak in the range $547-647^\circ\text{C}$ which is due to the decomposition of KNO_3 . This is in conformity with the one reported in literature¹².

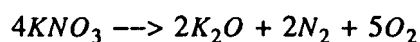


Figure 2 shows the DTA curves of B: KNO_3 :PEC₁ system and the compositions containing varying percentages of Si. The base composition shows a single sharp exothermic peak at 500°C , which could be due to the ignition reaction. The DTA curves of the main reaction are

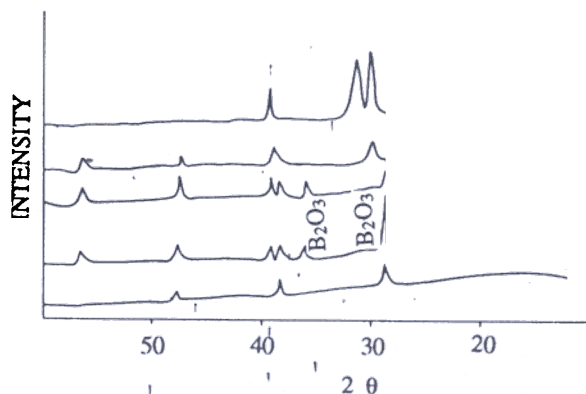


Figure 3. XRD patterns of slag containing % Si in B/ KNO_3 /PEC system.

shown in Fig. 2; the other peaks at 130 and 334°C are deleted. It is noted that the ignition reaction occurs at a lower temperature than the air oxidation of B. This is due to oxygen available from KNO_3 , which leads to a spontaneous reaction.

The peak temperature is observed to increase with increase in Si content. The reaction of the composition containing 5 per cent Si starts at 519°C and gets completed at 537°C . The inception temperature increases with increase in Si content. The peak width also increases and then finally the reaction does not show a spontaneous nature.

4. HEAT OF COMBUSTION

The heat of combustion was determined in air at 1 atm in a bomb calorimeter. The values obtained are given in Table 2. The value of heat of combustion of the base composition is 1696 cal/g, while that of the composition containing 30 per cent Si is 1158 cal/g. Substitution of Si in the base composition lowers the heat content. As the heat of formation of SiO_2 is -202 kcal/mole and that of B_2O_3 , -302 kcal/mole, the net heat of reaction for the oxidation of B is higher than that for the oxidation of Si.

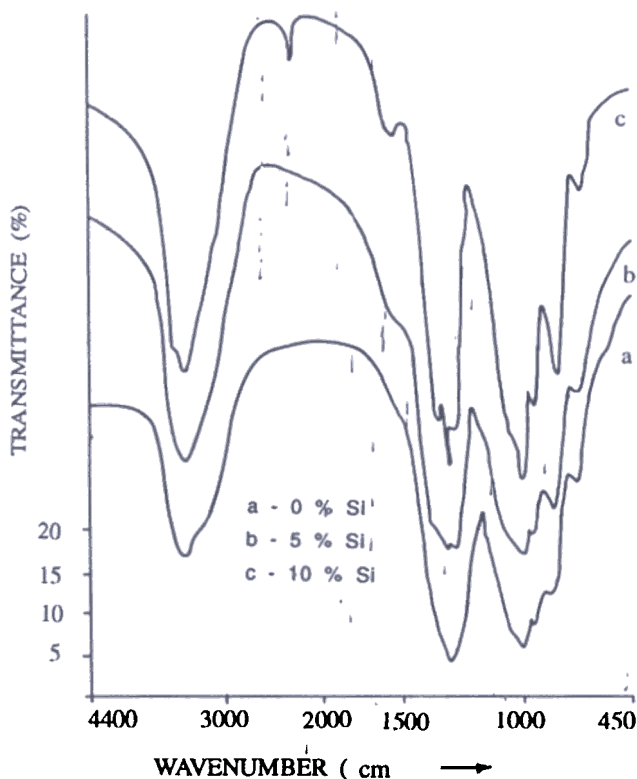
4. Rate of Burning

Data on rate of burning determined by the lead tube method are given in Table 2. The burning rate of the base composition is 7.03 mm/s. On adding

Table 3. FTIR data for slags of $B\text{-KNO}_3$ -PEC

Si, %	Frequency cm^{-1} and assignments							
20	3500 OH	2360 B-H	1712 B-H-B	1426 B-N	1004 B_4O_7	832 SiO_2	704 SiO_2	458 SiO_2
15	3502 OH		1710 B-H-B	1426 B-N	1004 B_4O_7	832 SiO_2	704 SiO_2	646 SiO_2
				1336 B-O	940			
10	3444 OH				1002 B_4O_7	834 SiO_2		
				1384 B-O				
5	3442 OH			1384 B-O	996 B_4O_7			
0	3440 OH			1382 B-O	1004 B_4O_7			

Si to the base composition, the burning rate gradually decreases from 7.03 to 1.73 mm/s. This can be correlated with the oxidation processes which are not the same. The oxidation of Si is slow, as compared to that of B.


 Figure 4. FTIR spectra of slags of $B/KNO_3/PEC$ system containing Si.

5. X-RAY DIFFRACTION & FTIR

The slags obtained in the combustion calorimetry experiment, were analysed by X-ray diffraction to identify the final products of the combustion reactions. X-ray diffraction patterns obtained are shown in Fig. 3. The 'd' values of the corresponding products compared with standard ASTM data cards¹³ are:

Compound	d (Å)
B_2O_3	3.2177 and 2.5066
KBO_2	3.0354, 2.8115
KB_5O_8	5.9804, 4.5026, 3.5036, 2.9568
SiO_2	1.515
$K_6Si_3O_9$	6.5053, 3.0335, 3.1291

From these data, only crystalline materials are identified. Further analysis was carried out employing FTIR spectroscopy. FTIR spectra of the same slags are shown in Fig. 4 and the values of frequencies along with assignments are given in Table 3. In all cases, hydrated salts of B and Si were identified. This indicates the formation of compounds like KBO_3 and $SiO_2 \cdot K_2O$, B_2NO_2 , free-silica and borohydrates. It is to be noted that only qualitative analysis of the products was done¹⁴.

6. SENSITIVITY

The results of impact and friction sensitivity measurements are presented in Table 2. Composition 1 is found to be less sensitive to impact, and addition of Si increases its sensitivity. Composition 7 is highly sensitive in comparison to the other compositions. This is probably due to the hard surface of Si (4-6 μ), which might be behaving as grit. This grit type material might be increasing the sensitivity by generating heat in the composition.

The friction insensitivity of these mixtures was observed up to 36 kg. It can be seen that these compositions are not very sensitive to friction.

7. CONCLUSION

The present study reveals that the addition of Si to the B-KNO₃-based ignition system increases ignition delay, ignition temperature and impact sensitivity, while it decreases maximum pressure, heat of combustion and rate of burning.

A unique feature observed in this study is that the addition of 5 per cent Si causes maximum increase in dp/dt value compared to the base and other compositions.

ACKNOWLEDGEMENT

The authors thank the Director, High Energy Materials Research Laboratory, Pune, for permitting them to publish this work.

REFERENCES

1. Daniel, J. Whelan; Maksacheff, M. & De Yong, L.V. Thermal decomposition of some pyrotechnic compositions, as studied by differential scanning calorimetry. Proceedings of the 16th International ICT-Jehrestagung Fraunhofer-Institute fur-Treib und Explosivstoffe, Karlsruhe, 1985. pp. 55/1-55/14.
2. Volk, F; Bathelt, H.M. & Muller, D. Inner ballistic evaluation of the effect of igniters. Proceedings of the 16th International ICT-Jehrestagung Fraunhofer-Institute fur-Treib und Explosivstoffe, Karlsruhe, 1985. pp. 6/1-6/19.
3. Brassy, C.; Megharti, M.; Roux, M. & Auzanneau. Thermal diffusivity of pyrotechnic compositions. Proceedings of the 16th International ICT-Jehrestagung Fraunhofer-Institute fur-Treib und Explosivstoffe, Karlsruhe, 1985. pp. 16/1-16/12.
4. Barnes, J.A.; Griffiths, T.T.; Charsley, E.L.; Hider, J.A. & Warrington, S.B. The properties and reactions of the B potassium nitrate pyrotechnic system. 11th International Pyrotechnics Seminar, Colorado, Illinois Institute of Technology Research, Chicago; 1986. pp. 27-45
5. Lindsley, G.L.; Robinson, E.A.; Charsley, E.L. & Warrington, S.B. The comparison of the ignition characteristics of selected metal/oxidant system. 11th International Pyrotechnics Seminar, Colorado, Illinois Institute of Technology Research, Chicago, 1986. pp. 425-46.
6. Laye, P.G. & Charsley, E.L. Thermal analysis of pyrotechnics. *Thermochimica Acta*, 1987, 12, 325-49
7. Rugunanan, R. Anil, *et al.* Combustion of binary and ternary Si/oxidant pyrotechnic systems, Part II, Binary systems with Sb₂O₃ and KNO₃ as oxidants. *Combustion Sci. Technol.*, 1994, 95(1-6), 85-99.
8. Rugunanan, R. Anil, *et al.* Combustion of binary and ternary Si/oxidant pyrotechnic systems, Part II, Binary systems with Sb₂O₃ and KNO₃ as oxidants. *Combustion Sci. Technol.*, 1994, 95(1-6), pp. 117-38
9. Rugunanan R. Anil & Brown Michel E., *Combust. Sci. Technol.*, 1994, 95 (1-6), 101-15.
10. Krishnamohan, G. *et al.* Thermal analysis and inverse burning rate studies on Si-KNO₃ systems. 8th International Pyrotechnics Seminar, Colorado, Illinois, Institute of Technology Research, Chicago, 1982. pp. 404 - 421.

BHINGARKAR, *et al* : ROLE OF SILICON IN BORON-POTASSIUM NITRATE SYSTEM

11. Heslop, R.H. & Robinson, R.L. Inorganic chemistry. Elsevier Publishing Co. 1960. pp. 262-83
12. Engineering Design Handbook: Military pyrotechnics series, Part III, Properties of materials used in pyrotechnic compositions. October 1963. pp 61 & 256. AMCP 706-187.
13. Joint committee on powder diffraction standards, X-ray Powder Diffraction File, 1967.
14. Colthup, N.B.; Daly, L.H. & Wiberley, S.E. Introduction to infrared and Raman spectroscopy. Academic Press, New York, 1964. pp. 291-98.

Contributors



Mrs VS Bhingarkar obtained her MSc (Organic Chemistry) from Poona University, in 1984. She is working as Scientist at the High Energy Materials Research Laboratory (HEMRL), Pune. The areas of his interest include design and development of pyrotechnic composition for ignition systems of solid rocket propellants.



Dr PP Sane did his PhD from Poona University, Pune, in 1978. He is working as Scientist E at HEMRL. The areas of his work include formulation, evaluation and qualification of pyrotechnic compositions and design and development of ignition systems for rocket propellants.



Dr RG Sarawadekar obtained his PhD from Shivaji University in 1981. He is working as Technical Officer B at HEMRL. The areas of his interest include thermal analysis, reaction kinetics, thermodynamics, solidstate chemistry, and thermo-chemical calculations using computers. Presently he is working on theoretical computations of pyrotechnic compositions.