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Thermal analysis studies on the zirconium/nickel alloy–potassium perchlorate–nitrocellulose pyrotechnic system [☆]

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Abstract

The zirconium/nickel alloy–potassium perchlorate–nitrocellulose pyrotechnic system has been studied using differential scanning calorimetry, simultaneous TG–DTA–mass spectrometry and chemical analysis using ion-specific electrodes. Quantitative measurements on the solid state reaction, in the region of 400°C, between zirconium/nickel alloy and potassium perchlorate have shown that a major component of the solid state reaction may be represented by the equation $9Zr + 14Ni + 8KClO_4 = 9ZrO_2 + 14NiO + 8KCl$. DSC has been confirmed as an excellent ancillary method for the determination of the amount of potassium perchlorate reacted.

Keywords: DSC; Ion-specific electrode; Pyrotechnics; TG–DTA–MS; Thermal analysis; X-ray diffraction; Zirconium/nickel alloy–potassium perchlorate–nitrocellulose mixture

1. Introduction

Previous studies on the zirconium–potassium perchlorate–nitrocellulose (NC) pyrotechnic system using simultaneous thermogravimetry–differential thermal analysis–mass spectrometry (TG–DTA–MS) showed that zirconium and potassium perchlorate

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gave an exothermic solid state reaction in the region of 400°C, which overlapped with the decomposition of unreacted potassium perchlorate at a higher temperature [1].

Quantitative measurements were made on this solid state reaction by differential scanning calorimetry (DSC) and by chemical analysis using ion-specific electrodes (ISE) to measure the potassium perchlorate and chloride content of the reaction products [2]. It was shown that the solid-state reaction could be represented by the equation $2Zr + KClO_4 \rightarrow 2ZrO_2 + KCl$ and that potassium chlorate, which has been found as an intermediate in the decomposition of potassium perchlorate, was not formed in significant quantities in the presence of zirconium.

In the present work, a similar approach has been applied to study the corresponding pyrotechnic system based on a zirconium/nickel alloy containing equal parts by weight of the two metals. During a study on the burning characteristics of a range of potassium perchlorate compositions containing zirconium or zirconium/nickel alloys, it was shown by DTA that an ignition temperature of between 433°C and 472°C was given for the present system, depending on the percentage of the fuel present [3].

2. Experimental

Compositions were prepared from a Zr/Ni alloy containing equal parts by weight of the metals (Degussa, average particle size 4 μm) and potassium perchlorate (particle size < 60 μm, purity $> 99\%$). The nitrocellulose was type 220.E, with a nitrogen content of 12.1%. The compositions were prepared in a Turbula mixer before granulation by the addition of 1% by weight of nitrocellulose (dissolved in an ethanol–acetone mixture) to give a grain size of about 0.5 mm.

DSC experiments were carried out using a Du Pont 9900 unit and a high-temperature unit developed for pyrotechnic studies. Simultaneous TG–DTA–MS work was performed using a Stanton Redcroft STA 1500 interfaced to a VG Micromass quadrupole mass spectrometer. Experiments were carried out in purified argon or helium, where possible using zirconium powder as an internal oxygen getter.

Analyses of reaction products, prepared by heating a composition to different temperatures in the Du Pont DSC apparatus, for perchlorate and chloride content were performed using ion-specific electrodes (ISE). Full details of the above experimental procedures have been given previously [1, 2].

3. Results

3.1. Preliminary thermal analysis studies.

The thermal behaviour of potassium perchlorate and nitrocellulose has been reported previously [1]. The oxidative behaviour of the zirconium/nickel alloy was studied by simultaneous TG–DTA in air and the results are shown in Fig. 1. It can be seen that there is evidence of a two stage oxidation process and X-ray diffraction measurements on the reaction products formed by heating the alloy to different

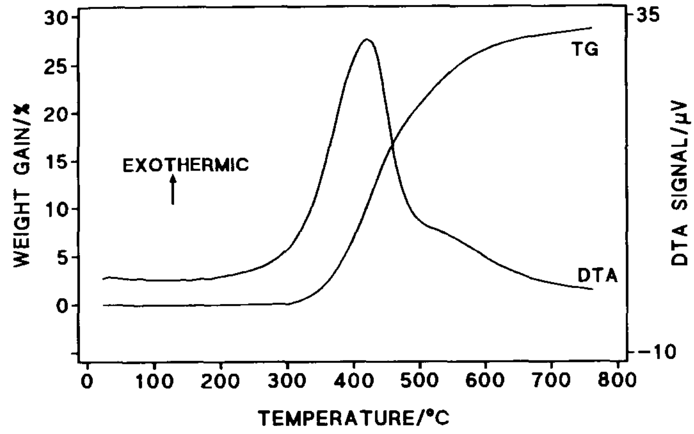

Fig. 1. Simultaneous TG-DTA curves for a zirconium-nickel alloy (50/50) (sample weight, 10 mg; heating rate, 5°C min^{-1}; atmosphere, air).

temperatures showed that zirconium oxide was produced initially, followed by the formation of nickel oxide at a higher temperature. The formation of an intermediate reaction product, which has still to be identified, was also indicated. It has been pointed out previously that the high reactivity of zirconium towards oxygen is not significantly modified by the presence of other metals such as nickel [4].

Preliminary DSC studies were carried out, using the high-temperature apparatus, on a range of ternary compositions containing 10% Zr/Ni and from 50-90% Zr/Ni. Typical results are shown in Fig. 2. The compositions showed a number of features in common with those observed for the corresponding system containing zirconium [1].

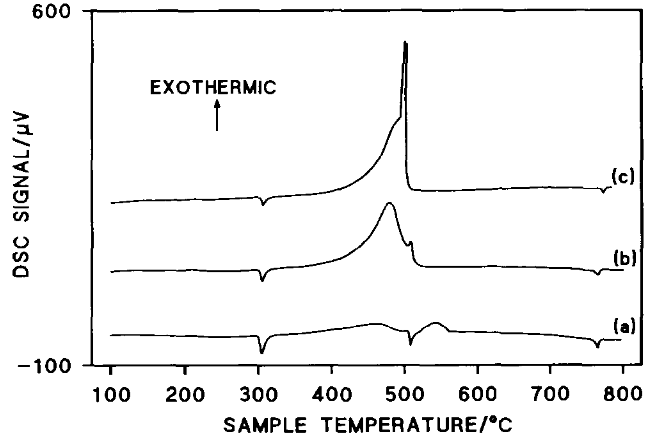

Fig. 2. High temperature DSC curves for (a) 10% Zr/Ni-89% $KClO_4$-1% NC, (b) 50% Zr/Ni-49% $KClO_4$-1% NC and (c) 70% Zr/Ni-29% $KClO_4$-1% NC compositions (sample weight, 5 mg; heating rate, 10°C min^{-1}; atmosphere, argon).

Thus the small exotherm corresponding to the decomposition of nitrocellulose at about 200°C was followed by the endothermic phase change of potassium perchlorate at 300°C. This transition was followed by the exothermic peak attributed to the reaction between zirconium/nickel alloy and potassium perchlorate, leading to the eutectic melt of $KClO_4$–KCl at about 505°C and the exothermic decomposition of unreacted potassium perchlorate.

The latter features decreased significantly as the zirconium/nickel content of the compositions was increased. The high temperature endotherm at about 770°C was due to the fusion of potassium chloride formed both in the solid-state reaction and in the decomposition of unreacted potassium perchlorate. The compositions containing 50% and above of the alloy showed an increase in heat output in the final stages of the reaction giving rise to a sharp peak and this became very rapid for the compositions with 70% and over of Zr/Ni.

TG–DTA–MS studies on the ternary composition containing 10% Zr/Ni showed the CO_2 evolution accompanying the breakdown of NC and the oxidation of the carbonaceous NC residue by $KClO_4$, in the region of 200°C and 400°C, respectively (Fig. 3). The O_2 curve indicated that the decomposition of unreacted $KClO_4$ started in the region of the DTA peak maximum. It was noticeable, in comparison with the corresponding zirconium system, that onset of decomposition of the unreacted perchlorate was accelerated in the presence of zirconium/nickel alloy. This was shown by the increased weight loss and the increase in magnitude of the DTA peaks given by the $KClO_4$–KCl eutectic.

The increased decomposition of the perchlorate was attributed to the catalytic effect of the nickel oxide, formed in the reaction, on the decomposition of the perchlorate and this was confirmed by TG studies where nickel oxide was added to potassium

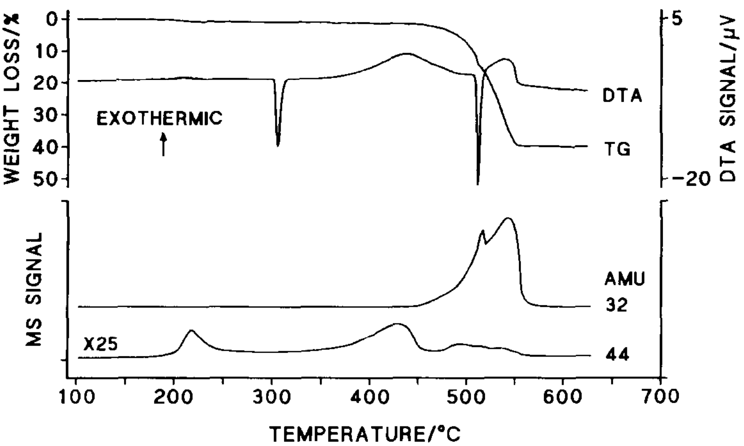

Fig. 3. Simultaneous TG, DTA and EGA curves for O_2 (32 amu) and CO_2 (44 amu), for a 10% zirconium/nickel alloy–89% potassium perchlorate–1% nitrocellulose composition (sample weight, 10 mg; heating rate, 10°C min^{-1}; atmosphere, helium).

perchlorate. This produced a further increase in the rate of weight loss when compared with the addition of ZrO_2

The eutectic $KClO_4$–KCl melt and the vigorous bubbling decomposition of the unreacted $KClO_4$ were observed for the 10% Zr/Ni composition by thermomicroscopy and are illustrated by the video prints in Fig. 4. Due to the larger particle size of the Zr/Ni alloy compared with the zirconium (4 μm vs 1.7 μm) there was significantly less movement of the oxidised metal particles during the decomposition of the unreacted perchlorate.

3.2. Measurements of reaction exothermicities by DSC

Experiments were carried out on the Du Pont 9900 DSC to estimate the variation in the reaction exothermicity as a function of zirconium/nickel content for compositions containing 50–90% zirconium/nickel. The instrument was calibrated using the enthalpies of fusion of high purity indium, tin, lead, zinc and aluminum. The measurements on the pyrotechnic compositions showed good reproducibility and typical DSC curves are shown in Fig. 5.

The DSC measurements, together with values obtained previously by combustion calorimetry in argon [3], are shown in Fig. 6. The combustion calorimetry measurements gave maximum exothermicity values for compositions containing 60–65%

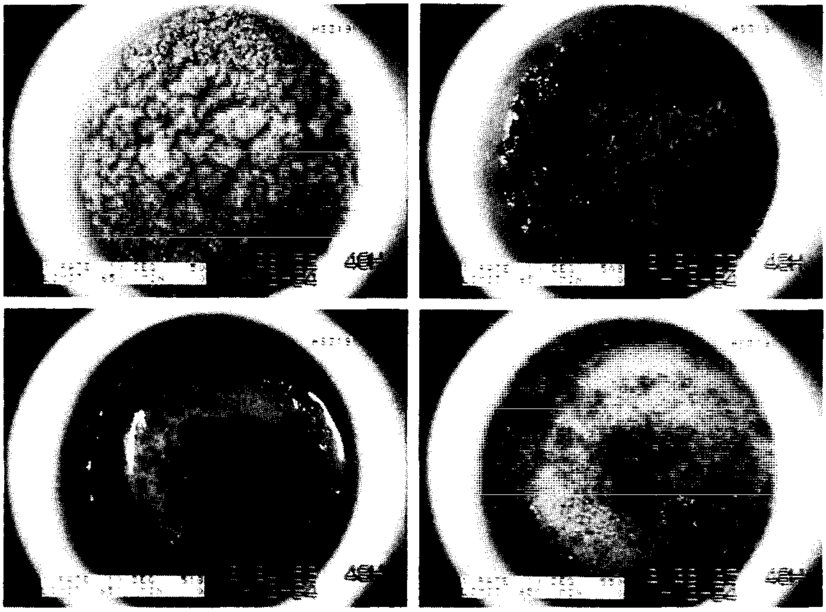

Fig. 4. Video prints from a thermomicroscopy study on a 10% zirconium/nickel alloy–89% potassium perchlorate–1% nitrocellulose composition. Top left, 50°C; top right, 508°C; bottom left, 518°C; bottom right, 550°C (sample weight, 5.0 mg; heating rate, 10°C min^{-1}; atmosphere, argon).

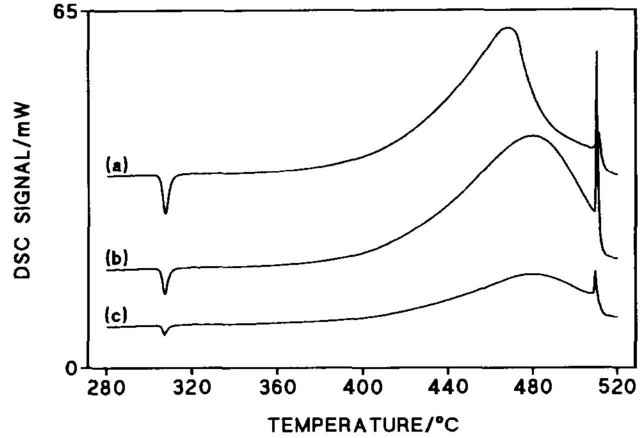

Fig. 5. DSC curves for (a) 50% Zr/Ni-49% $KClO_4$-1% NC, (b) 75% Zr/Ni-24% KClO-1% NC and (c) 90% Zr/Ni-9% $KClO_4$-1% NC compositions (sample weight, 5 mg; heating rate, 5°C min^{-1}; atmosphere, argon).

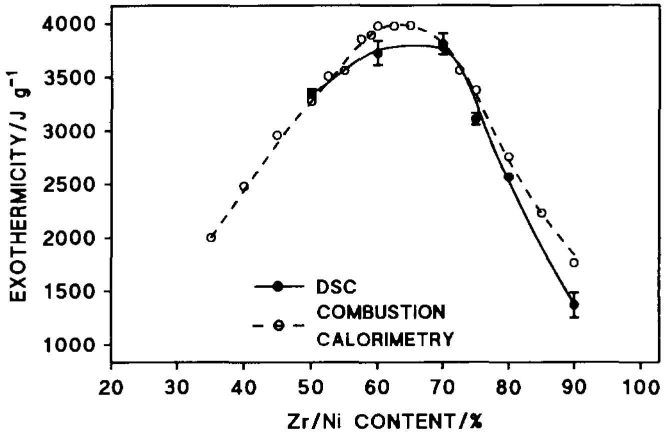

Fig. 6. Comparison of reaction exothermicities in argon, obtained by DSC, for a range of zirconium/nickel alloy-potassium perchlorate-nitrocellulose compositions with those from adiabatic combustion calorimetry studies.

Zr/Ni while the maximum values from the DSC studies were in the 60-70% Zr/Ni region. These values were in reasonable agreement with the calculated reaction stoichiometry of 59.7% Zr/Ni given by the equation

$$9Zr + 14Ni + 8KClO_4 = 9ZrO_2 + 14NiO + 8KCl$$

The agreement between the DSC and combustion calorimetry measurements suggested that the reaction in the region 350°C to 510°C, observed by DSC under non-ignition conditions, represented the major component of the pyrotechnic combustion reaction.

3.3. Measurement of the extent of reaction in the 50% zirconium/nickel alloy–49% potassium perchlorate–1% nitrocellulose composition as a function of temperature

Following the preliminary high-temperature DSC experiments, measurements on the extent of reaction as a function of temperature were carried out on the 50% Zr/Ni–49% $KClO_4$–1% NC composition by DSC and by chemical analysis using ion-specific electrodes.

The percentage of the potassium perchlorate reacted, as determined from the ISE measurements on samples heated to different temperatures, is plotted in Fig. 7. The values can be seen to lie on a well defined curve and thus provide a quantitative measure of the extent of reaction as a function of temperature. The reaction was observed to start slightly above 300°C, accelerated rapidly above 440°C and was completed by about 500°C.

DSC measurements on the residues showed well defined peaks for the solid–solid transition of unreacted perchlorate although, as was observed for the zirconium system [2], the single transition given by the perchlorate alone showed evidence of a double peak in the reaction products. The measurements on the amount of perchlorate reacted by DSC were in good agreement with those measured by ISE, as can be seen in Fig. 8, thus confirming that the DSC technique provides a useful method for the determination of the perchlorate content of pyrotechnic reaction products.

Measurement of the amount of potassium chloride formed in the reaction at different temperatures gave a curve that was similar in shape to that obtained for the amount of

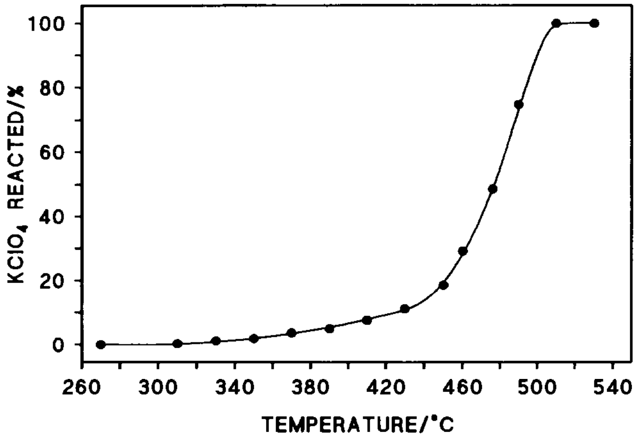

Fig. 7. Plot of % $KClO_4$ reacted against temperature for a 50% Zr/Ni–49% $KClO_4$–1% NC composition (measurements by ISE on 5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

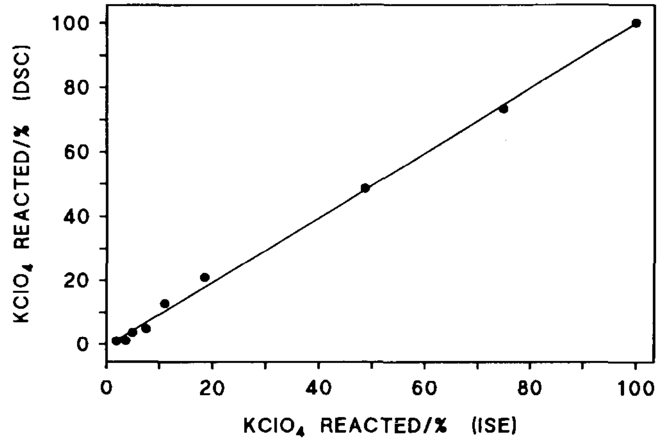

Fig. 8. Plot of % $KClO_4$ reacted measured by DSC against % $KClO_4$ reacted measured by ISE, for the 50% Zr/Ni–49% $KClO_4$–1% NC composition (5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

perchlorate reacted as a function of temperature. In order to test the validity of the reaction equation postulated previously, the chloride values have been expressed as a percentage of the amount of chloride that would be formed from the total amount of perchlorate present according to the above equation.

In Fig. 9 the calculated values for the % KCl formed have been plotted against the % $KClO_4$ reacted. The correlation between the perchlorate and chloride measurements lends quantitative support to the postulated reaction equation and suggests that an intermediate reaction involving the formation of potassium chlorate, which had

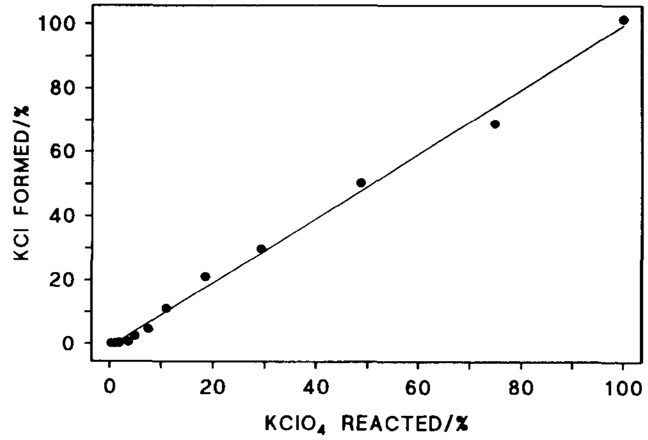

Fig. 9. Plot of % KCl formed against % $KClO_4$ reacted for the 50% Zr/Ni—49% $KClPO_4$–1% NC composition (5 mg samples heated at 5°C min^{-1} in argon to different temperatures).

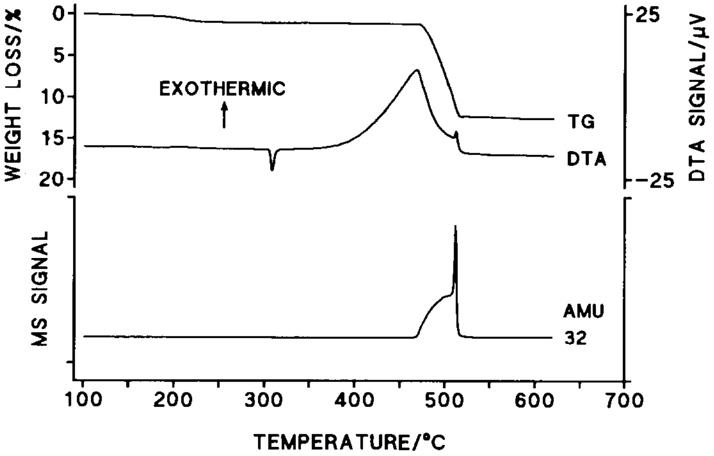

Fig. 10. Simultaneous TG, DTA and EGA curves for O_2 (32 amu) for a 50% zirconium/nickel alloy–49% potassium perchlorate–1% nitrocellulose composition (sample weight, 10 mg; heating rate, 10°C min^{-1}; atmosphere, helium).

been observed at low levels in the decomposition of potassium perchlorate [5], did not take place to a significant extent in the presence of the zirconium/nickel alloy.

This observation was supported by X-ray diffraction measurements on the residues formed at different temperatures, which showed ZrO_2, NiO and KCl as the reaction products, as well as the unidentified intermediate phase formed in the aerial oxidation of the Zr/Ni alloy.

It can be seen from the simultaneous TG–DTA–MS plot for the 50% Zr/Ni alloy (Fig. 10) that decomposition of the perchlorate began in the region of the DTA peak maximum at about 455°C. The MS trace showed that the small exothermic peak in the final stages of reaction was accompanied by a sharp increase in the rate of oxygen evolution.

4. Conclusions

Studies on the zirconium/nickel alloy–potassium perchlorate–nitrocellulose system have shown that it is possible to make quantitative measurements on the solid-state reaction between the zirconium/nickel alloy and potassium perchlorate. The perchlorate analysis by ISE has enabled the amount of potassium perchlorate reacted to be established quantitatively as a function of temperature. Comparison of these results with those obtained by DSC peak area measurements on the potassium perchlorate transition has confirmed the DSC technique as an excellent ancillary method for the determination of the extent of the perchlorate reaction.

The variation in the exothermicity of reaction with zirconium/nickel content has been measured by DSC for mixtures in the range 50–90% Zr/Ni. The Zr/Ni alloy contents corresponding to the maximum exothermicities given by the DSC and combustion calorimetry measurements were in reasonable agreement with the reaction stoichiometry of 59.7% Zr/Ni calculated from the equation

$$9Zr + 14Ni + 8KClO_4 \rightarrow 9ZrO_2 + 14NiO + 8KCl$$

In addition there was a linear correlation between the amount of $KClO_4$ reacted and the amount of KCl formed based on the above equation. X-ray diffraction studies showed that the zirconium component was oxidised initially, followed by the nickel component in the later stages of the reaction.

The agreement between the DSC and adiabatic combustion calorimetry studies suggested that the reaction in the region 350°C to 510°C, observed by DSC under non-ignition conditions, represented the major component of the pyrotechnic combustion reaction.

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