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# Thermomicroscopy studies on the zirconium–potassium perchlorate–nitrocellulose pyrotechnic system ☆

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**Abstract**

Thermomicroscopy has been used to assist in the characterisation of the reactions occurring in the zirconium–potassium perchlorate–nitrocellulose pyrotechnic system. The components of the system and their binary and ternary combinations have been studied using a stereoscopic microscope, under conditions of controlled heating rate and atmosphere, and the observations recorded using a colour video camera in conjunction with a time-lapse video recorder. Measurements were also made of the intensity of the light reflected from the surface of the sample as a function of temperature. The results are discussed in the light of the studies made by DSC and simultaneous TG–DTA–mass spectrometry.

*Keywords:* DSC; Pyrotechnic system; TG–DTA–MS; Thermomicroscopy; Time-lapse photography; Video recording; Zirconium–potassium perchlorate–nitrocellulose mixture

## 1. Introduction

Previous studies on the zirconium–potassium perchlorate–nitrocellulose pyrotechnic system, using simultaneous thermogravimetry–differential thermal analysis–mass spectrometry, showed that zirconium and potassium perchlorate gave an exothermic solid state reaction in the region of 400 °C, which overlapped with the decomposition of unreacted potassium perchlorate [1].

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Differential scanning calorimetry and chemical analysis using ion-specific electrodes were used to follow quantitatively the solid state reaction in the region of 400°C between zirconium and potassium perchlorate [2]. Comparison of the amount of potassium chloride formed in the reaction with the amount of perchlorate reacted showed that the solid state reaction could be represented by the equation $2Zr + KClO_4 \rightarrow 2ZrO_2 + KCl$. DSC was found to provide an excellent ancillary method for the determination of the amount of potassium perchlorate reacted.

Thermomicroscopy was used to assist in the characterisation of the physical changes taking place during these reactions. In this paper we report the results of these studies, which were carried out under reflected light conditions using a modified version of a system developed for pyrotechnic studies [3].

Observations were carried out in an argon atmosphere on the components of the zirconium–potassium perchlorate–nitrocellulose system and on their binary and ternary combinations. In addition, measurements were made of the intensity of the light reflected from the surface as a function of temperature. Results from this technique have been described for a number of inorganic materials [3] and more recently for polymer samples [4].

## 2. Experimental

The hot stage unit used in these studies (Stanton Redcroft Model HSM-5) has been described previously [3]. This unit enables samples, contained in standard DSC-type pans, to be examined using reflected light, under conditions of controlled heating rate and atmosphere, over the temperature range ambient to 1000°C. The sample temperature is recorded directly from a plate-type platinum vs platinum/13% rhodium thermocouple which supports the sample crucible.

Although the original hot stage design was used, the remainder of the system, which is shown as a block diagram in Fig. 1, has been completely updated. The sample was viewed using a stereoscopic zoom-microscope (Olympus model SZ1145TR CTV) which gave a range of magnifications from × 18 to × 110 using a × 10 eyepiece. The sample was illuminated using a twin fibre optic system (Olympus Highlight 3000) connected to a voltage stabiliser. The observations were recorded using a CCD colour video camera (JVC model TK-1085E) in conjunction with a time-lapse S-VHS video cassette recorder (JVC model BR-S920E). The camera output was viewed using a high-resolution colour monitor (JVC model TM-1500PS).

Temperature programming was carried out using a Linkam programmer (modified model TMS91). This in conjunction with a video text overlay unit (Linkam model VTO 232) enabled the sample temperature to be continuously displayed on the video recording. In addition to sample temperature, the time and date were also displayed using the video recorder facilities to enable the unambiguous identification of individual frames.

The changes in the reflected light intensity (RLI) from the sample were monitored using a silicon photo-detector (IPL model 16B) which was filtered to give an approximate eye response using a green filter (Schott type BG38). The photocell signal and the

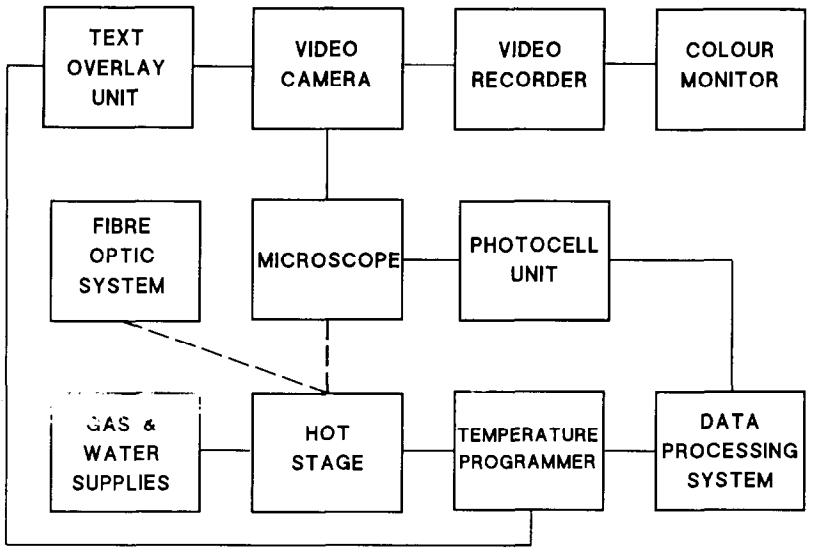


Fig. 1. Block diagram of reflected light thermomicroscopy system.

sample temperature output from the temperature programmer were recorded using a PC-compatible computer (Elonex PC-425X) fitted with a 16-bit data acquisition board (Strawberry Tree model MINI-16). The data was acquired using icon-driven software provided with the board (Quicklog PC, version 2.1.0). The resulting data in ASCII format was processed using a DOS-based graphics package (Biosoft Fig. P, version 6.0). A photograph of the complete assembly is shown in Fig. 2.

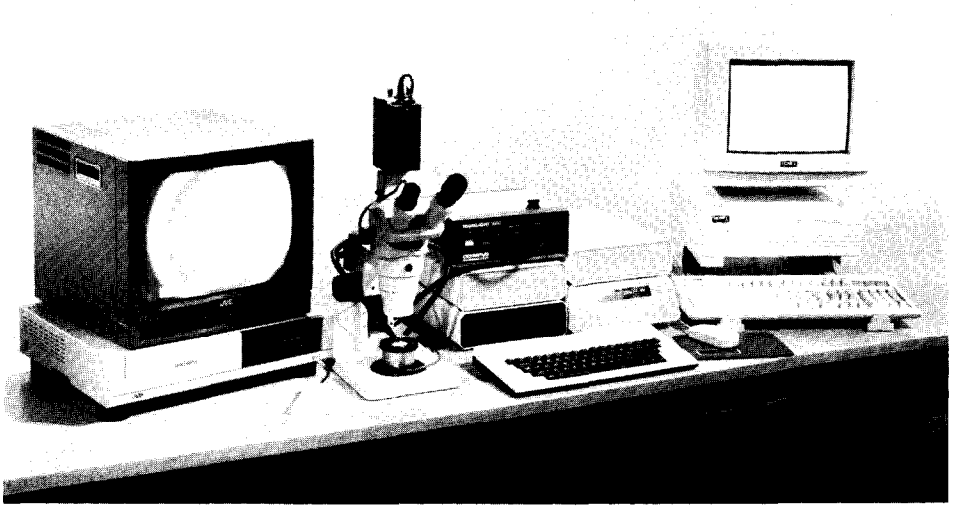

Fig. 2. Photograph of reflected light thermomicroscopy system.

The video recordings were edited by copying the S-VHS recording to Betacam-SP (broadcast format). The latter copy was then edited using an edit controller (Sony BV910). Prints were made using a video printer (Sony model UP5000) from the original S-VHS copy. This unit enabled up to four frames to be recorded on a single print.

In the present work, since preliminary observations showed that the samples containing potassium perchlorate had a tendency to bubble and creep, samples were contained in alumina crucibles 4 mm high by 6 mm diameter instead of the normal 2 mm high crucibles. Experiments were normally carried out in an argon atmosphere at a heating rate of 10°C $min^{-1}$ using sample weights in the range 2–5 mg. Having obtained suitable sample illumination, the photocell signal amplification was adjusted to give a pre-determined signal using precipitated barium sulphate as a reflectance standard. The sample to be studied was then inserted in place of the barium sulphate sample without altering the light system. In this way the reflected light intensity measurements were approximately related to a common scale.

### *2.1. Materials*

The zirconium (Degussa grade CX) had a mean particle size of 1.7 μm, and a purity of 96.5% (as total Zr + Hf). The potassium perchlorate had a particle size of < 60 μm, and a purity of > 99%. The nitrocellulose was type 220.E, with a nitrogen content of 12.1%. The compositions were prepared in a Turbula mixer before granulation with the nitrocellulose to give a grain size of about 0.5 mm.

## 3. Results and discussion

### *3.1. Zirconium*

Studies were carried out on the oxidation of zirconium where approximately 4 mg samples were heated at 10°C $min^{-1}$ in an atmosphere of flowing air. The sample, which was initially a dark grey powder, remained unchanged until approximately 250°C when a slight darkening was observed which was also shown on the reflected light intensity curve. The sample became lighter above 450°C and reached a maximum reflected light intensity around 800°C. Some expansion of the sample was seen in the temperature range 370°C to 550°C.

### *3.2. Potassium perchlorate*

The first change observed in this white crystalline material was a movement in the sample in the region of 300°C due to expansion associated with the solid–solid phase transition. Melting was observed to start at about 570°C, leading to a vigorous bubbling reaction and the evolution of white fumes.

The sample had completely melted by about 590°C to give a clear liquid in which the rapid production of fine bubbles could be observed. The bubbling reaction became increasingly vigorous as the temperature was increased. It was shown in additional

experiments, by focusing the microscope on the edge of the ceramic crucible, that during this bubbling reaction a fine spray of droplets was ejected from the crucible and condensed on the cell window. These experiments also showed that the sample crept over the edge of the crucible. These observations explained the higher than theoretical weight losses given in TG studies on this compound. The reaction was complete by about 630°C leaving a white residue. Fig. 3. shows a set of video prints illustrating the melting and decomposition of the perchlorate.

The RLI curve for potassium perchlorate is shown in Fig. 4, together with a curve for a 50% $KClO_4$–50% KCl mixture showing the sharp deflection due to the eutectic melt at 507°C.

### 3.3. *Nitrocellulose*

The onset of decomposition of nitrocellulose was observed in the region of 190°C by a change in the white fibrous material to a cream colour accompained by some shrinkage. At about 205°C, the sample melted to form a vigorously bubbling mass which expanded out of the crucible. The bubbling was accompanied by the evolution of white fumes condensed on the hot stage window as small droplets. The dark brown decomposition product could be seen in the melt around 220°C and bubbling stopped at about 235°C leaving a blackish-brown porous residue. These reactions are illustrated by the video prints shown in Fig. 5.

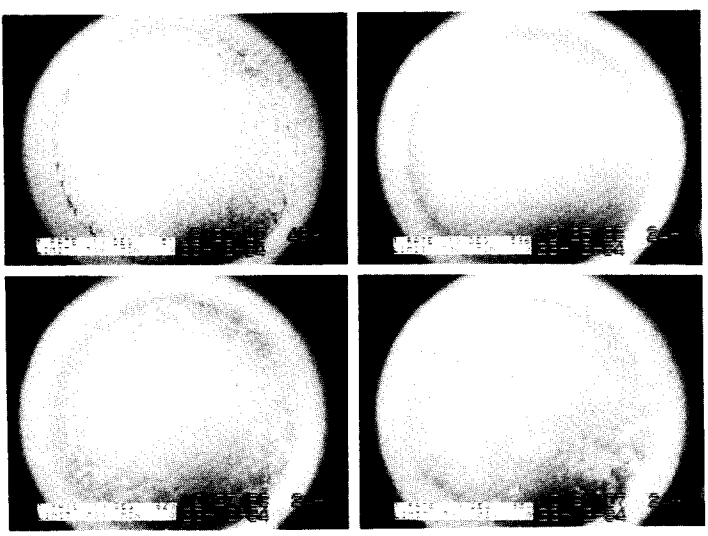

Fig. 3. Video prints showing the fusion and decomposition of potassium perchlorate. Top left, 51°C; top right, 596°C; bottom left, 620°C; bottom right, 650°C. (Sample weight, 5.0 mg; heating rate, 10°C $min^{-1}$; atmosphere, argon).

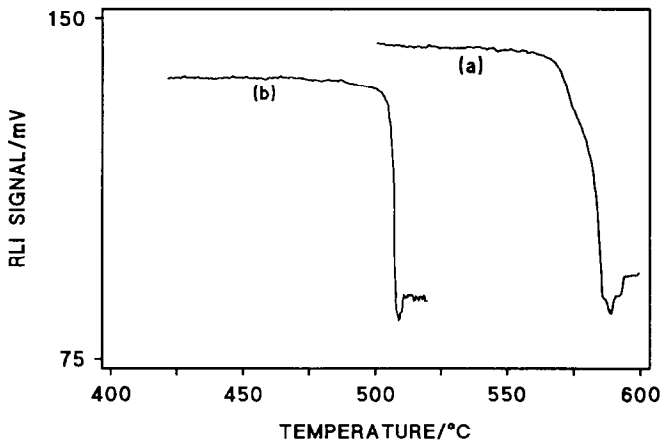


Fig. 4. Reflected light intensity curve for (a) potassium perchlorate and (b) a 50% potassium perchlorate–50% potassium chloride mixture. (Sample weight, 5.0 mg; heating rate, 10°C $min^{-1}$; atmosphere, argon).

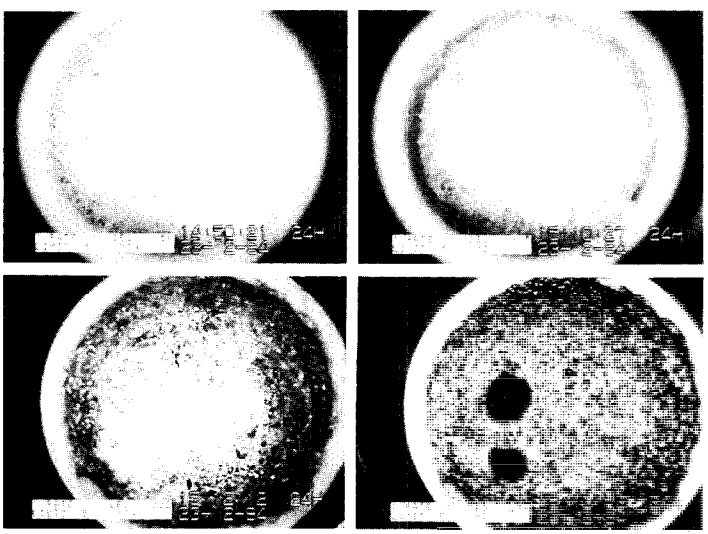

Fig. 5. Video prints showing the decomposition of nitrocellulose. Top left, 50°C; top right, 205°C; bottom left, 222°C; bottom right, 234°C (Sample weight, 2.6 mg; heating rate, 10°C $min^{-1}$; atmosphere, argon).

### 3.4. *10% Zirconium–90% potassium perchlorate composition*

Following movement in this medium grey granular material in the region of 300°C, due to the phase change in $KClO_4$, the reaction of the zirconium with potassium perchlorate was observed as a change in colour to light-grey over the range 430°C to 500°C. This is shown in the video prints in Fig. 6 and in the RLI curve in Fig. 7. At

about 506 °C there was a small amount of melting due to the formation of $KClO_4$–KCl eutectic mixture; this is also shown on the RLI curve. This was followed by the fusion of the unreacted potassium perchlorate to give a vigorously bubbling mixture. The reaction was complete in the region of 570 °C, giving an off-white solid. The decrease in

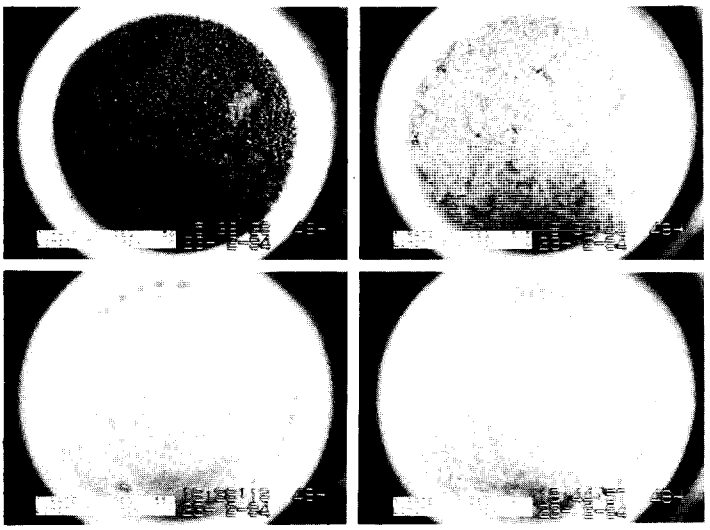

Fig. 6. Video prints for a 10% zirconium–90% potassium perchlorate composition. Top left, 50 °C top right, 515 °C; bottom left, 550 °C; bottom right, 610 °C (Sample weight, 5.0 mg; heating rate, 10 °C $min^{-1}$; atmosphere, argon).

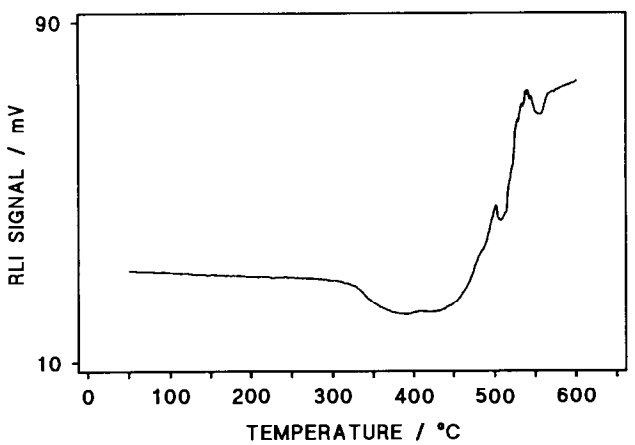


Fig. 7. Reflected light intensity curve for a 10% zirconium–90% potassium perchlorate composition. (Sample weight, 5.0 mg; heating rate, 10 °C $min^{-1}$; atmosphere, argon).

the RLI in the region of 300°C, which was also observed in the zirconium oxidation studies, requires further investigation.

### 3.5. Potassium perchlorate–nitrocellulose mixtures

The reaction of the carbonaceous residue from the decomposition of nitrocellulose with potassium perchlorate, which had been shown previously to overlap with the reaction of zirconium with potassium perchlorate [1], was studied for mixtures containing potassium perchlorate and nitrocellulose in the ratios 10:1, 30:1 and 100:1. As can be seen from the RLI and derivative (DRLI) curves for the 10:1 mixture, shown in Fig. 8, the darkening of the initially white sample, due to the decomposition of nitrocellulose in the region of 200°C, was followed by a rapid change to a white powder accompanying the oxidation of the carbonaceous nitrocellulose residue by potassium perchlorate.

At lower nitrocellulose levels, darkening of the sample in the region of 240°C to 360°C, associated with further decomposition of the nitrocellulose residue, was seen more clearly. The sensitivity of the RLI technique was demonstrated by studies of reactions in samples containing as little as 5 μg of nitrocellulose. Above 500°C the melting and decomposition of residual potassium perchlorate was observed. Only in the case of the 10:1 mixture had sufficient potassium chloride been formed in the reaction between potassium perchlorate and the nitrocellulose residue to show the $KClO_4$–KCl eutectic melting above 500°C.

### 3.6. Zirconium–potassium perchlorate–nitrocellulose compositions

A range of ternary compositions containing from 10–60% zirconium and 1% nitrocellulose was studied. The reactions observed in the composition containing 10%

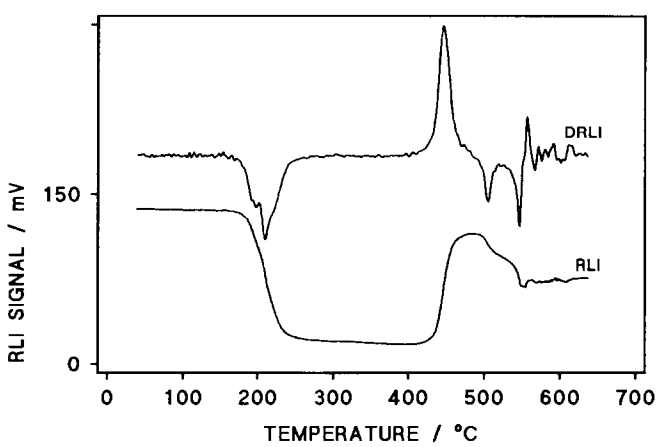


Fig. 8. Reflected light intensity and derivative RLI curves for a 10:1 potassium perchlorate–nitrocellulose mixture. (Sample weight, 5.1 mg; heating rate, 10°C $min^{-1}$; atmosphere, argon).

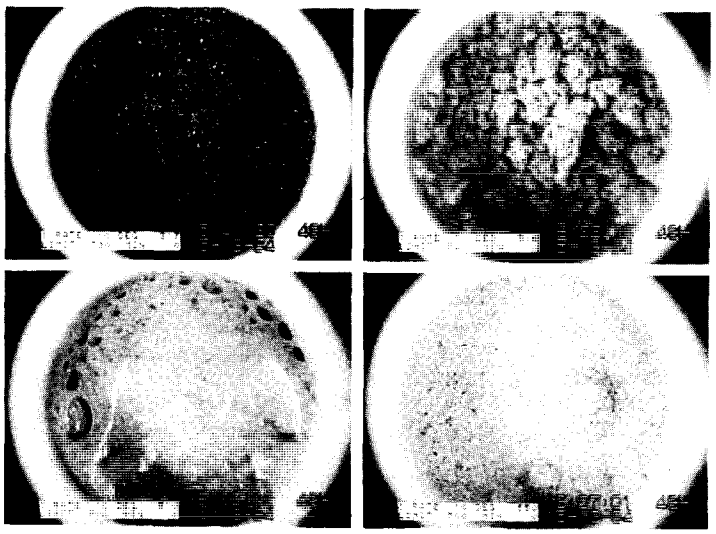

Fig. 9. Video prints for the 20% zirconium–79% potassium perchlorate–1% nitrocellulose composition. Top left, 317 °C; top right, 506 °C; bottom left, 510 °C; bottom right, 550 °C (Sample weight, 5.1 mg; heating rate, 10 °C $min^{-1}$; atmosphere, argon).

zirconium were similar to those observed for the 10% zirconium binary composition. However, the solid–solid phase transition produced more movement in the granulated composition and the bubbling reaction in the final stage appeared to be more vigorous.

In the 20% zirconium composition, the increased reaction between the zirconium and potassium perchlorate resulted in an increase in the extent of eutectic fusion and this is clearly seen in the sequence of video prints shown in Fig. 9. The bubbling mixture in the final stages of reaction could be seen to be considerably more viscous. Studies on the 30% and 40% zirconium compositions showed that the amount of liquid phase present in the final stages of the reaction was further reduced with increasing zirconium concentration and in the case of the 40% zirconium composition only a small amount of eutectic fusion could be seen.

At the 60% zirconium level, the sharp exothermic peak recorded by high temperature DSC in the final reaction stages [2], was shown to be associated with the instantaneous evolution of a white vapour which was ejected onto the window of the hot stage. The identification of this material, which may be unreacted potassium perchlorate, is in progress and it is hoped to study the reaction using a high speed video system.

## 4. Conclusions

Thermomicroscopy studies have proved to be of considerable value in assisting in the interpretation of the reactions taking place in the zirconium–potassium perchlor-

ate–nitrocellulose system and have identified a number of features that were not evident from the other thermal analysis techniques used. The RLI curves have provided additional complementary information and are useful when comparing the thermomicroscopy results with those obtained from other thermal analysis techniques. The RLI technique has been shown to be particularly sensitive in studying reactions of the carbonaceous product produced by the decomposition of the nitrocellulose. Further work needs to be carried out to establish the quantitative potential of the technique.

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