

Binary and ternary pyrotechnic systems of Mn and/or Mo and BaO₂ and/or SrO₂. Part 2. Combustion studies

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Abstract

The binary and ternary pyrotechnic systems of manganese, molybdenum, BaO₂ and SrO₂, which had been previously studied under the controlled temperature conditions of thermal analysis, have been studied further by ignition in packed channels and recording of temperature–time profiles during combustion. The Mn/BaO₂, Mo/BaO₂ and Mn/SrO₂ systems burn over a wide range of compositions, but the range of ignitable compositions for the Mo/SrO₂ system is very limited. The linear burning rates, for all these systems, range from 2 to 12 mm s⁻¹ and burning rates are increased by the use of smaller particle-sizes of fuel and greater loading pressures. Inert additives generally decrease the burning rate.

INTRODUCTION

The use of BaO₂ and SrO₂ as oxidants in pyrotechnic mixtures is briefly reviewed in Part 1 of this series [1]. Spice and Staveley [2] showed that several pyrotechnic systems undergo a pre-ignition reaction (PIR) and that solid–solid reactions occurred in at least the Fe/BaO₂ and Fe/K₂Cr₂O₇ systems. They noted that the linear burning rates of different compositions of the same system varied over a far wider range of values than either the specific heat or the thermal conductivity of the different compositions. They suggested that the burning rate is determined mainly by the kinetics of the PIR, and that the burning characteristics of a binary pyrotechnic mixture are more dependent on the properties of the oxidant than of the fuel. They also reported some results for the Mn/BaO₂, the Mo/BaO₂ and the S/BaO₂ systems.

Hill et al. [3, 4] also studied combustion of the Mo/BaO₂, Fe/BaO₂ and S/BaO₂ systems. They found good agreement between the observed linear burning rates for the Fe/BaO₂ system and those calculated from the

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shapes of the temperature profiles, and fair agreement for the Mo/BaO₂ system. Improved correlation between observed and calculated burning rates was achieved for the 80% Fe/KMnO₄ system by greater control over materials and experimental conditions. Kinetic analysis of the temperature profiles gave low values for the activation energy (13–33 kJ mol⁻¹) and a thermal conduction mechanism was proposed to account for the burning rates.

Yoshinaga et al. [5] quoted values for the ignition temperature of the Mo/BaO₂ system ranging from 425 to 500°C and for the ignition energy of from 11 to 12 kJ mol⁻¹. They also recorded linear burning rates ranging from 1.0 to 2.4 mm s⁻¹ for some compositions of Mo/BaO₂ at different densities.

Beyens and Dubois [6] noted the variations in the linear burning rates of Mg/BaO₂ compositions which had been made from different batches of BaO₂. Although no chemical differences between the batches could be detected, they did notice a link between different shapes of BaO₂ particles and the linear burning rates. They also identified the presence, in the oxidant, of BaCO₃ formed by exposure to the air.

EXPERIMENTAL

Materials

The materials used were those as used in Part 1 of this series [1]. Four different binary pyrotechnic systems were studied in detail: Mn/BaO₂, Mo/BaO₂, Mn/SrO₂ and Mo/SrO₂. Compositions are stated as percentages by mass of the fuel. Ternary pyrotechnic systems, consisting of either two fuels and one oxidant, or a single fuel with both oxidants, were also studied. The compositions of the ternary systems are quoted as percentages by mass of each constituent. The constituents of all the pyrotechnic mixtures were mixed by end-over-end tumbling, or by brushing through a sieve.

Median particle diameters and surface areas are given in Table 1.

TABLE 1

Particle sizes of constituents of all four systems

Material	Surface area (m ² kg ⁻¹)	Diameter (μm)	Material	Surface area (m ² kg ⁻¹)	Diameter (μm)
Mn large	8.0	112.6	BaO ₂ large ^a	62	36.6
Mn small ^a	85	16.6	BaO ₂ small	800	10.2
			BaO ₂ (BDH)	490	24.1
Mo large	9.3	64.0			
Mo medium ^a	19	34.4	SrO ₂ large ^a	1370	3.5
Mo small	64	13.8	SrO ₂ small	1300	3.0

^a Standard particle sizes used through this work, unless stated otherwise.

Apparatus

Samples of the powdered pyrotechnic compositions were hydraulically pressed (1 min at 50–250 MPa) into a rectangular stainless-steel channel (internal dimensions 30 mm × 6 mm × 5 mm) and ignited at one end using a starter increment (1 mm of 50% Mn/KMnO₄) and a safety match. The resulting temperature changes in the composition were recorded as a function of time [7, 8] as the combustion front passed a Pt/10% Rh–Pt thermocouple (wire diameters used were 0.05, 0.1, 0.2 and 0.3 mm) imbedded, prior to pressing, at a fixed point in the mixture. Two additional slits in the channel sides enabled burning times and hence burning rates to be measured through the triggering and stopping of a timing circuit by infrared detectors.

The unreacted starting materials and the solid products of reaction were characterized, where possible, using X-ray powder diffraction (XRD) and infrared (IR) spectroscopy. Scanning electron microscopy (SEM) was also used to detect the changes in external appearance after combustion.

Thermal conductivities of the compositions before combustion were also determined [9].

RESULTS AND DISCUSSION

Binary systems

For all four binary systems, compositions could be prepared which burnt under the experimental conditions described above.

The solid residues after combustion contained a complex mixture of metal oxides in addition to unreacted starting materials. The residues from the Mn/BaO₂ system contained a manganese spinel with the formula MnO · Mn₂O₃. The residues from the mixtures containing molybdenum tended to absorb water on cooling to form hydroxides. The presence of molybdates was also observed.

The range of compositions which sustained combustion in the standard stainless-steel channel under 50 MPa compaction varied from system to system as shown in Table 2. The ranges of measured burning rates v_{obs} , and maximum excess temperature rises U_{max} (where $U = T - T_a$ and T_a is the ambient temperature) [7, 8] for these compositions are also given in Table 2.

The mass burning rate increased with compaction for all four systems. Densities, void fractions, linear and mass burning rates are given in Table 3. McLain [10] has suggested that an increase in the mass burning rate (g s^{-1}) with increased compaction may indicate the occurrence of a genuine solid–solid reaction. It can also be argued that the increased compaction could prevent the escape of the gaseous products of decom-

TABLE 2

Effect of composition on burning rates of binary systems

M ^a (%)	v (mm s ⁻¹)			
	Mn/BaO ₂	Mo/BaO ₂	Mn/SrO ₂	Mo/SrO ₂
15	6.4 ± 0.6			
20	11.7 ± 0.2	2.8 ± 0.2	4.5 ± 1.0	
25	9.7 ± 0.5	4.1 ± 0.4	5.1 ± 1.3	
30	9.5 ± 0.4	4.5 ± 0.5	6.6 ± 1.0	
35	7.2 ± 0.4	4.9 ± 0.2	4.8 ± 0.2	
40	6.7 ± 0.4	4.7 ± 1.0	7.5 ± 1.0	2.3 ± 0.1
45	6.6 ± 0.4	10.1 ± 1.0	7.1 ± 1.3	2.2 ± 0.2
50	9.2 ± 0.4	6.0 ± 0.2	6.8 ± 1.2	
55	7.8 ± 0.6	6.2 ± 0.5	8.3 ± 0.7	
60	3.3 ± 0.8	6.8 ± 0.7	10.1 ± 1.6	
65	1.8 ± 0.5	5.5 ± 0.6	9.5 ± 0.3	
70		4.8 ± 0.4	12.0 ± 2.3	
75			12.3 ± 2.1	
80			7.2 ± 1.1	
<i>Range</i>				
M (%)	15–65	20–70	20–80	40–45
v (mm s ⁻¹)	1.7–11.7	2.7–10.1	4.5–12.3	2.2–2.3
U _{max} (°C)	700–>1760	860–1710	620–1730	1410–1600
v _{max} at	20% Mn	45% Mo	75% Mn	40% Mo

^a M = Mn or Mo.

TABLE 3

Effect of compaction on burning rate (BR)

System	Pressure (MPa)	Density (g cm ⁻³)	Void fraction	Linear BR (mm s ⁻¹)	Mass BR (g s ⁻¹)
25% Mn/BaO ₂	0	3.53 ± 0.18	0.42	6.57 ± 0.13	0.562
	50	4.18 ± 0.11	0.32	9.68 ± 0.45	0.728
	100	4.57 ± 0.24	0.25	9.80 ± 0.60	0.898
	150	5.13 ± 0.12	0.16	11.0 ± 0.4	1.32
30% Mo/BaO ₂	0	3.87 ± 0.07	0.45	2.84 ± 0.12	0.270
	50	4.60 ± 0.31	0.41	4.51 ± 0.50	0.502
	100	5.13 ± 0.26	0.27	6.74 ± 0.11	0.838
	150	5.36 ± 0.10	0.24	5.5 ± 2.8	0.711
20% Mn/SrO ₂	0	1.24 ± 0.27	0.76	3.92 ± 0.71	0.226
	50	2.51 ± 0.08	0.52	4.5 ± 1.0	0.259
	100	2.78 ± 0.31	0.47	4.58 ± 0.29	0.309
	250	3.49 ± 0.16	0.34	4.76 ± 0.87	0.402
40% Mo/SrO ₂	0	1.56 ± 0.02	0.78	2.23 ± 0.22	0.116
	50	3.34 ± 0.10	0.52	2.30 ± 0.06	0.182
	100	3.45 ± 0.37	0.50		

position of the oxidant and hence promote the oxidation of the fuel. The increase in the mass burning rate for the Mn/BaO₂ system was proportionally the largest of all the four binary systems.

Mixtures containing the larger particle-size range of manganese with the standard particle size of both oxidants (i.e. 50% Mn/BaO₂ and 20% Mn/SrO₂) did not burn. The three particle-size ranges of molybdenum metal were also mixed individually with the standard particle-size oxidants. The two smaller ranges produced mixtures which sustained burning in both systems (i.e. 50% Mo/BaO₂ and 40% Mo/SrO₂), but both mixtures made using the largest particle-size range of molybdenum would not burn. The linear burning rates and the maximum excess temperatures, for the molybdenum mixtures which sustained combustion are given in Table 4.

Samples of oxidant with the smaller particle size were mixed with the standard particle size of the fuels and burnt in the channel. Within the limits of reproducibility, neither the burning rate nor the maximum excess temperature were significantly different for these mixtures.

Temperature profiles for various compositions for all four binary systems were recorded. Profiles were generally sigmoidal. Despite attempts to standardize the measurement procedure, the reproducibility of the recorded temperature profiles of all four binary systems was not particularly good. Figures 1–4 show the variability within the temperature–time data for the 20% compositions of three of the binary systems and for 40% Mo/SrO₂.

The effects of composition on the shape of the temperature profiles are shown in Figs. 5–8 for the four binary systems. The maximum temperature generally decreased as the proportion of fuel was increased.

Comparison of temperature profiles based on the mole ratio of fuel to oxidant are probably chemically more significant than comparisons based on similar percentages by mass of fuel. A mole ratio of $\sim 4:1$ includes the following compositions: 55% Mn/BaO₂, 40% Mo/BaO₂, 60% Mn/SrO₂ and 55% Mo/SrO₂. This last composition did not sustain combustion under the experimental conditions. The temperature profiles (Fig. 9) had similar gradients at low temperature but differed in the

TABLE 4

Effect of molybdenum particle size on v_{obs} and U_{max}

System	v_{obs} (mm s ⁻¹)	U_{max} (°C)
50% Mo (medium)/BaO ₂	5.9 ± 0.2	1358 ± 65
50% Mo (small)/BaO ₂	12.9 ± 1.2	1457 ± 66
40% Mo (medium)/SrO ₂	2.3 ± 0.1	1502 ± 99
40% Mo (small)/SrO ₂	5.8 ± 0.6	1480 ± 156

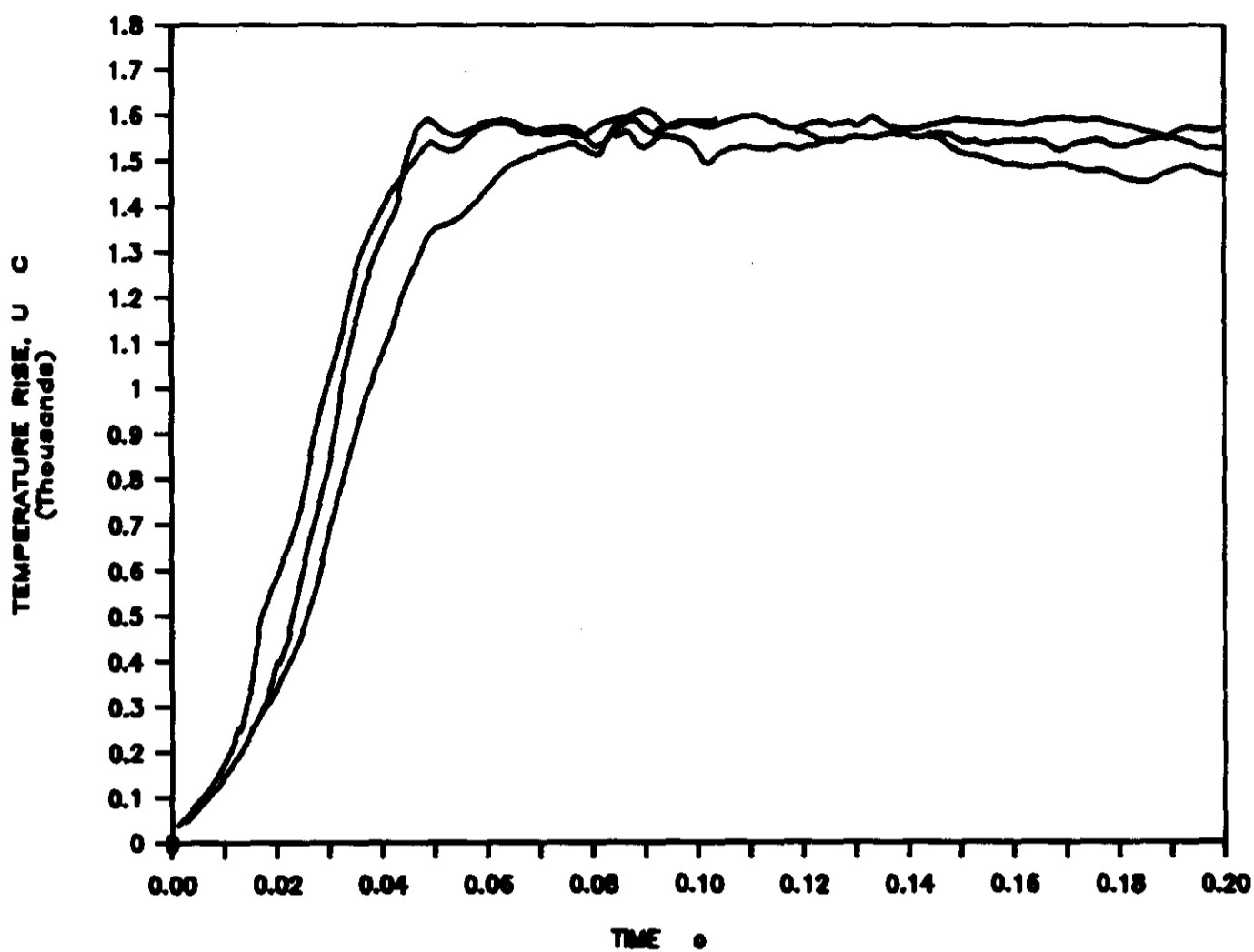


Fig. 1. Reproducibility of temperature profiles for 20% Mn/BaO₂.

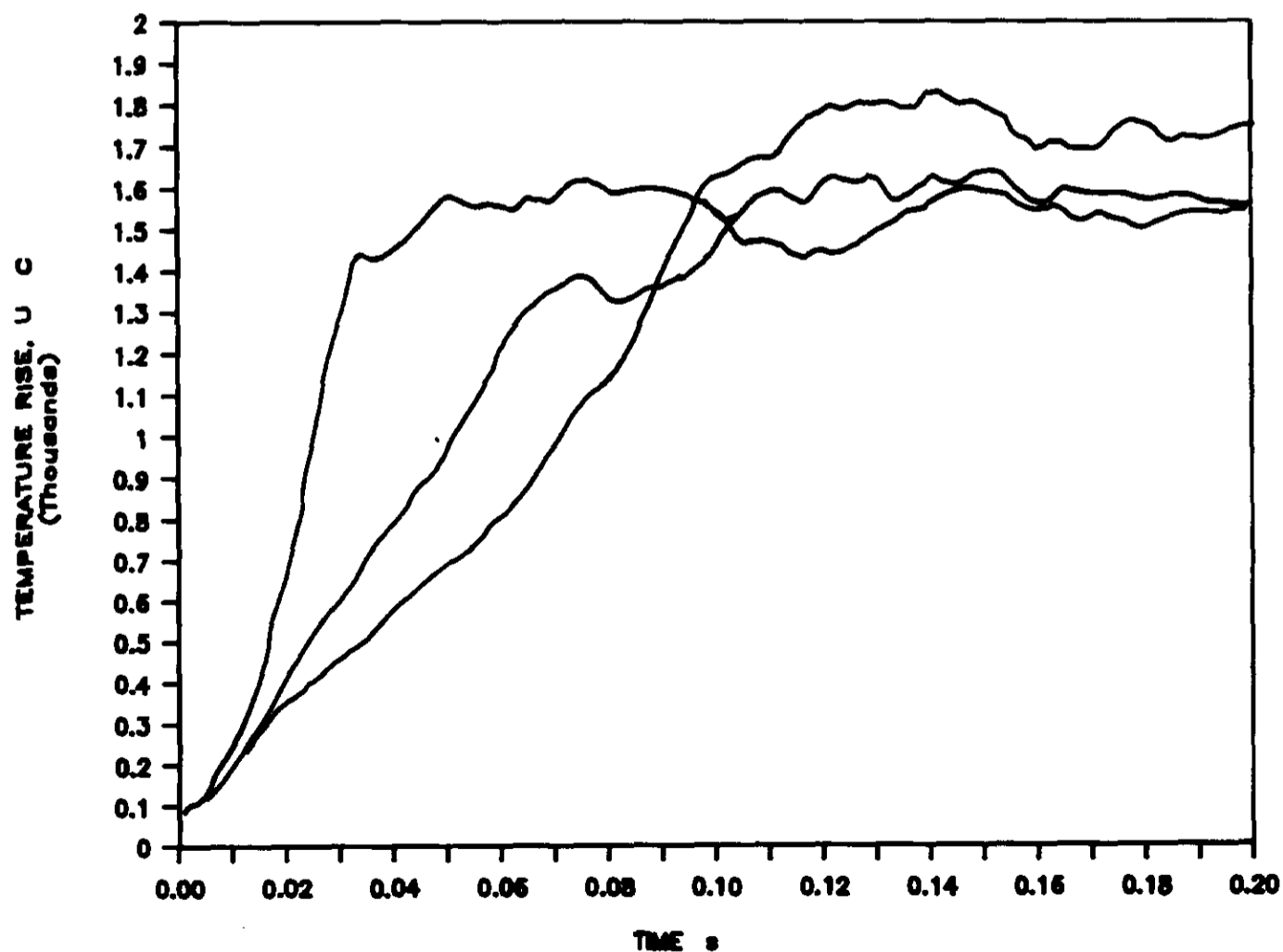


Fig. 2. Reproducibility of temperature profiles for 20% Mo/BaO₂.

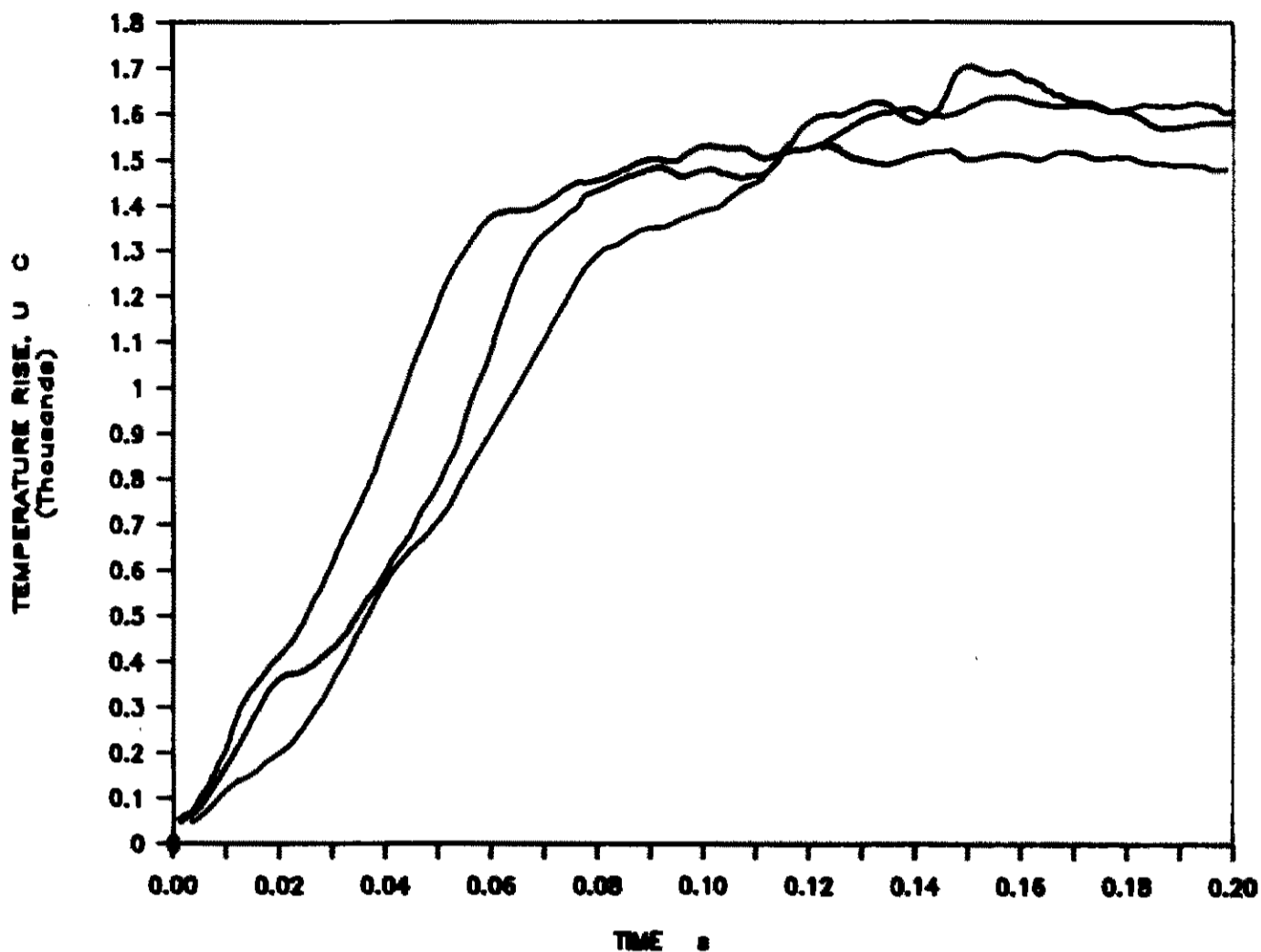


Fig. 3. Reproducibility of temperature profiles for 20% Mn/SrO₂.

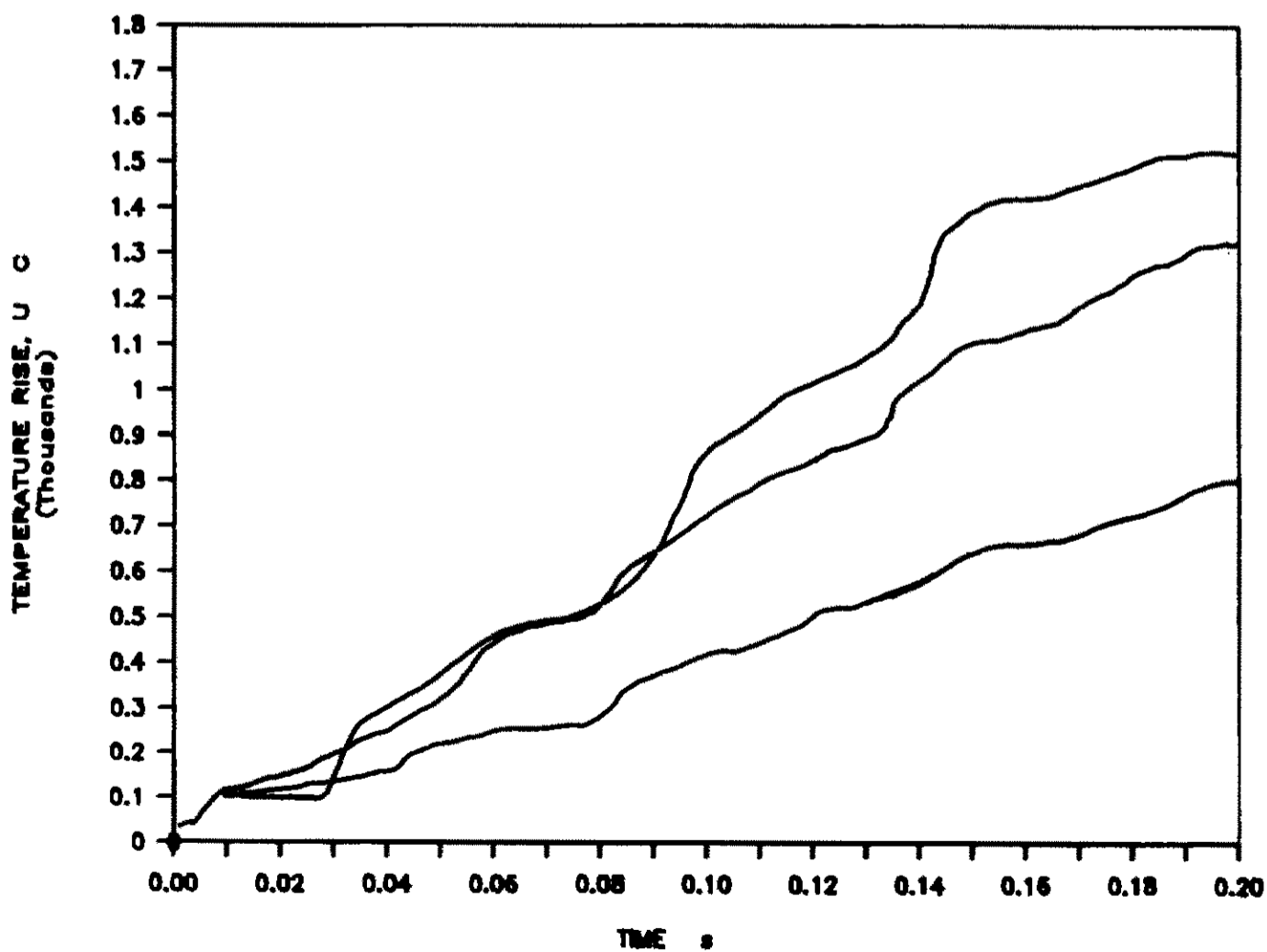


Fig. 4. Reproducibility of temperature profiles for 40% Mo/SrO₂.

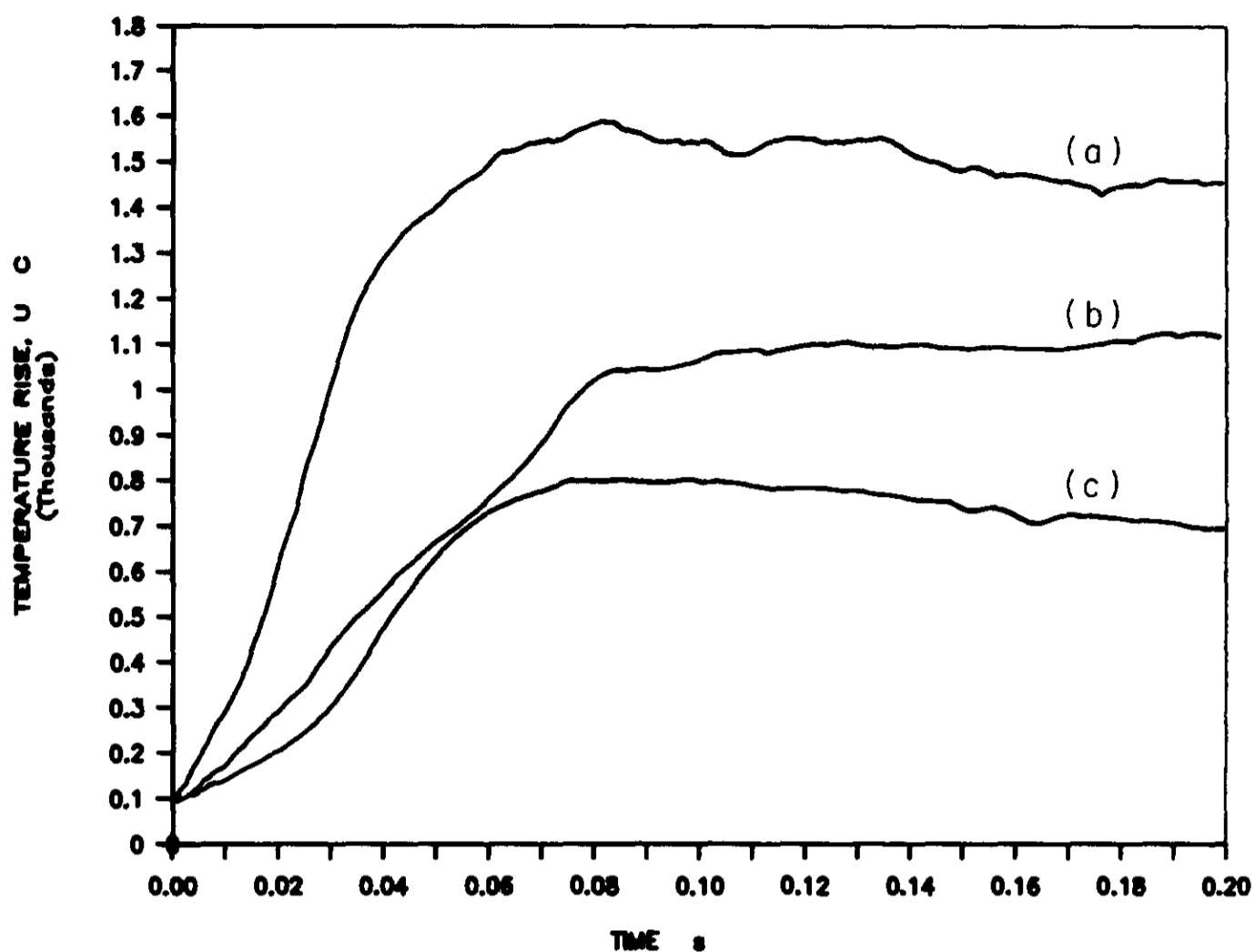


Fig. 5. Effect of composition on the temperature profiles of the Mn/BaO₂ system: curve a, 20% Mn; curve b, 50% Mn; curve c, 60% Mn.

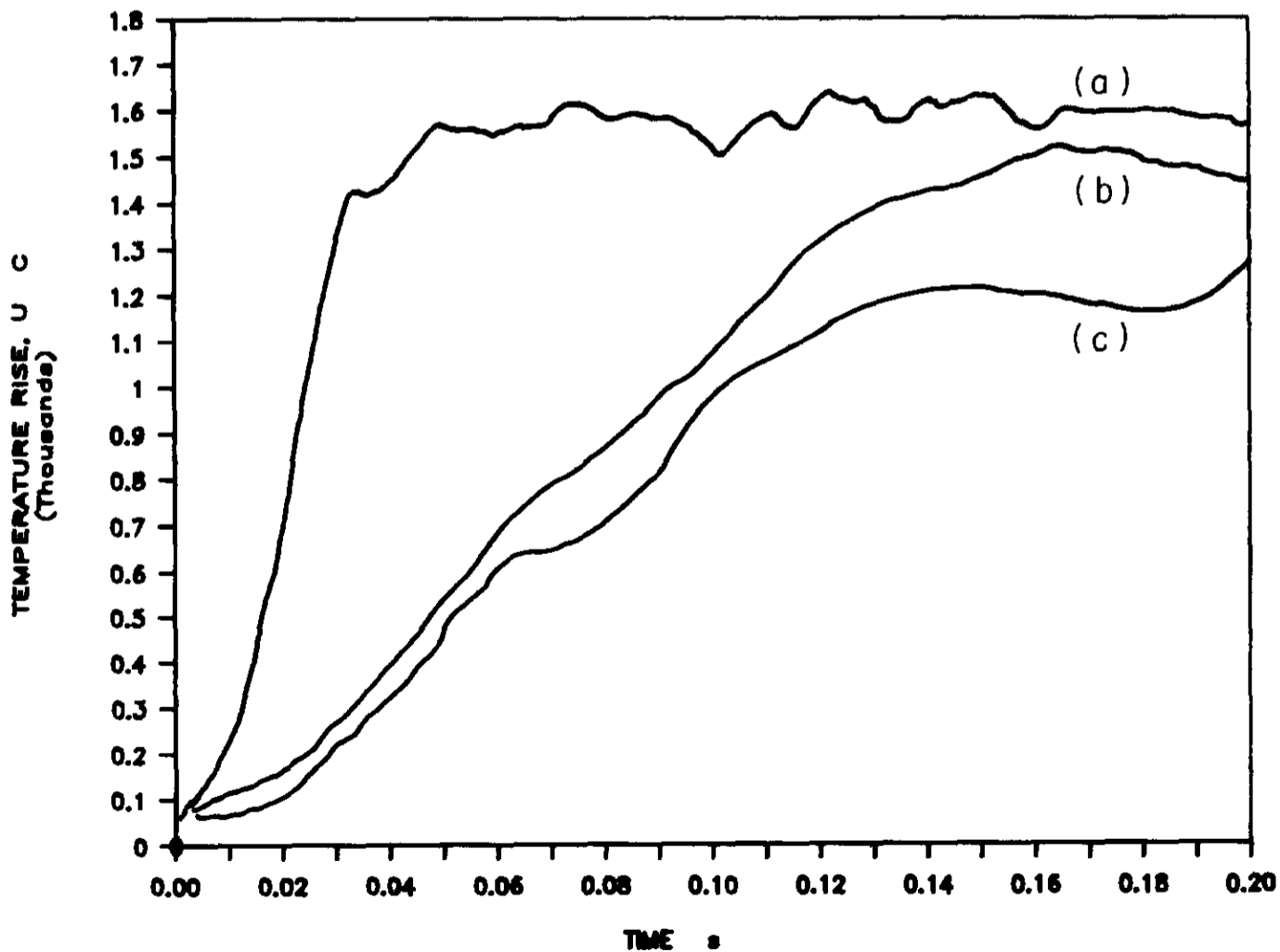


Fig. 6. Effect of composition on the temperature profiles of the Mo/BaO₂ system: curve a, 20% Mo; curve b, 50% Mo; curve c, 60% Mo.

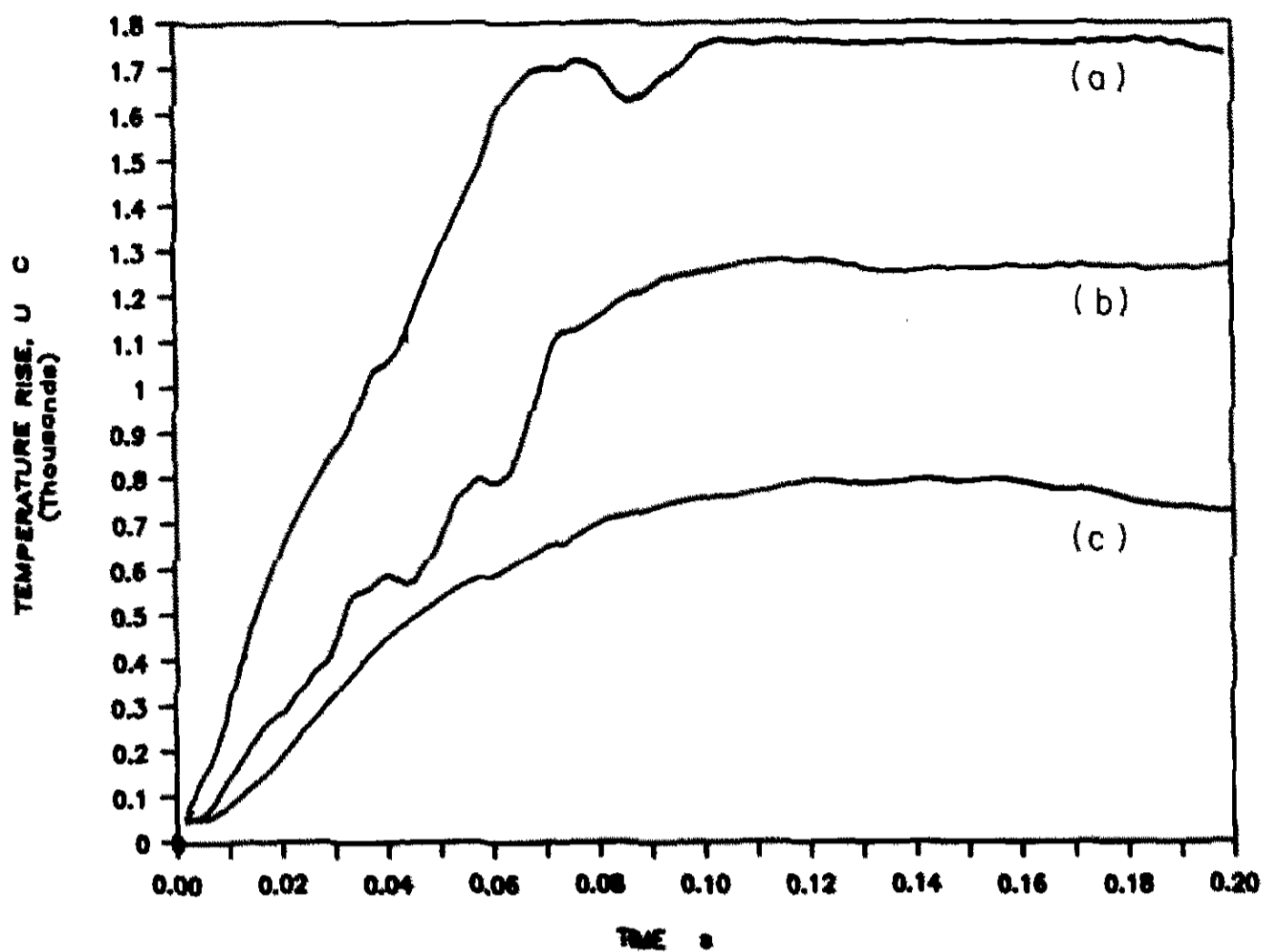


Fig. 7. Effect of composition on the temperature profiles of the Mn/SrO₂ system: curve a, 20% Mn; curve b, 50% Mn; curve c, 60% Mn.

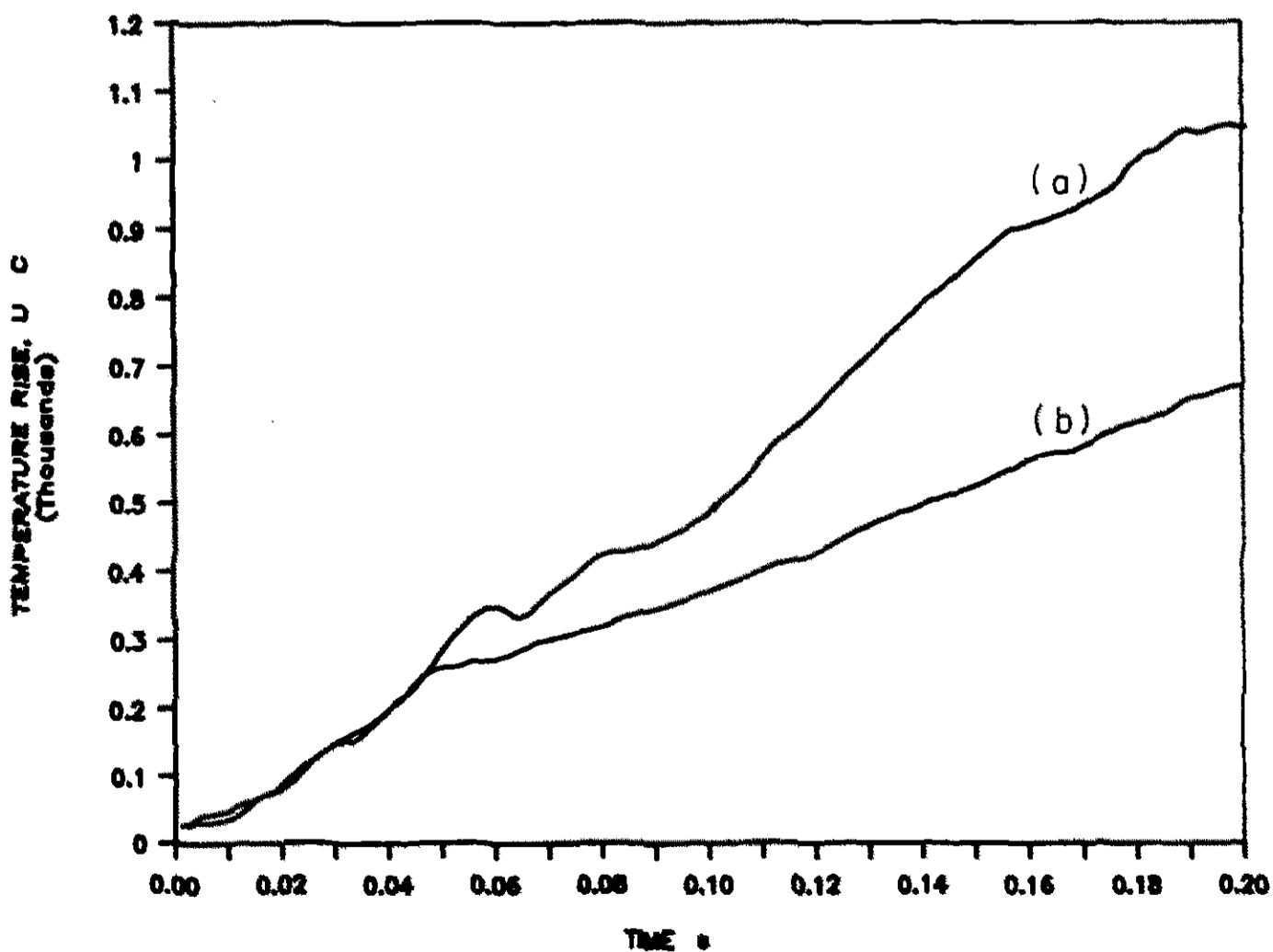


Fig. 8. Effect of composition on the temperature profiles of the Mo/SrO₂ system: curve a, 40% Mo; curve b, 45% Mo.

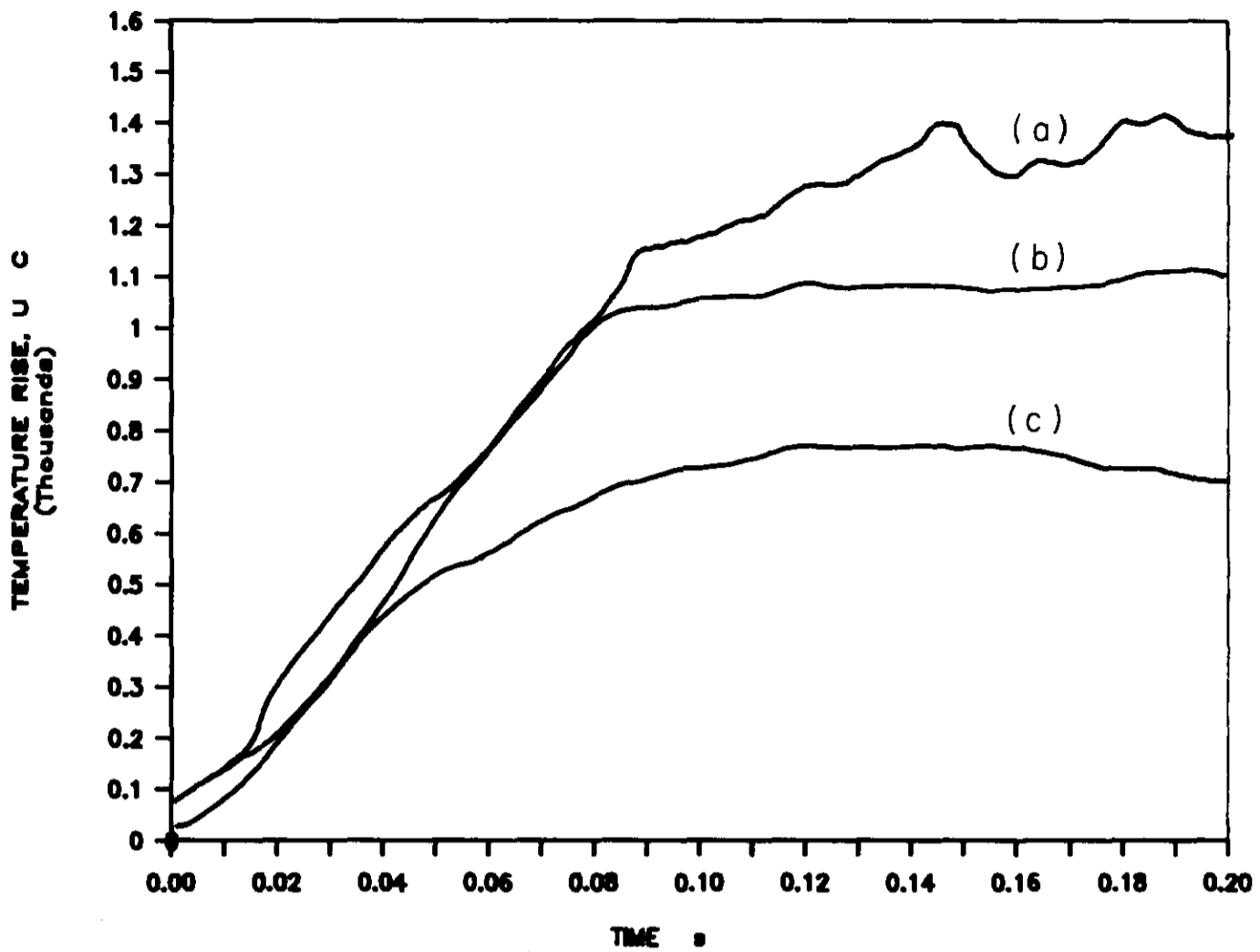


Fig. 9. Comparison of temperature profiles for a mole ratio of 4:1: curve a, Mo/BaO₂; curve b, Mn/BaO₂; curve c, Mn/SrO₂.

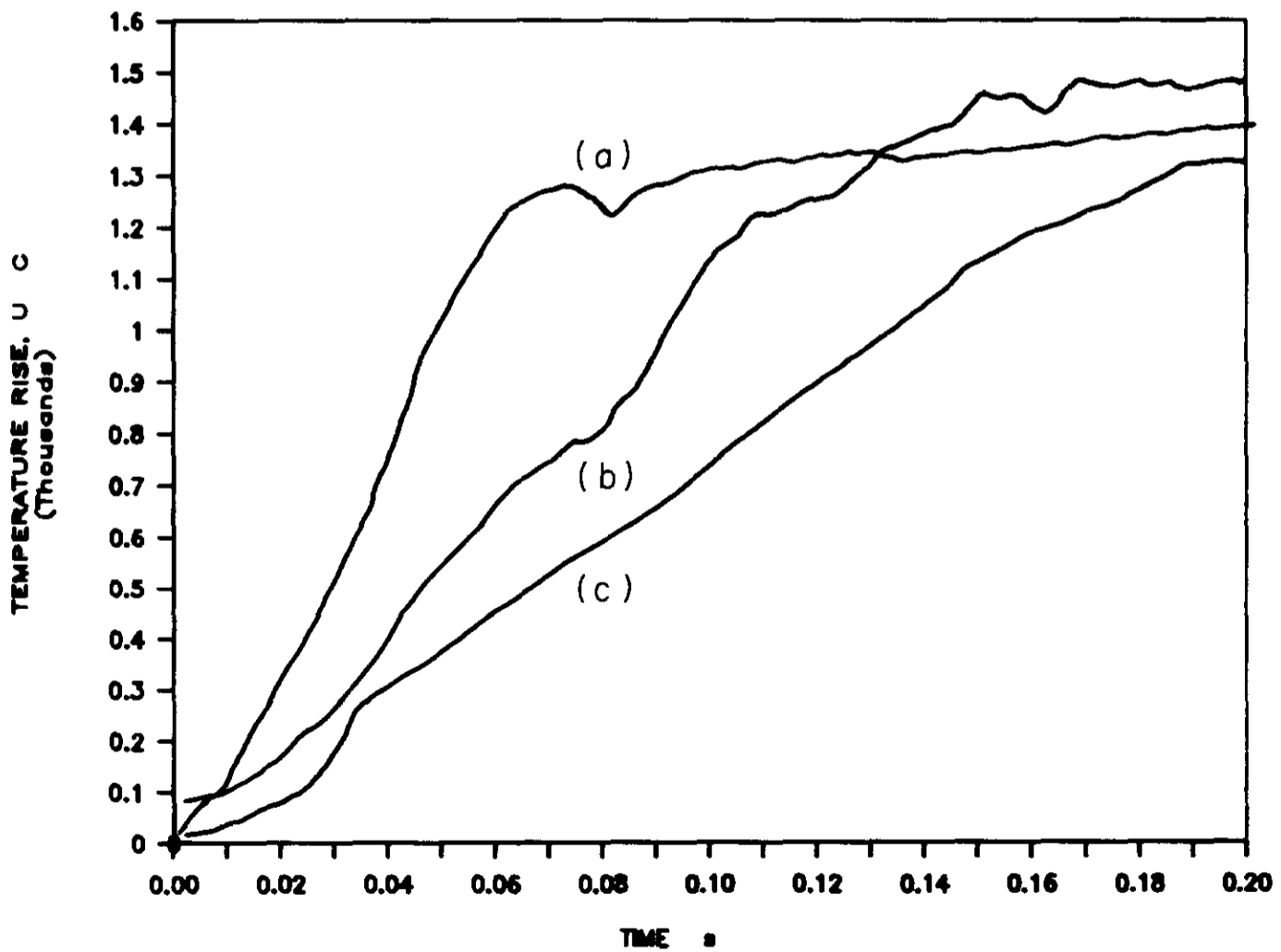


Fig. 10. Comparison of temperature profiles for a mole ratio of 2:1: curve a, Mo/BaO₂; curve b, Mn/SrO₂; curve c, Mo/SrO₂.

recorded maximum temperatures, $\text{Mo}/\text{BaO}_2 > \text{Mn}/\text{BaO}_2 > \text{Mn}/\text{SrO}_2$. A mole ratio of approximately 2:1 includes the following compositions: 25% Mo/BaO_2 , 45% Mn/SrO_2 , 40% Mo/SrO_2 and 35% Mn/BaO_2 . This last composition burnt at temperatures above the melting point of the platinum thermocouple wire ($\approx 1760^\circ\text{C}$) and, therefore, no profiles could be recorded. Although the temperature profiles have similar maximum temperatures (Fig. 10), the gradients in the rise zone are noticeably different, $\text{Mo}/\text{BaO}_2 > \text{Mn}/\text{SrO}_2 > \text{Mo}/\text{SrO}_2$.

Exceptions to the regular sigmoidal temperature profiles were recorded in all four systems, especially in compositions near to the end of the range which supported combustion. Irregular temperature profiles were less reproducible than those for the majority of compositions. In general, irregularities in a temperature profile may be related to phase changes, such as melting of the fuel and/or oxidant in the rise zone, or recrystallization of molten products in the cooling zone. For example, the temperature profile of 40% Mn/SrO_2 showed an exothermic process in the cooling zone which could arise from further exothermic reaction, or from product recrystallization. The temperature is in the range where recrystallization of Mn_3O_4 or MnO (melting points 1560 and 1785°C , respectively) is possible. The temperature profiles of 60% Mo/BaO_2 showed endothermic deviations from about 400 to about 800°C which includes the decomposition temperature of BaO_2 ($\approx 600^\circ\text{C}$) [1].

Effect of additives on burning

The burning rate of a pyrotechnic mixture may be altered by changing its composition, or the pressure under which the mixture was compacted, or the particle size of the fuel, or by introducing a suitable additive. Additives may act as inert diluents, or may be possible reaction intermediates or products, e.g. MnO_2 , MoO_3 , etc.

The additives tested for their effect on the burning characteristics of the BaO_2 systems, with 20% Mn or Mo , were Al_2O_3 , BaO , BaCO_3 and $\text{Ba}(\text{OH})_2$, as well as MoO_3 for the Mo/BaO_2 system and MnO_2 for the Mn/BaO_2 system. As the proportion of the additive was increased in steps (1%, 5% and 10% of the total mass of the binary mixture), the maximum excess temperature of the Mn/BaO_2 was lowered, the burning rate decreased and the rise time correspondingly increased. Effects of each of the additives were similar. Small amounts (<10%) of the additives chosen decreased the burning rate of the 20% Mn/BaO_2 composition. Additives may inhibit the reaction by decreasing the contact area between the fuel and oxidant particles, or by changing the heat capacity and/or the thermal conductivity of the mixture sufficiently to alter the burning rate of the mixture. Alternatively, the additive may take part in the reaction and compete for the unreacted materials, in which case, depending on the heat of this competitive reaction, the rate of burning may be either increased

or decreased. Changes in heat capacity and thermal conductivity at ambient temperature for the systems examined are small enough to be negligible and cannot account for the large differences in burning rate.

Thermal analysis [1] of the Mn/BaO₂ system suggested that the combustion reaction could be influenced by the decomposition of Ba(OH)₂ at a temperature of about 360°C. Small quantities of Ba(OH)₂ mixed in with the Mn/BaO₂ system did not enhance the combustion.

The additives used for the two SrO₂ systems were Al₂O₃ and the strontium equivalents of those added to the BaO₂ systems, i.e. SrO, SrCO₃ and Sr(OH)₂, as well as MnO₂ and MoO₃ in their respective systems. Similar amounts (i.e. 1%, 5% and 10% of the total mass of the binary mixture) were added to 20% Mn/SrO₂ and to 40% Mo/SrO₂ (the 20% Mo/SrO₂ composition did not sustain combustion under the experimental conditions). As before, increasing proportions of additive slowed the burning rate and lowered the maximum excess temperature of 20% Mn/SrO₂. The 40% Mo/SrO₂ system failed to ignite in the presence of as little as 5% of most of the additives. The addition of as much as 10% of MoO₃ had no observable effect on the burning rate or the maximum excess temperature of the 40% Mo/SrO₂ system.

The Mo/BaO₂ system was much more sensitive to the presence of additives than the Mn/BaO₂ system. All the additives, except BaO, prevented combustion from taking place when even as little as 1% was added.

Ternary systems

Ternary pyrotechnic systems with various compositions were prepared and burnt in the open channel. Burning rates and temperature profiles were recorded. The compositions were chosen on the basis of the results obtained for the four binary systems. Thus it was known, for example, that the 50% Mn/BaO₂ composition burnt faster than the 50% Mn/SrO₂ composition and that the 30% Mo/BaO₂ composition sustained combustion while the 30% Mo/SrO₂ composition did not burn in the open channel. The aim of these experiments, therefore, was to investigate how the addition of the second fuel or second oxidant modified the burning of the binary systems.

Mixed oxidant systems

Mn/BaO₂/SrO₂ system. The composition of this system was varied by increasing the proportion of SrO₂ at the expense of the proportion of BaO₂. All the compositions from 50:50:0 (i.e. 50% Mn, 50% BaO₂ and 0% SrO₂) through to 50:0:50 (with 12.5% steps) burnt under the normal experimental conditions. The composition affected the burning rate and maximum excess temperature of the Mn/BaO₂/SrO₂ system as shown in Table 5. The mole ratios of the three constituents are also listed.

TABLE 5

Effects of composition of the ternary systems on the burning rate and maximum excess temperature

Composition (%)	v_{obs} (mm s ⁻¹)	U_{max} (°C)	Mole ratio
<i>Mn : BaO₂ : SrO₂</i>			
50:50:0	9.1 ± 0.4	1182 ± 57	1.00:0.32:0.00
50:37.5:12.5	3.5 ± 0.7	1173 ± 3	1.00:0.24:0.11
50:25:25	4.1 ± 0.5	1228 ± 5	1.00:0.16:0.23
50:12.5:37.5	4.8 ± 0.2	1340 ± 20	1.00:0.08:0.34
50:0:50	6.8 ± 1.2	1198 ± 27	1.00:0.00:0.46
<i>Mo : BaO₂ : SrO₂</i>			
30:70:0	4.4 ± 0.8	1678 ± 14	1.00:1.32:0.00
30:60:10	^a	^a	1.00:1.13:0.27
30:50:20	^a	^a	1.00:0.94:0.53
30:40:30	^a	^a	1.00:0.76:0.80
30:30:40	^a	^a	1.00:0.57:1.07
30:20:50	1.8 ± 0.1	1593 ± 127	1.00:0.38:1.34
30:10:60	^a	^a	1.00:0.19:1.60
30:0:70	^a	^a	1.00:0.00:1.87
<i>Mo : Mn : BaO₂</i>			
30:0:70	4.4 ± 0.8	1678 ± 14	0.76:0.00:1.00
10:10:70	^a	^a	0.50:0.44:1.00
10:20:70	2.0 ± 0.1	1481 ± 78	0.25:0.88:1.00
0:30:70	9.4 ± 0.4	>1760	0.00:1.32:1.00
<i>Mo : Mn : SrO₂</i>			
30:0:70	^a	^a	0.53:0.00:1.00
25:5:70	^a	^a	0.45:0.16:1.00
22.5:7.5:70	2.3 ± 0.3	1489 ± 85	0.40:0.23:1.00
20:10:70	2.2 ± 0.4	1508 ± 206	0.36:0.31:1.00
10:20:70	5.2 ± 0.3	1557 ± 9	0.18:0.62:1.00
0:30:70	6.6 ± 1.0	1547 ± 129	0.00:0.93:1.00

^a Would not burn.

The temperature profiles for the different compositions of this ternary system were all very similar, and more like the profiles of the Mn/BaO₂ system than of the Mn/SrO₂ system.

That all of the compositions mixed of the Mn/BaO₂/SrO₂ system should sustain combustion might be expected, since both the 50% Mn/BaO₂ and the 50% Mn/SrO₂ systems burnt, although with different burning rates. Burning rates are plotted against the percentage of both oxidants in Fig. 11. The burning rate of the 50% Mn/BaO₂ composition decreased initially on addition of SrO₂, reached a minimum when a quarter of the BaO₂ had been replaced by SrO₂, and gradually increased as the proportion of SrO₂ was increased. Values of U_{max} were not significantly altered.

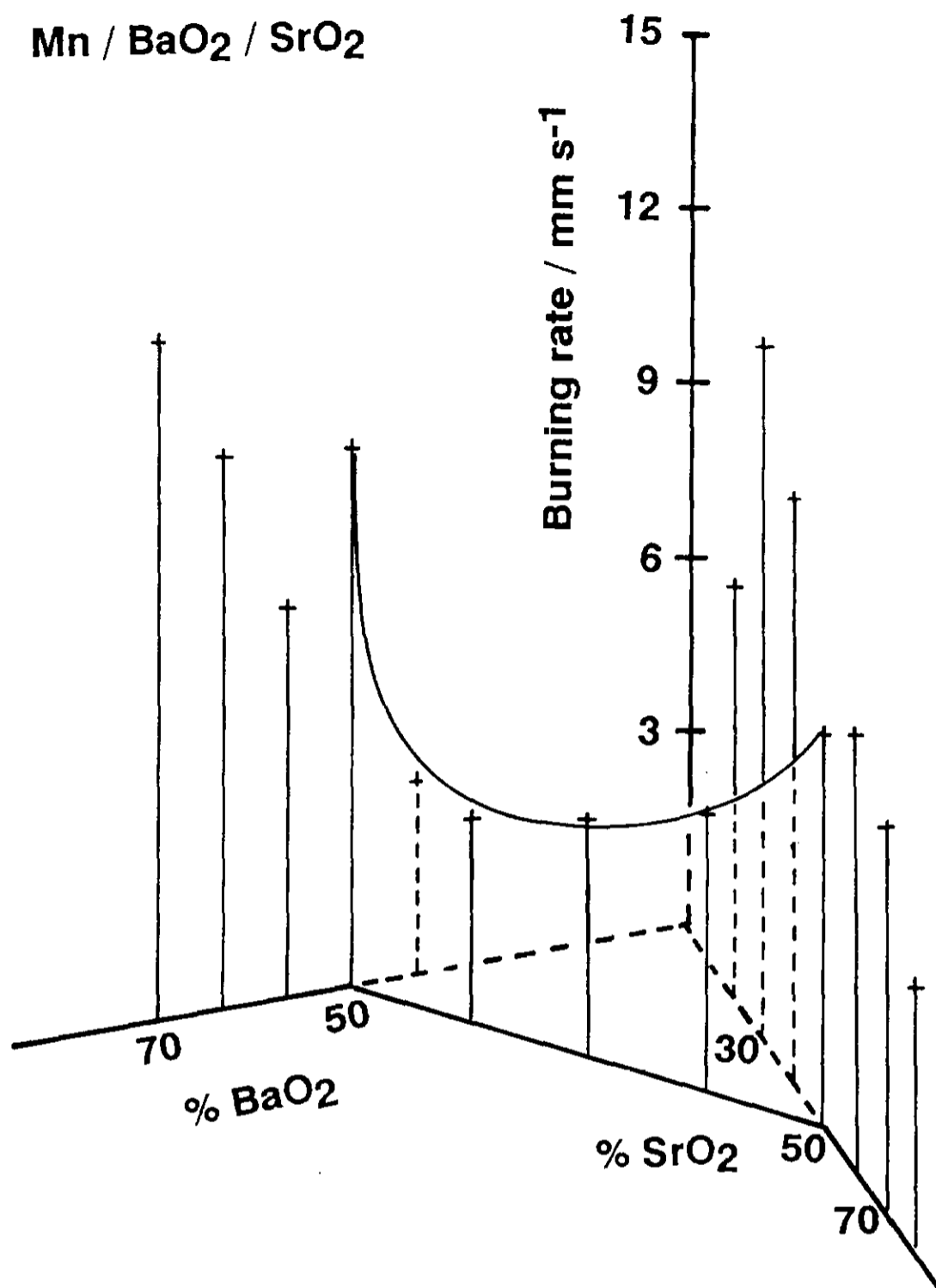


Fig. 11. Burning rates of ternary compositions of Mn/BaO₂/SrO₂.

Mo/BaO₂/SrO₂ system. The proportions by mass of the two oxidants were changed in steps of 10% from 30:70:0 (i.e. 30% Mo, 70% BaO₂ and 0% SrO₂) to 30:0:70. The Mo/BaO₂/SrO₂ ternary system was of interest because 30% Mo/BaO₂ burns, but 30% Mo/SrO₂ does not burn. Combustion of the 30% Mo/BaO₂ composition failed when the proportion of the BaO₂ was decreased to 60% of the total mass (i.e. only 10% SrO₂). Only one further composition (30:10:60) of this system sustained combustion reproducibly, and the reason for this is not clear. The burning rates and U_{\max} values are included in Table 5.

Mixed fuel systems

Mo/Mn/BaO₂ system. The composition was varied by increasing the proportion of manganese, at the expense of the proportion of molybde-

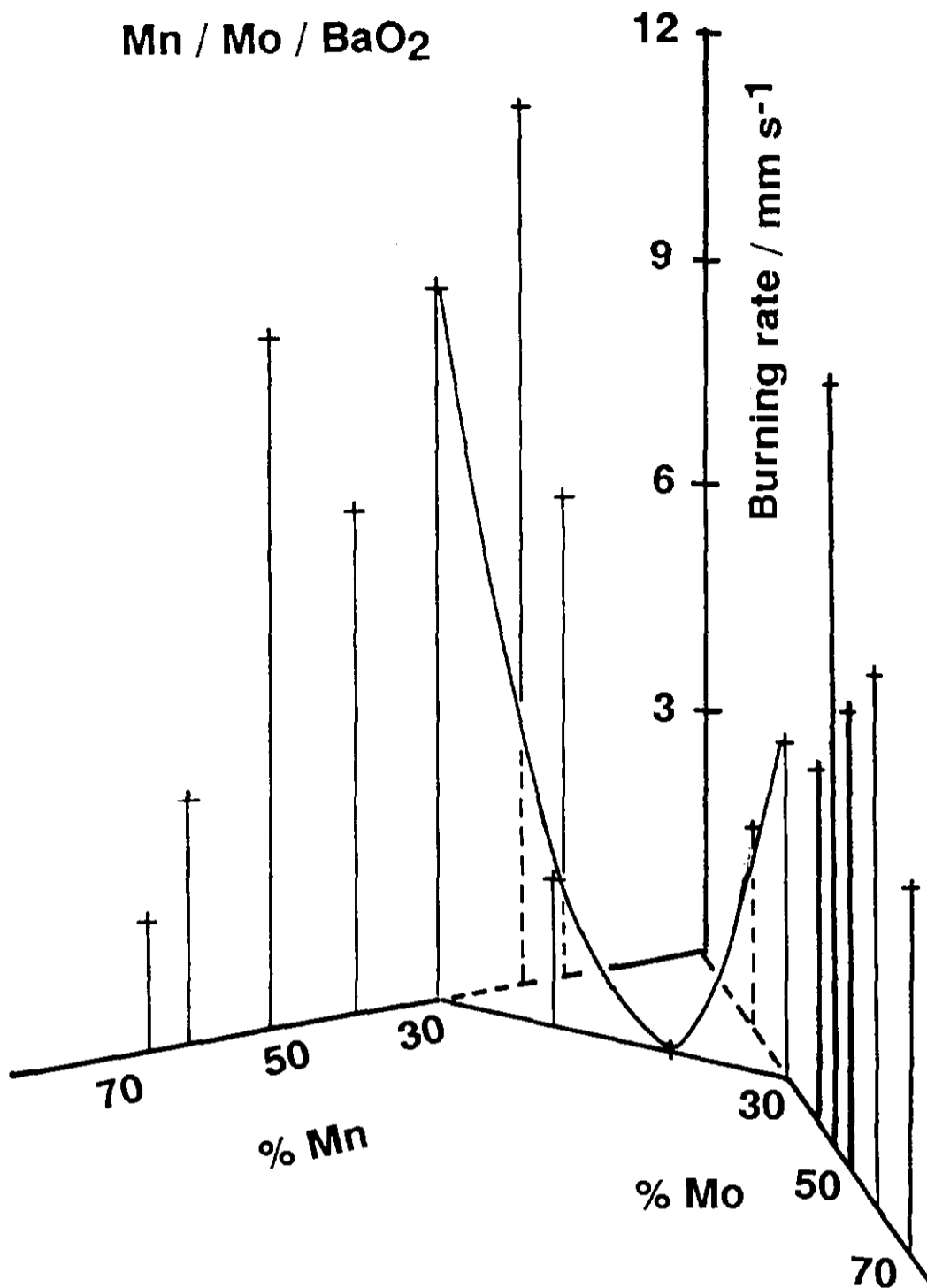


Fig. 12. Burning rates of ternary compositions of Mn/Mo/BaO₂.

num, in steps of 10% from 30:0:70 (i.e. 30% Mo, 0% Mn and 70% BaO₂) to 0:30:70. Both ternary compositions were difficult to ignite and only one (10:20:70) sustained combustion. The results are given in Table 5.

The mixed fuel systems burnt with significantly slower burning rates than expected from the relevant binary systems. Three-dimensional plots of the burning rates against the composition of both fuels are shown in Figs. 12 and 13.

All the compositions of the Mo/Mn/BaO₂ system were expected to burn since the two relevant binary compositions (30% Mo/BaO₂ and 30% Mn/BaO₂) both sustained combustion. With a mass ratio of 2:1 (Mo:Mn) the Mo/Mn/BaO₂ system failed to burn, but, as the proportion of manganese was increased the burning rate increased (Fig. 12).

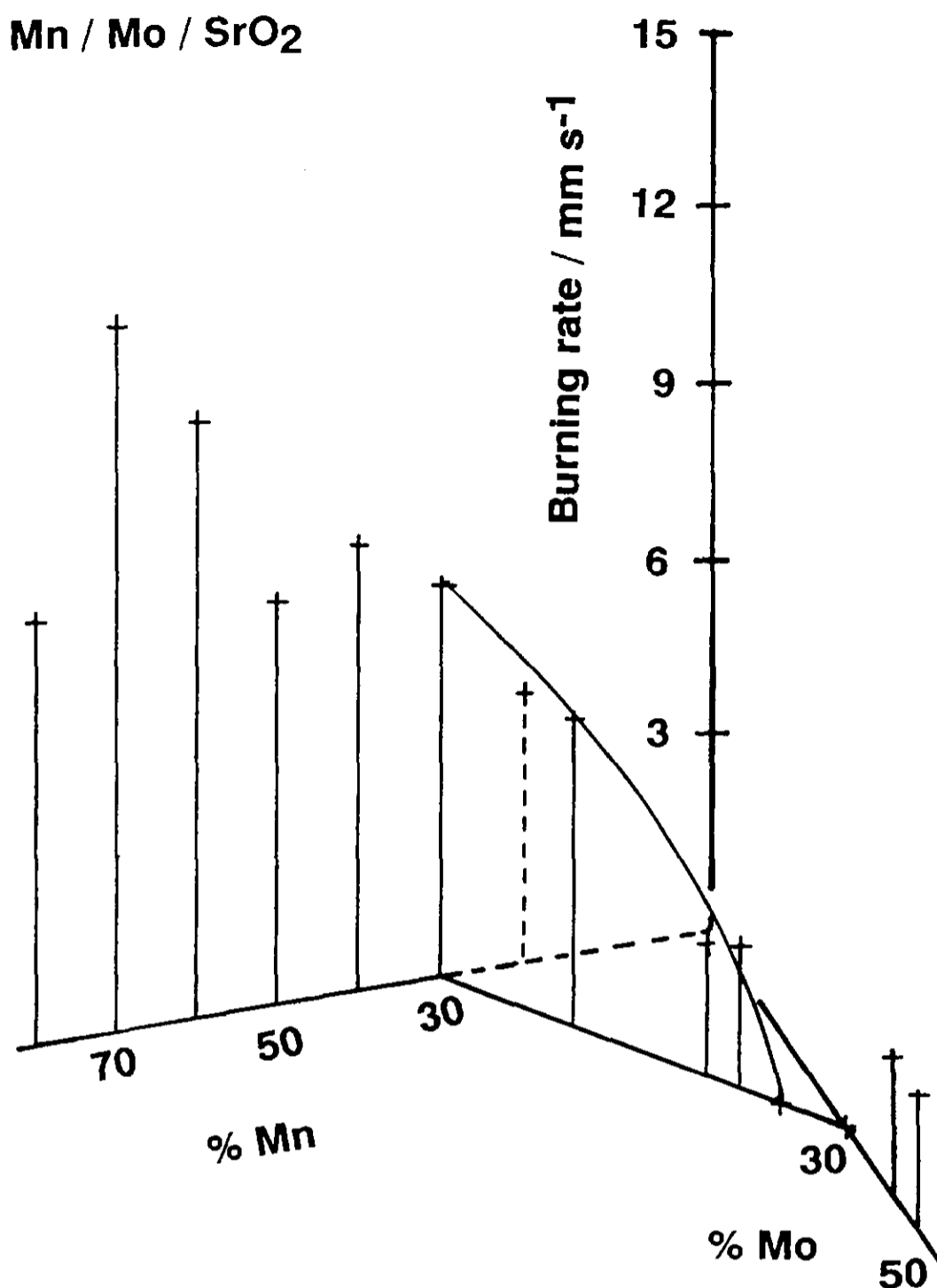


Fig. 13. Burning rates of ternary compositions of Mn/Mo/SrO₂.

Mo/Mn/SrO₂ system. Ternary compositions of this system were made up in a similar way to the system above, but two extra compositions (25:5:70 and 22.5:7.5:70) were included. The effects of composition on the burning rate and U_{\max} are shown in Table 5.

The 30% Mo/SrO₂ composition was known not to burn, but 30% Mn/SrO₂ burnt at a rate of about 7 mm s⁻¹. Only 7.5% manganese needed to be added before combustion was sustained with a burning rate of about 2 mm s⁻¹ and as the percentage manganese was increased so did the burning rate.

One possible explanation for the slow burning rates of mixed fuel ternary systems is the possible interference between manganese and molybdenum due to the formation of an alloy which is reported [11] to form at 1175°C containing between 62% and 73% manganese. The

melting point of manganese ($1244 \pm 3^\circ\text{C}$) is close to the prevailing reaction temperatures (>1000 and $<1700^\circ\text{C}$) and thus could also affect the burning of ternary mixtures.

No indications or reports were found of any interaction between BaO_2 and SrO_2 .

Thermochemical information from temperature profiles

The total heat evolved by the combustion wave in a pyrotechnic mixture [7, 8] is given by

$$Q = cU_{\text{ad}} \quad (1)$$

where U_{ad} is calculated by integration of the excess temperature function between arbitrary times t_1 and t_2 in the remote rise and decay zones respectively. The specific heat capacities c of the powdered pyrotechnic mixtures can be estimated from the composition, masses and the specific heat capacities of the pure bulk solids. Plots of Q (corrected for the thermocouple diameter) against composition are given in Figs. 14 and 15 for the two manganese systems and the two molybdenum systems, respectively.

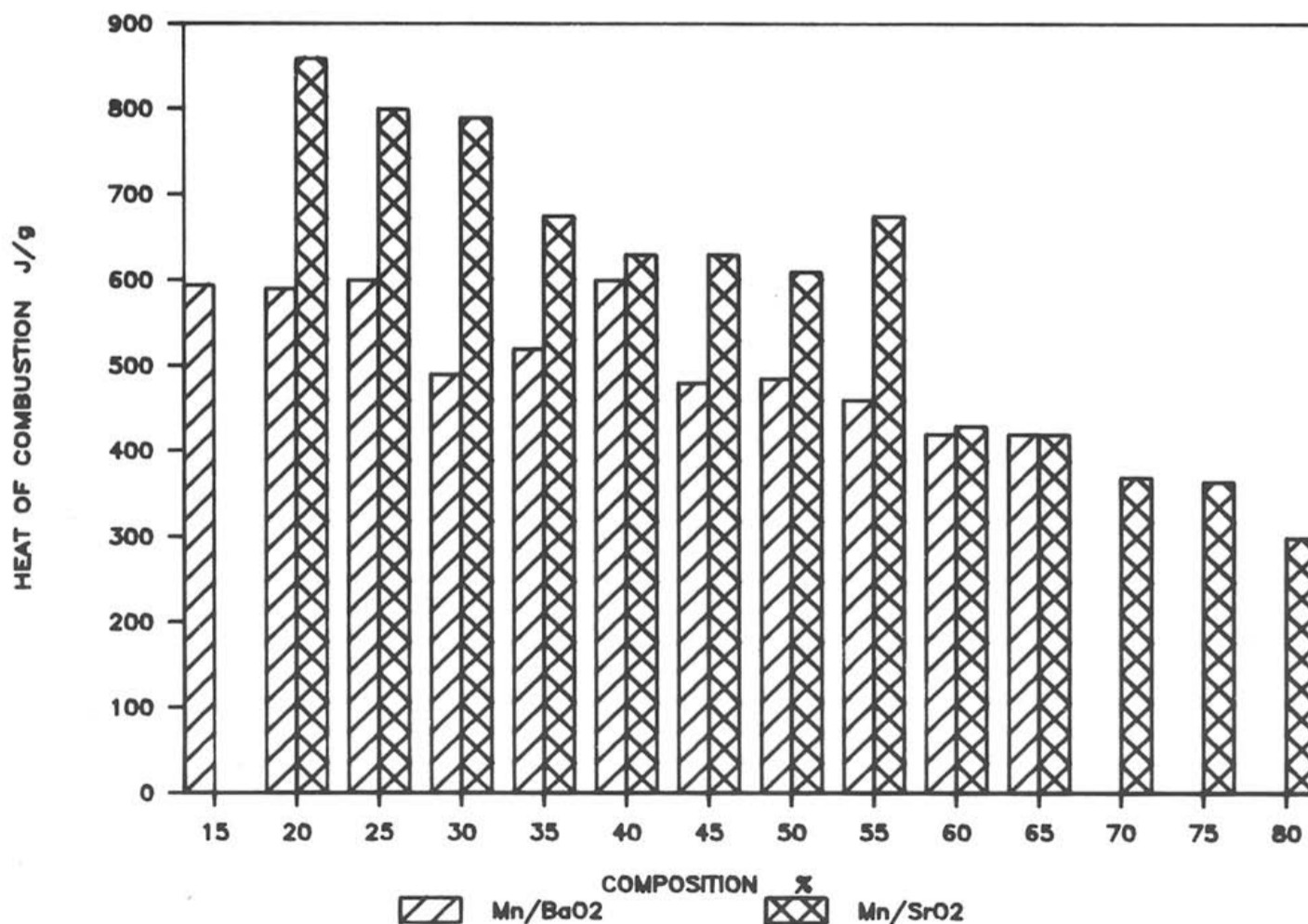


Fig. 14. Effect of composition on the heat of combustion of the binary systems containing Mn as fuel.

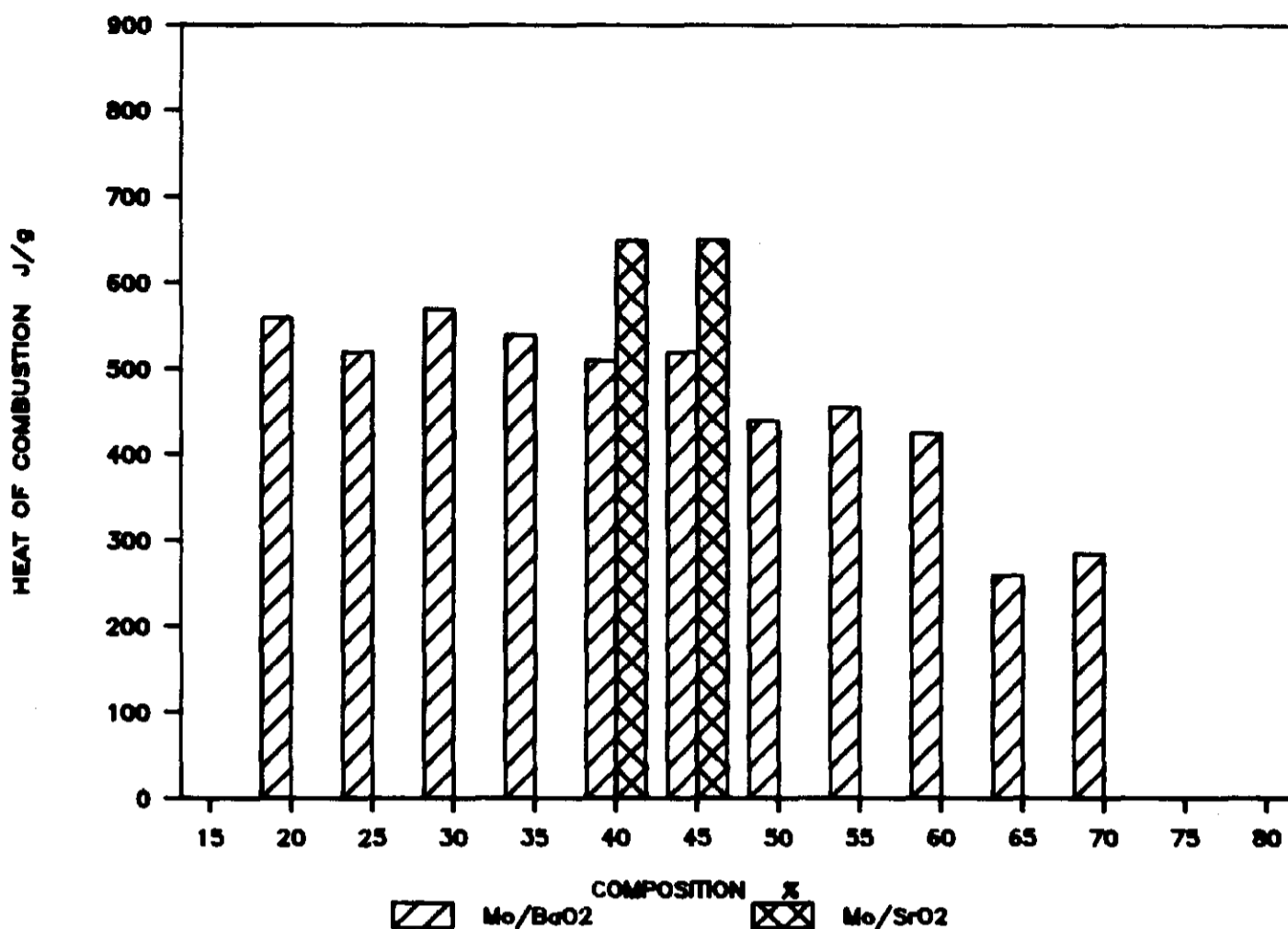


Fig. 15. Effect of composition on the heat of combustion of the binary systems containing Mo as fuel.

Values calculated from eqn. (1) are compared with values determined by differential scanning calorimetry [1] and bomb calorimetry in Table 6.

The bomb calorimetry values are generally higher than the Q values determined using DSC and those calculated from temperature profiles, probably because the reactions in the bomb were reasonably complete and

TABLE 6

Comparison of heats of reaction

Sample	$-\Delta H = Q$ (kJ g ⁻¹)			
	Bomb cal.	DSC	Profiles	
			Calculated ^a	Corrected ^b
40% Mn/BaO ₂	1.42 ± 0.32	0.44 ± 0.22	0.42 ± 0.06	0.46 ± 0.02
40% Mo/BaO ₂	1.07 ± 0.03	1.04 ± 0.11	0.44 ± 0.03	0.52 ± 0.03
40% Mn/SrO ₂	1.54 ± 0.24	0.27 ± 0.84	0.79 ± 0.04	1.02 ± 0.02
40% Mo/SrO ₂			0.63 ± 0.03	0.71 ± 0.03

^a Q values calculated from temperature profiles measured with a thermocouple wire of 0.1 mm diameter.

^b Q values corrected to negligible thermocouple wire diameter.

any heat losses were accounted for. The slow heating of the sample in the DSC may have allowed formation of a protective oxide layer around the fuel which prevented complete combustion. Many of the temperature profiles had a long (≈ 0.1 s) maximum temperature “plateau” which may indicate incomplete reaction as the burning front passes the thermocouple followed by further combustion which maintains the maximum temperature.

Spice and Staveley [2], using bomb calorimetry, obtained values for the heats of reaction of 40% Mn/BaO₂ and 40% Mo/BaO₂ in air of 1.20 and 0.90 kJ g⁻¹, respectively, which are similar to the values in Table 6. Yoshinaga et al. [5] used an inert atmosphere of argon gas and reported a value of 0.50 kJ g⁻¹ for 50% Mn/BaO₂.

Stoichiometry

The standard enthalpies of reaction (based on 1 mol of fuel) for the various possible fuel/oxidant combinations, calculated from published [12] standard enthalpies of formation, are given in Table 7. Some of the standard values for the oxides were found to vary quite widely from one compilation to another. Also given are the percentage fuel values for the corresponding stoichiometric compositions (assuming 100% purity of the

TABLE 7

Reaction stoichiometry for binary systems

Reaction	ΔH (kJ per mol fuel)	Stoichiometry (%)	Q^a (kJ g ⁻¹)
<i>Mn/BaO₂ system</i>			
Mn(s) + BaO ₂ (s) → BaO(s) + MnO(s)	-328.5	24	1.16
3Mn(s) + 4BaO ₂ (s) → 4BaO(s) + Mn ₃ O ₄ (s)	-352.4	20	0.94
2Mn(s) + 3BaO ₂ (s) → 3BaO(s) + Mn ₂ O ₃ (s)	-355.9	18	0.84
Mn(s) + 2BaO ₂ (s) → 2BaO(s) + MnO ₂ (s)	-352.2	14	0.62
<i>Mo/BaO₂ system</i>			
Mo(s) + 2BaO ₂ (s) → 2BaO(s) + MoO ₂ (s)	-472.8	22	0.84
Mo(s) + 3BaO ₂ (s) → 3BaO(s) + MoO ₃ (s)	-576.2	16	0.68
<i>Mn/SrO₂ system</i>			
Mn(s) + SrO ₂ (s) → SrO(s) + MnO(s)	-334.1	31	1.68
3Mn(s) + 4SrO ₂ (s) → 4SrO(s) + Mn ₃ O ₄ (s)	-359.6	26	1.35
2Mn(s) + 3SrO ₂ (s) → 3SrO(s) + Mn ₂ O ₃ (s)	-364.0	23	1.22
Mn(s) + 2SrO ₂ (s) → 2SrO(s) + MnO ₂ (s)	-363.0	19	0.91
<i>Mo/SrO₂ system</i>			
Mo(s) + 2SrO ₂ (s) → 2SrO(s) + MoO ₂ (s)	-486.9	29	1.22
Mo(s) + 3SrO ₂ (s) → 3SrO(s) + MoO ₃ (s)	-592.7	21	0.99

^a For 40% fuel composition.

oxidants) and the expected heat output in kilojoules per gram for the 40% fuel compositions used in the calorimetric experiments.

Enthalpies of reaction, calculated for different oxides as products, vary less for the manganese systems than for the molybdenum systems. The experimental values for heats of reaction of the pyrotechnic reactions (Table 6) were compared with values given in Table 7. The best agreement occurs for the reactions which produce MnO(s) for the Mn/BaO₂ system, MoO₂(s) for the Mo/BaO₂ system, and Mn₃O₄(s) for the Mn/SrO₂ system. No bomb calorimetry and DSC results were obtained for the Mo/SrO₂ system.

Thermal conductivity

The thermal conductivities λ of the bulk metals manganese (7.81 W m⁻¹ K⁻¹) and molybdenum (13.8 W m⁻¹ K⁻¹) are decreased to low values of 0.39 and 0.46 W m⁻¹ K⁻¹, respectively, characteristic of powders, where the main contribution to the thermal insulation is the void fraction in the powder. Hill et al. [3] reported a value of 0.76 W m⁻¹ K⁻¹ for iron powder compared to 67 W m⁻¹ K⁻¹ for bulk iron. Their value for pellets of BaO₂ powder was 0.67 W m⁻¹ K⁻¹ compared to our values of from 0.33 to 0.59 W m⁻¹ K⁻¹ as the compaction was increased from 0 to 50 MPa. Beck et al. [9] reported values of λ from 0.22 to 0.40 W m⁻¹ K⁻¹ for the Sb/KMnO₄ system and Boddington et al. [8] 0.13 to 0.17 W m⁻¹ K⁻¹ for the W/K₂Cr₂O₇ system. Comparison of the individual powders showed that, over the relatively small range, BaO₂ had the highest thermal conductivity (0.55 W m⁻¹ K⁻¹) and SrO₂ the lowest (0.31 W m⁻¹ K⁻¹). SrO₂ has the smallest median particle size and largest void fraction.

Substitution of up to 40% of the BaO₂ by manganese in a binary pyrotechnic composition had little effect on the thermal conductivity (or the void fraction). In general, a decrease in the particle size increased the void fraction (under the same compaction pressure). The median particle diameters of the manganese and BaO₂ differ only by a factor of about 2. The minimum amount of compaction of BaO₂ had a greater effect on λ than did the addition of manganese.

Although the molybdenum powder had a slightly lower thermal conductivity than BaO₂, substitution of up to 40% of BaO₂ by molybdenum slightly increased the value of λ . Median particle diameters were similar, as were void fractions. Similar substitution of SrO₂ by molybdenum did not have the same effect. The SrO₂ particles are about 0.1 times the diameter of the molybdenum particles.

The thermal conductivity λ and the burning rates v of pyrotechnic compositions are related by

$$v = (\lambda S / \rho c)^{1/2} = (\lambda / \rho c t_r)^{1/2} \quad (2)$$

TABLE 8

Comparison of thermal conductivity and burning rate

Sample	Thermal conductivity (W m ⁻¹ K ⁻¹)	Burning rates (mm s ⁻¹)	
		Measured	Calculated
20% Mn/BaO ₂	0.52 ± 0.03	11.7 ± 0.2	6.3 ± 0.4
40% Mn/BaO ₂	0.48 ± 0.03	6.7 ± 0.4	4.3 ± 1.1
20% Mo/BaO ₂	0.70 ± 0.04	2.8 ± 0.2	6.8 ± 1.8
40% Mo/BaO ₂	0.67 ± 0.07	4.7 ± 1.0	3.9 ± 1.1
20% Mn/SrO ₂	0.28 ± 0.02	4.5 ± 1.0	3.2 ± 0.4
40% Mn/SrO ₂	0.31 ± 0.02	7.5 ± 1.0	7.5 ± 0.6
40% Mo/SrO ₂	0.30 ± 0.02	2.3 ± 0.1	4.6 ± 0.5

where S (used in the Hill approach [3, 4]) is $1/t_r$ (used in the Leeds approach [7, 8]), ρ is the density and c is the specific heat capacity. The value of t_r has to be corrected for the diameter of the thermocouple wire d .

Comparison of measured thermal conductivities of various compositions of the four binary systems with both measured and calculated burning rates for the same systems in Table 8, showed that the relatively small variations in the thermal conductivity of the compositions do not account for the changes in the measured burning rates.

CONCLUSIONS

Three of the four binary pyrotechnic systems sustained combustion over a wide range of compositions (Table 2). The Mo/SrO₂ system was the exception; only two compositions (40% and 45%) of this system sustained combustion and they were the most susceptible to any changes in the experimental procedure. The reason for this restricted range is not obvious since the fuel molybdenum in the Mo/BaO₂ system supports combustion over a wide range of compositions and, similarly, SrO₂ burns well in the Mn/SrO₂ system.

The linear burning rates of all four binary systems are in the 2 to 12 mm s⁻¹ range and the maximum recorded combustion temperatures (with the exception of some Mn/BaO₂ compositions) lie in the 1600 to 1750°C range.

Heat outputs per gram of composition were in the range from 220 to 850 J.

Compaction and the use of smaller particle sizes of fuel increased the burning rates.

The observed burning rates for the Mn/BaO₂ system were similar to those reported by Spice and Staveley [2]. The maximum burning rate occurs at around 20% manganese. This corresponds approximately to the stoichiometric composition for complete reaction to BaO(s) and Mn₃O₄(s).

Barium and strontium carbonates and hydroxides retarded the burning of the corresponding pyrotechnic mixtures as has been previously reported [5]. Prolonged exposure of peroxides to a moist atmosphere promotes [6, 10] the production of carbonates and hydroxides, so adequate storage of both peroxides is vital for the effective and reproducible functioning of pyrotechnic systems containing these oxidants.

The measured burning rates for the Mo/BaO₂ system were consistently lower than the values published by Spice and Staveley [2], and by Nakahara and Hikita [13]. The Mo/BaO₂ system had a reproducible maximum burning rate at a composition of about 45%. This composition is well above the stoichiometric compositions of 16% and 22% corresponding to complete reactions to produce BaO(s) and MoO₃(s) or MoO₂(s), respectively.

Incomplete reaction of the fuel particles can also shift the fuel proportion to higher values for the same overall stoichiometry. For metals such as manganese and molybdenum which can readily exist in several oxidation states, the occurrence of different reactions in fuel-rich or oxidant-rich compositions, or even fuel-rich or oxidant-rich regions of a nominally fixed composition, is possible.

The mass burning rate of the Mo/BaO₂ system increased as the compaction was increased from 0 to 100 MPa, but further compaction caused no further increase in the burning rate.

The burning rate of the Mo/BaO₂ system was approximately doubled when, in the same composition, a smaller (14 μm) particle-size range of Mo was substituted for the standard size (34 μm). There was no change in the burning rates of mixtures containing two BaO₂ samples of different particle sizes (17 μm and 10 μm).

No published values for the burning rates of the Mn/SrO₂ system were found. The maximum burning rate for the Mn/SrO₂ system was at about 75% manganese. This is well above the highest stoichiometric composition for all probable reactions (e.g. 31% for the production of MnO(s)). The measured thermal conductivities for various compositions of Mn/SrO₂ increased slightly with increasing proportions of manganese.

The Mo/SrO₂ system supported combustion over the smallest range of compositions. No published values for the burning rates of this system were found.

Compositions of the Mo/SrO₂ system, which burnt under the normal experimental conditions, failed to ignite when they had been compacted under loads greater than 50 MPa.

The burning rate was approximately doubled when, in the same composition, a smaller particle-size range of molybdenum was substituted for the standard size. This behaviour was also observed for the Mo/BaO₂ system (above).

The additives tested, except MoO₃, progressively decreased the linear burning rates until finally combustion failed. Addition of up to 10% MoO₃ in 40% Mo/SrO₂ did not decrease the linear burning rate or maximum excess temperature of the composition. The MoO₃ may play some part as an alternative oxidant. It is also volatile at high temperatures (>750°C) and hence may not hamper reaction.

Examination of the residues after combustion of the binary systems showed that reaction was incomplete in all systems. The products consisted of mixtures of simple metal oxides of various stoichiometries and of complex oxides of the form XMO₄, where X = Ba or Sr and M = Mn or Mo. Onset of exothermic reaction appears to be associated with onset of decomposition of the respective oxidants, but is generally at temperatures below the onset of oxidation of the metal powders by gaseous oxygen. Indications are that reactions are initially solid–solid reactions, in agreement with the proposals of Spice and Staveley [2]. This is supported by the slowing effect of inert additives.

Differences between the manganese and molybdenum systems may be related to some formation of MoO₃ which may volatilize at higher temperatures and thus not contribute to the formation of protective layers of product on the metal.

Values of the thermal conductivity of the various powders, measured at ambient temperature, did not show sufficient variation to account for the range of burning rates observed. Little information is available on the temperature dependences of the thermal conductivities of the materials used in pyrotechnic systems, and any such information would have to take into account the effects of phase transitions, decomposition and mass transport.

Some compositions of ternary systems with either mixed fuels or mixed oxidants could be ignited. No interactions between the fuels or between the oxidants were observed. The reactions which take place in the ternary systems are likely to be similar to the reactions in the binary systems, complicated by competition between two fuels or two oxidants. The reaction in a mixed oxidant ternary system will depend on the relative stability of the two oxidants and the influence of the reverse reactions.

Further complicating factors are the possibility of catalytic effects on the decomposition of the peroxides and the possible formation of either solid solutions or complex oxides during reaction. The thermally more stable of the two oxidants could act simply as an inert diluent at the start of combustion. At higher temperatures the role of this compound may then change to that of the second oxidant. As the median particle size of

the SrO₂ particles was approximately one tenth of the median size of the BaO₂ particles (Table 3), the SrO₂ particles may pack into the spaces formed by the metal/BaO₂ mixture and therefore change their contact area.

An ideal binary pyrotechnic system for detailed study would have a metal fuel which is oxidized predominantly to a single product. Manganese and molybdenum are not ideal fuels in that they can readily exist in several oxidation states, thus complicating attempts at determining reaction stoichiometry. Further complications arise from the formation of non-crystalline products and from rapid reactions of the products with water and CO₂ in the atmosphere.

Kinetic aspects of the reactions in the binary pyrotechnic systems are discussed in Part 3 of this series [14].

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