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# THERMOANALYTICAL STUDY OF SOLID STATE $Al_4C_3$–$X_2S_2O_8$ AND $B_4C$–$X_2S_2O_8$ (X = Na, K) BINARY SYSTEMS

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## ABSTRACT

TG, DTG and DTA studies for $Al_4C_3$ and $B_4C$ alone and in binary molar ratios (under static air and dynamic $N_2$) mixtures with $Na_2S_2O_8$ or $K_2S_2O_8$ has shown that $Al_4C_3$ undergoes gradual degradation from 50 °C upwards The small exo-peak observed around 800 °C belongs to the polymorphic modification of the freshly prepared $Al_2O_3$ The main decomposition step starts around 880 °C Under $N_2$, $B_4C$ is thermally stable up to the ceiling temperature of the heating programme (1050 °C), in air it gains appreciable weight (35 5%) over the temperature span 580–1050 °C Under either atmospheres, pyrosulphates of Na and K react with $Al_4C_3$ ($T_{max} = 625$ °C) forming $Na_3Al(SO_4)_3$ and $K_3Al(SO_4)_3$ which are stable up to 590 and 630 °C, respectively Stoichiometric equations for their formation have been suggested A eutectic mixture ($K_3Al(SO_4)_3 + K_2SO_4$), $T_{max} = 600$ °C, is found $B_4C$ reacts with molten $Na_2S_2O_7$ and $K_2S_2O_7$ forming, respectively, $Na_2B_4O_7$, $\gamma$-$Na_2B_4O_7$ and $K_2B_4O_7$ as major products The by-products, $Na_2SO_4$ and $K_2SO_4$, react around 800 °C with $B_2O_3$ forming extra $Na_2B_4O_7$ and $K_2B_4O_7$, with aluminium oxide, meta aluminates of Na and K are formed It seems that the ionic carbide ($Al_4C_3$) is less stable and more reactive than the covalent carbide ($B_4C$) This suggests that they have different stereochemistry, resonating structures and molecular shapes

## INTRODUCTION

Aluminium carbide ($Al_4C_3$) belongs to the salt-like ionic class of carbides (methanides) [1] At 1800 °C it reacts with $N_2$ to form $Al_5C_3N$ [2] It is used for the preparation of many organometallic compounds [2] The Al–C bond length is 190–222 pm, the C–C bond is much longer, 316 pm [3] $B_4C$ is a semiconductor covalent-class carbide [4–5] with rhombic crystalline structure and is a good neutron absorber [6] It is used for lining high-temperature and reactive containers and to increase the coherence strength of cement and ceramic materials

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A recent literature survey has not revealed any thermoanalytical investigations of $Al_4C_3$ and $B_4C$ alone or in mixtures This work investigates the non-isothermal behaviour of the two carbides individually or in binary mixtures with persulphates of Na and K under static air and dynamic $N_2$ atmospheres

## EXPERIMENTAL

### *Reagents*

Commercial $Al_4C_3$ and $B_4C$ (Fluka AG Buchs), sodium and potassium peroxodisulphates (Hopkin and Williams) were used Alpha-$Al_2O_3$ (MOM) desiccated at 1300 °C for two hours was used as reference for DTA

### *Apparatus and procedure*

The thermal analyser, the procedure and X-ray diffractometer used for the identification of reactants and products of thermal analysis were as described previously [7] Dry nitrogen flow rate was 370 $cm^3$ $min^{-1}$

## RESULTS AND DISCUSSION

### *Thermoanalysis of $Al_4C_3$ and $B_4C$*

The thermoanalytical behaviour of both carbides is reported in Fig. 1 and Table 1 A very slow weight loss up to 4 45 wt% (over the temperature range 50–450 °C) due to catalytic decomposition of $Al_4C_3$ by persulphates, is indicated by the TG curve Afterwards, the TG exhibits a sudden weight

TABLE 1

Preparation and results of $Al_4C_3$–$Na_2S_2O_8$ molar ratio binary mixtures

| $Al_4C_3$–$Na_2S_2O_8$ molar ratio | Weight of sample (mg) | Weight of $Al_4C_3$ in sample (mg) | Weight of $Na_2S_2O_8$ in sample (mg) | Weight of $O_2$ lost (mg) | | Temp of $O_2$ lost (°C) | |
|---|---|---|---|---|---|---|---|
| | | | | Theo | Exp | $T_i$ | $T_f$ |
| 0 1 | 200 | – | 200 | 13 4 | 13 | 160 | 200 |
| 1 2 | 200 | 46 43 | 153 57 | 10 3 | 10 | 175 | 215 |
| 1 1 | 200 | 75 4 | 124 6 | 8 37 | 8 | 175 | 220 |

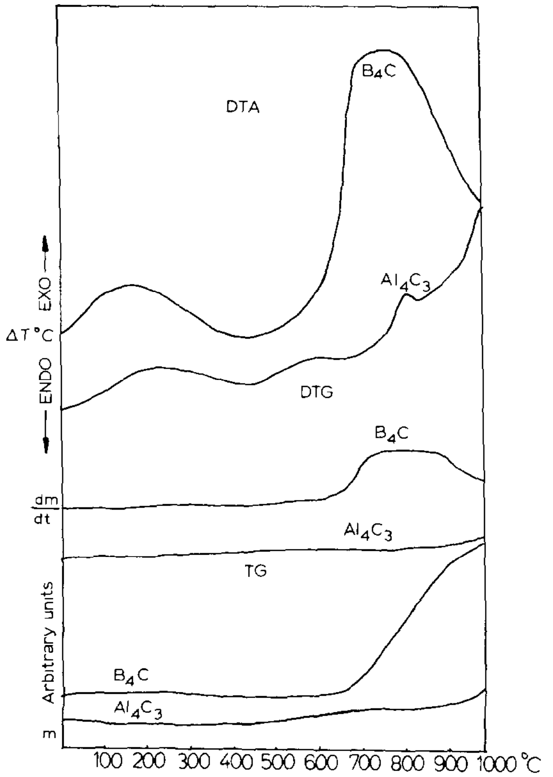

Fig 1 Thermoanalysis curves of $Al_4C_3$ and $B_4C$ under (static) air atmosphere

gain (7 5 wt%) attributable to two consecutive slow air oxidation processes of $Al_4C_3$, both of which are described below

$$Al_4C_3 + 6O_2 \xrightarrow{\Delta} 2Al_2O_3 + 3CO_2 + \text{heat} \qquad (1)$$

The XRD patterns of the final decomposition products confirm the presence of $Al_2O_3$ and unreacted $Al_4C_3$ [8,9] At 810 °C a small sharp exo-peak of

| Decomposition of $Al_4C_3$ (°C) | Formation temp of $Na_3Al(SO_4)_2$ (°C) | | Decomposition temp of $Na_3Al(SO_4)_2$ (°C) | | Melting point of $Na_2S_2O_7$ (°C) | Melting point of $Na_2SO_4$ (°C) | $Al_4C_3$ oxidation (°C) |
|---|---|---|---|---|---|---|---|
| | $T_i$ | $T_f$ | $T_i$ | $T_f$ | | | |
| – | – | – | – | – | 370 | 880 | – |
| 50 | 350 | 400 | 590 | 760 | – | 630 | ⩾ 880 |
| 50 | 310 | 360 | 590 | 660 | – | 610 | ⩾ 880 |

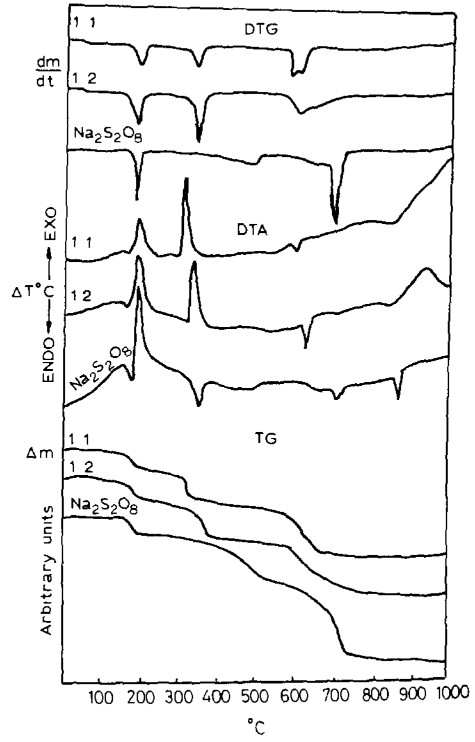

Fig 2 Thermoanalysis curves of ($Al_4C_3$–$Na_2S_2O_8$) molar ratio binary systems

polymorphic modification of $Al_2O_3$ appears under air, and under $N_2$, at $T_{max}$ = 786 °C which means that dynamic $N_2$ promotes the process

The TG and DTG traces of $B_4C$ in air show that it is thermally stable up to 580 °C Thereafter, a large weight gain of 35 5 wt% obtained beyond 580 °C belongs to the combustion of $B_4C$. This is accompanied by a large exo-peak that appears on the DTA curve between 650 and 780 °C X-ray diffractometry of the final products identifies the presence of $B_2O_3$ [10] and unreacted $B_4C$ [11] The oxidative decomposition follows

$$B_4C + 4O_2 \xrightarrow{\Delta} 2B_2O_3 + CO_2 + \text{heat} \qquad (2)$$

The broad exotherm before 540 °C is believed to be due to variation of specific heats of boron carbide with rise of temperature A negligible weight gain is observed after 700 °C in $N_2$, the corresponding DTA reveals no enthalpy change.

### *Thermoanalysis of $Al_4C_3$–$Na_2S_2O_8$*

Figure 2 and Table 1 show the results of $Al_4C_3$ $Na_2S_2O_8$ molar ratios heated in air The $T_i$ and $T_f$ for the decomposition of the persulphate in mixtures exceeds that for $Na_2S_2O_8$ alone by 15 and 20 °C for the ratios 1 2 and 1 1, respectively, so that the heat resistance of the latter is catalytically improved in the presence of $Al_4C_3$ Appreciable decomposition of the latter starts at 50 °C and is catalysed by $Na_2S_2O_8$ The acute exotherms at 350 and 310 °C accompanied by weight losses of 14 and 12 mg for 1 2 and 1 1 ratios, respectively, represent an unresolved redox reaction between molten $Na_2S_2O_7$ and $Al_4C_3$

$$Al_4C_3 + 3Na_2S_2O_7 + 6O_2 \xrightarrow{\Delta} 2Na_3Al(SO_4)_3 + 3CO_2 + \text{heat} \quad (3)$$

X-ray analysis for samples of 1 1 and 1 3 ratios heated up to 440 °C reveals the presence of $Na_3Al(SO_4)_3$ [12], traces of $Al_2O_3$ and unused $Al_4C_3$ The double salt is found to be thermally stable up to 590 °C, afterwards it undergoes simultaneous melting ($T_{max} = 625$ °C) [13], volatilization and decomposition

$$2Na_3Al(SO_4)_3 \xrightarrow{\Delta} 3Na_2SO_4 + 3SO_3 + Al_2O_3 \quad (4)$$

At 590–615 °C, a decrease of 60 wt% occurs, and at 615–660 °C the remaining 40 wt% is gone For the 1 2 ratio the decomposition occurs in

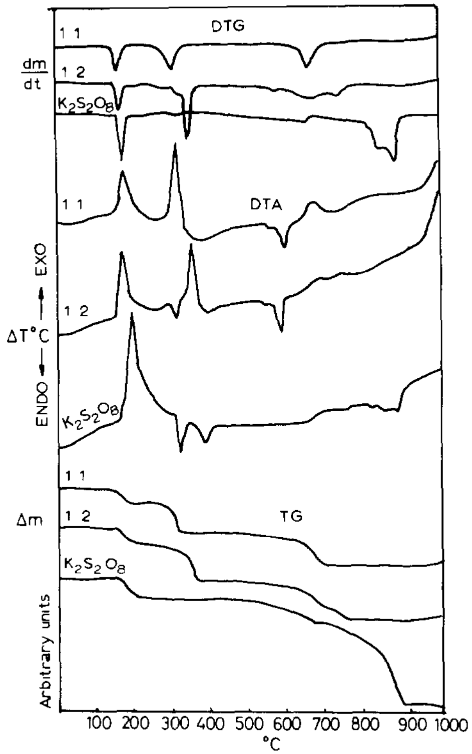

Fig 3 Thermoanalysis curves of $Al_4C_3$–$K_2S_2O_8$ binary system under (static) air atmosphere

one step After 870 °C, a weight gain due to oxidation of excess $Al_4C_3$ occurs In nitrogen, the TG and DTG curves (not shown for brevity) infer that between 50 and 110 °C a small weight loss of sample is observed for the 1 1 ratio, the $T_i$ and $T_f$ for the persulphate decomposition are shifted to 165–195 °C, respectively The $Na_2S_2O_7$–$Al_4C_3$ reaction (1 1 ratio) takes place in two exothermic stages, a major one between 270 and 350 °C and a minor one between 370 and 410 °C, revealing the complex route for the formation of $Na_3Al(SO_4)_3$ in $N_2$ or air Under $N_2$, a smaller exotherm appears ($T_{max}$ = 910 °C) after the melting endotherm of $Na_2SO_4$ attributable to the reaction

$$Na_2SO_4 + Al_2O_3 \xrightarrow{\Delta} 2NaAlO_2 + SO_3 + \text{heat} \qquad (5)$$

A monotonic behaviour is observed for the 1 2 ratio, except that the formation of the double salt occurs in one step and the burning exotherm of unreacted $Al_4C_3$ (after 860 °C) is larger in air but completely demolished in $N_2$ Higher ratios, such as 2 1, behave similarly, except that the combustion step beyond 820 °C becomes enormously large, and in $N_2$ two sharp exo-peaks, a large one between 800 and 910 °C and a smaller between 910 and 980 °C appear (see eqn (5)) The latter represents a crystallization process Naturally, in air the combustion exotherm of the carbide overlaps these exo-peaks

*Thermoanalysis of $Al_4C_3$–$K_2S_2O_8$*

$Al_4C_3$ has catalytically lowered the $T_i$ of persulphate degradation (Fig 3 and Table 2) by about 22 °C for either ratio Unexpectedly, no weight loss of the analysed sample was observed up to 200 °C, which means that $K_2S_2O_8$ delays the decomposition of the carbides Distinct exotherms ($T_{max}$ = 320 °C for the 1 1 and 365 °C for the 1 2 ratios, respectively) are observed on DTA and represent the exo-reaction between carbide and pyrosulphate It is worth noting that $T_{max}$ increases as the $Al_4C_3$ $K_2S_2O_8$ ratio decreases,

TABLE 2

Preparation and results of thermal analysis of $Al_4C_3$–$K_2S_2O_8$ binary systems

| $Al_4C_3$–$K_2S_2O_8$ molar ratio | Weight of sample (mg) | Weight of $Al_4C_3$ (mg) | Weight of $K_2S_2O_8$ (mg) | Temp of $O_2$ lost from $K_2S_2O_8$ (°C) | | Weight of $O_2$ lost from $K_2S_2O_8$ (mg) | | Decomposition temp of $K_2S_2O_7$ (°C) |
|---|---|---|---|---|---|---|---|---|
| | | | | $T_i$ | $T_f$ | Theo | Exp | |
| 0 1 | 200 | – | 200 | 182 | 205 | 10 82 | 10 5 | 455–865 |
| 1 2 | 200 | 42 | 158 | 160 | 200 | 8 54 | 8 | 260 |
| 1 1 | 200 | 69 5 | 130 5 | 160 | 200 | 7 | 7 | 260 |

indicating the catalytic role of the carbide played in decreasing the activation of the system The $d$-lines for samples heated up to 340 °C identify $K_3Al(SO_4)_3$ [14], in addition to $\alpha$-$Al_2O_3$ and unburned $Al_4C_3$ Calculations suggest the following stoichiometric reaction

$$3K_2S_2O_8 + Al_4C_3 + 6O_2 \xrightarrow{\Delta} 2K_3Al(SO_4)_4 + Al_2O_3 + 3CO_2 + \text{heat} \qquad (6)$$

The exo-peak for the 1 1 ratio infers a reaction in the solid state, whereas that for the 1 2 ratio occurs after melting of the pyrosulphate Calculation shows that not all the pyrosulphate reacts with $Al_4C_3$ Unreacted $K_2S_2O_7$ pyrolyses, forming $K_2SO_4$ whose B–a endotherms [15] appear at $T_{max}$ of 560 and 580 °C $K_3Al(SO_4)_3$, melting $T_{max} = 600$ °C (m p of pure compound = 690 °C) [14], starts decomposition at 630 °C, which goes on to 690 °C for the 1 1 ratio (weight loss = 16 mg), and, for the 1 2 ratio, continues to 760 °C in two steps (weight loss = 18 mg) The overall decomposition steps are exothermic, this includes a polymorphic modification of the freshly-formed $\alpha$-$Al_2O_3$ X-ray diffraction for samples heated up to 690 °C, in $N_2$ or air, confirms the absence of $K_3Al(SO_4)_3$ $d$-lines and the presence of those of $K_2SO_4$, $Al_2O_3$ and $Al_4C_3$ Beyond 940 °C a weight gain due to combustion of $Al_4C_3$, accompanied by evolution of heat, is obtained in air In $N_2$ two distinct exo-peaks similar to those previously obtained (Fig 2) are due to the formation and crystallization of $NaAlO_2$

In conclusion, it seems that the $C_3^{4-}$ ion persists longer during decomposition in the presence of $K_2S_2O_8$ than with $Na_2S_2O_8$

A distinct feature of this system is that the melting endotherm of the double salt precedes the decomposition exotherms, in the previous system the two peaks are overlapped (same $T_{max}$)

### *Thermoanalysis of $B_4C$–$Na_2S_2O_8$*

Table 3 shows the preparation and results of thermal analysis of this binary system Figure 4 indicates that $B_4C$ has shifted the temperature for

| Temp of reaction (°C) | | Phase change of pyro (°C) | Melting point of pyro (°C) | Decomposition temp of $K_3Al(SO_4)_3$ (°C) | | Phase change of $K_2SO_4$ (°C) | Melting point of $K_3Al(SO_4)_3$ | Oxidation of $Al_4C_3$ |
|---|---|---|---|---|---|---|---|---|
| $T_i$ | $T_f$ | | | $T_i$ | $T_f$ | | | |
| – | – | 320 | 390 | – | – | – | – | |
| 340 | 380 | 320 | – | 630 | 760 | 560 | 600 | 940 |
| 290 | 320 | – | – | 630 | 690 | 580 | 600 | 940 |

TABLE 3

Preparation and results of $B_4C$–$Na_2S_2O_8$ molar ratios binary systems

| $B_4C$–$Na_2S_2O_8$ molar ratio | Weight of $B_4C$ in sample (mg) | Weight of $Na_2S_2O_8$ in sample (mg) | Weight of sample (mg) | Temp of $O_2$ lost from $Na_2S_2O_8$ (°C) | | Weight of $O_2$ lost from $Na_2S_2O_8$ (mg) | |
|---|---|---|---|---|---|---|---|
| | | | | $T_i$ | $T_f$ | Theo | Prac |
| 0 1 | – | 200 | 200 | 160 | 200 | 13 4 | 13 |
| 1 2 | 21 | 179 | 200 | 170 | 210 | 12 | 12 |
| 1 1 | 37 8 | 162 2 | 200 | 175 | 210 | 10 9 | 10 5 |
| 2 1 | 63 64 | 136 36 | 200 | 180 | 210 | 9 16 | 9 |

the decomposition of the persulphates and pyrosulphate towards higher values Afterwards, a two-step overlapped exothermic reaction occurs between carbide and pyrosulphate, accompanied by a weight loss of 22 and 24 wt% for the 1 1 and 1 2 ratios, respectively *d*-Lines for samples heated up

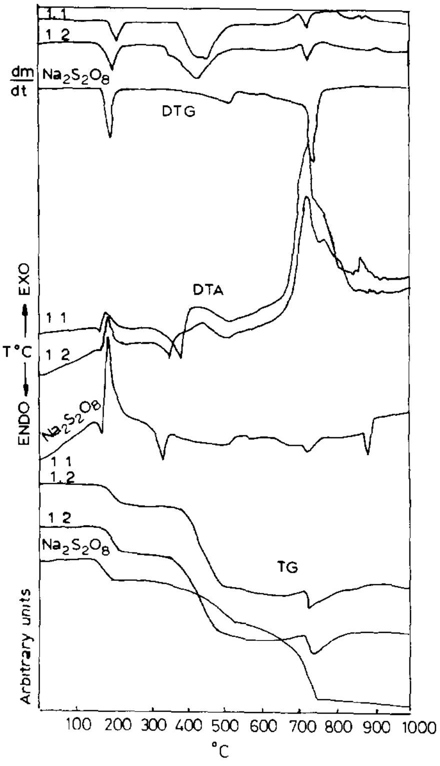

Fig 4 Thermoanalysis curves of $B_4C$–$Na_2S_2O_8$ binary systems under (static) air atmosphere

| Melting point of $Na_2S_2O_7$ | Reaction temp of $B_4C$ and $Na_2S_2O_7$ (°C) | Reaction temp of $B_4C$ and $Na_2SO_4$ (°C) | Temp of $B_4C$ oxide (°C) | | Melting point of $Na_2SO_4$ |
|---|---|---|---|---|---|
| | | | 1st step | 2nd step | |
| 320 | – | – | – | – | 880 |
| 355 | 355 | 720 | 690 | 870 | 855 |
| 380 | 380 | 720 | 670 | 850 | 830 |
| 365 | 365 | 700 | 640 | 875 | 850 |

to 520 °C show the presence of $Na_2B_4O_7$ [16], $\gamma$-$Na_2B_4O_7$ [17], $Na_2SO_4$ [18] and excess $B_4C$

Calculations indicate that the stoichiometric ratio is 1 1 and the redox reaction is

$$Na_2S_2O_7 + B_4C + 4O_2 \xrightarrow{\Delta} Na_2B_4O_7 + 2SO_3 + CO_2 + \text{heat} \qquad (6)$$

The combustion of unreacted $B_4C$ begins at 560 °C and reaches a maximum at 690 °C A sharp but comparatively smaller decomposition exotherm (Fig 5) is obtained in $N_2$ (no $B_4C$ combustion) as follows

$$Na_2B_4O_7 \xrightarrow{\Delta} Na_2O + 2B_2O_3 + \text{heat} \qquad (7)$$

The exothermicity of the above reaction is ascribed to polymorphic crystallization of $B_2O_3$ at high temperatures The disappearence of $Na_2SO_4$ is due to its reaction with $B_2O_3$

$$Na_2SO_4 + 2B_2O_3 \xrightarrow{\Delta} Na_2B_4O_7 + SO_3 \qquad (8)$$

Under dynamic $N_2$ a reaction similar to the above takes place X-ray diffraction patterns of the final product infer the presence of unreacted $B_4C$ The same decomposition trend has been found for the 2 1 ratio (Fig 5) in air and $N_2$, under the latter the large combustion exotherm of $B_4C$ completely vanishes

### *Thermoanalysis of $B_4C$–$K_2S_2O_8$*

The preparation and results of various molar ratios of this binary system are shown in Table 4 and Fig 6 The $T_i$ and $T_f$ of $K_2S_2O_8$ and $K_2S_2O_7$ decomposition are catalytically lowered by $B_4C$, the effect increases as the ratio $B_4C$ $K_2S_2O_8$ increases The exo-peaks at 460 (1 1) and 480 °C (1 2) ratios represent the triple-step exothermic reaction between pyrosulphate

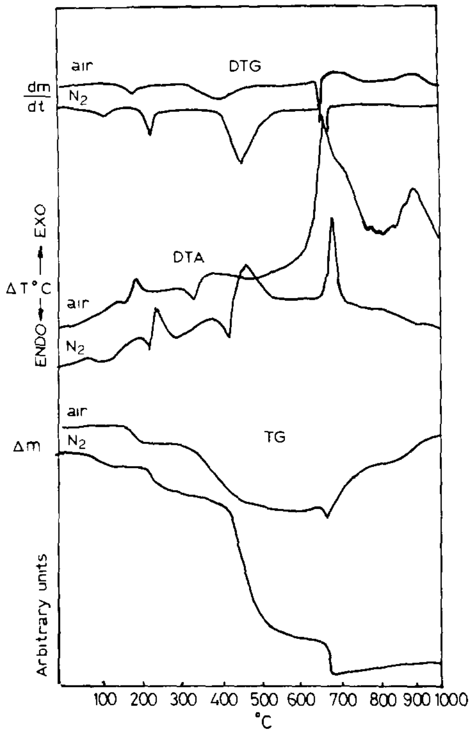

Fig 5 Thermoanalysis curves of $B_4C$-$Na_2S_2O_8$ (2 1 ratio) in (static) air and (dynamic) $N_2$ atmospheres

and carbide X-ray diffractometry for samples heated to 530, 550, 580 and 680 °C identifies $K_2B_4O_7$ [19] and unreacted $B_4C$ and $K_2SO_4$ (from pyrolysis of excess $K_2S_2O_7$) Thermogravimetric computations suggest the following stoichiometric reaction

$$K_2S_2O_7 + B_4C + 4O_2 \xrightarrow{\Delta} K_2B_4O_7 + 2SO_3 + CO_2 + \text{heat} \tag{9}$$

TABLE 4

Preparation and results of $B_4C$-$K_2S_2O_8$ molar ratio binary systems

| $B_4C$-$K_2S_2O_8$ molar ratio | Weight of sample (mg) | Weight of $B_4C$ (mg) | Weight of $K_2S_2O_8$ (mg) | Temp of $O_2$ lost °C | | Weight of $O_2$ lost (mg) | | Phase change of $K_2S_2O_7$ (°C) |
|---|---|---|---|---|---|---|---|---|
| | | | | $T_i$ | $T_f$ | Theo | Exp | |
| 0 1 | 200 | – | 200 | 182 | 205 | 11 83 | 10 5 | 310 |
| 1 2 | 200 | 18 6 | 181 4 | 160 | 170 | 10 7 | 10 5 | 320 |
| 1 1 | 200 | 34 | 165 9 | 160 | 180 | 9 8 | 9 5 | 320 |

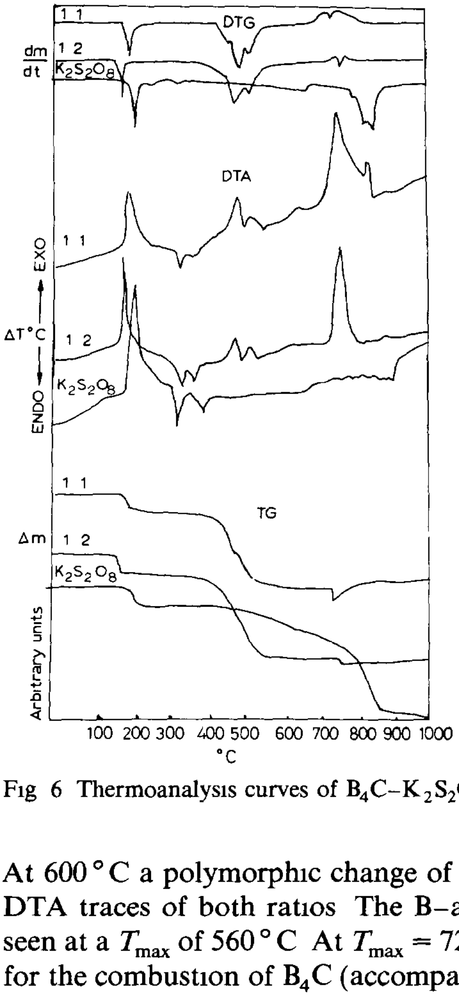

Fig 6 Thermoanalysis curves of $B_4C$–$K_2S_2O_8$ molar ratios under (static) air atmosphere

At 600 °C a polymorphic change of $K_2B_4O_7$ is seen as a small exo-peak on DTA traces of both ratios The B–a phase change endotherm of $K_2SO_4$ is seen at a $T_{max}$ of 560 °C At $T_{max}$ = 720 and 876 °C, the overlapped exo-peaks for the combustion of $B_4C$ (accompanied by weight gain) and reaction of the freshly-formed $B_2O_3$, with $K_2SO_4$, are observed, respectively

$$K_2SO_4 + 2B_2O_3 \xrightarrow{\Delta} K_2B_4O_7 + SO_3 + \text{heat} \qquad (10)$$

| M P of $K_2S_2O_7$ (°C) | Decomposition temp of $K_2S_2O_7$ (°C) | | Reaction temp of $B_4C$ and $K_2S_2O_7$ (°C) | | Reaction temp of $B_4C$ and $K_2SO_4$ (°C) | | Phase change of $K_2SO_4$ (°C) | Temp of $B_4C$ oxidation (°C) |
|---|---|---|---|---|---|---|---|---|
| | $T_i$ | $T_f$ | $T_i$ | $T_f$ | $T_i$ | $T_t$ | | |
| 395 | 455 | 865 | – | – | – | – | – | – |
| 385 | 400 | 570 | 480 | 570 | 750 | 760 | 560 | 600 |
| 380 | 380 | 550 | 460 | 550 | 720 | 725 | 560 | 600 |

X-ray diffraction patterns for samples heated up to 730 °C reveal increase of intensity of *d*-lines of $K_2B_4O_7$ and quenching of those of $K_2SO_4$

A decomposition trend similar to that of the previously discussed $B_4C$–$Na_2S_2O_8$ system has been found in the $N_2$ atmosphere

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