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High temperature thermal analysis of a Pyronol composition [1]

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Abstract

In this study, differential scanning calorimetry (DSC) has been used for the measurement of thermal properties of fuel/oxidant pairs. Pyronol, a modified thermite, has been synthesized and studied by thermoanalytical techniques to determine the onset of ignition and the enthalpy of reaction. The data reveal the role of internal oxidant, metallics, and thermite under inert and active atmospheres. The study suggests that uncombined aluminum preferentially reacts with polytetrafluoroethylene (Teflon) or its thermal decomposition products. Depletion of free aluminum minimizes the opportunity for thermite and intermetallic reactions. The study indicates that composition revisions such as the replacement of Teflon with a non-reactive polymer or a binary composition based on Teflon and aluminum would lead to improved energetics and possibly to enhanced performance.

INTRODUCTION

In the Pyronol system (a modified ferric oxide/aluminum thermite), Teflon serves to pressurize the effluent of the incendiary composition. The main reaction product of Pyronol is reported as being molten iron, which then acts as a cutting fluid [1]. The consolidated composition, packaged in appropriate canisters, has been used by salvage crews at sea to cut through cables and steel structures. The Pyronol composition owes its origin to H. Goldschmidt, who in an 1895 patent [2] described the reduction of solid Fe_3O_4 by Al.

In this thermoanalytical study, we obtain data which suggest a complex role for Teflon in the Pyronol composition as well as some interesting thermal features of ferric oxide, aluminum and nickel.

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EXPERIMENTAL

All DTA/DSC thermograms were obtained with a Perkin-Elmer (P.E.) 1700 high temperature DTA system comprised of a P.E. System 7/4 Thermal Analysis Controller, a P.E. Differential Thermal Analyzer, a P.E. Graphics Plotter 8, and an IBM model 80 PS-2 loaded with standard P.E. DTA software. For these studies the DTA 1700 was used in the DSC mode. The DTA furnace was temperature calibrated and the heat flow was calibrated with high purity silver (99.999%) obtained from Englehard Industries. Calibration was obtained initially by running this standard with a calibration factor of unity and comparing known heats of fusion with those experimentally observed. The calibration factor thus determined was further refined by iterative experiments, repetition and averaging. This procedure yielded a calibration factor of 1.394 with silver. All DSC experiments were performed in 100 mm^3 ceramic liners placed in the instrument's platinum sample holder cups. The dynamic purge atmosphere was air or argon. All experiments were conducted at a heating rate of 20°C min^{-1}. Initially, samples were doped with calcined alumina, but this procedure yielded non-reproducible results and tended to mask the thermogram. Simply using undoped samples and an empty ceramic liner as reference yielded improved results. Most thermograms were run in duplicate. Features and their locations were found to be reproducible. The exothermic and endothermic peak energy values did vary, however. Agreement was within 20%.

RESULTS AND DISCUSSION

Table 1 shows the composition investigated in these thermal analysis studies. The Pyronol composition is formulated to produce molten iron effluent from the Fe_2O_3/Al thermite reaction. Aluminum is also incorporated to alloy exothermically with Ni so as to preheat the thermitic reactive pair. Teflon is incorporated so that, upon decomposition, the gas produced will pressurize the molten reaction products, thereby ejecting molten metal which serves as a cutting fluid. To understand better the complex chemistry of the composition and to optimize its performance, we have grouped the

TABLE 1

Composition of Pyronol

Component	Weight%
Teflon	7.0
Ferric Oxide	34.3
Aluminum	27.4
Nickel	31.3

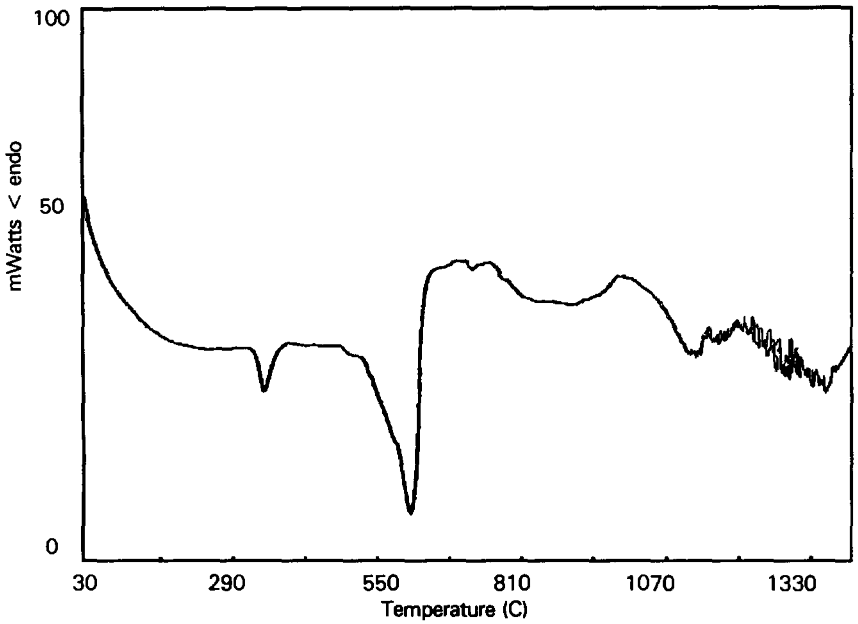

Fig. 1. Thermogram (DSC) of Teflon under argon. Weight: 11.35 mg; scan rate: 20°C min^{-1}; atmosphere: argon, 18 cm^3 min^{-1}.

composition into appropriate components and pairs of compositions and studied these by thermoanalytical techniques.

The comparison of DSC pyrolysis experiments with Teflon in argon and air atmospheres (Figs. 1 and 2) indicates a combustion reaction in air with onset at 513.9°C yielding in excess of 1271 J g^{-1}. Figure 1 illustrates that Teflon undergoes simple decomposition under an inert atmosphere. The appearance of a broad exothermic peak followed by a sharper exothermic shoulder in Fig. 2 suggests a combustion process with formation of several combustion products. Apparently Teflon, even in the presence of trace quantities of oxygen, decomposes vigorously to $(CF_x)_nO$ free radical compounds [3], where $x = 2$ or 3 and $n = 1$. In a cutting torch application, entrapped air could easily serve as a source of oxygen for formation of such free radicals.

Figure 3 represents a DSC thermogram obtained for the stoichiometric Fe_2O_3/Al thermite studied under an argon atmosphere. This thermogram clearly demonstrates that Fe_2O_3 is reduced to Fe^0 in a stepwise manner as evidenced by an initial exotherm with onset at 925.8°C followed by two additional exothermic reductions in the vicinity of 1300°C. A composition based on Al_2Ni stoichiometry was prepared. The calorimetry experiments with this composition did in fact indicate an alloy being formed at 955.5°C (Fig. 4) with appreciable exothermicity (in excess of 9072 J g^{-1}).

It is well known that Teflon reacts with metals. This reaction has been demonstrated with magnesium metal [4] in missile decoy applications. Two

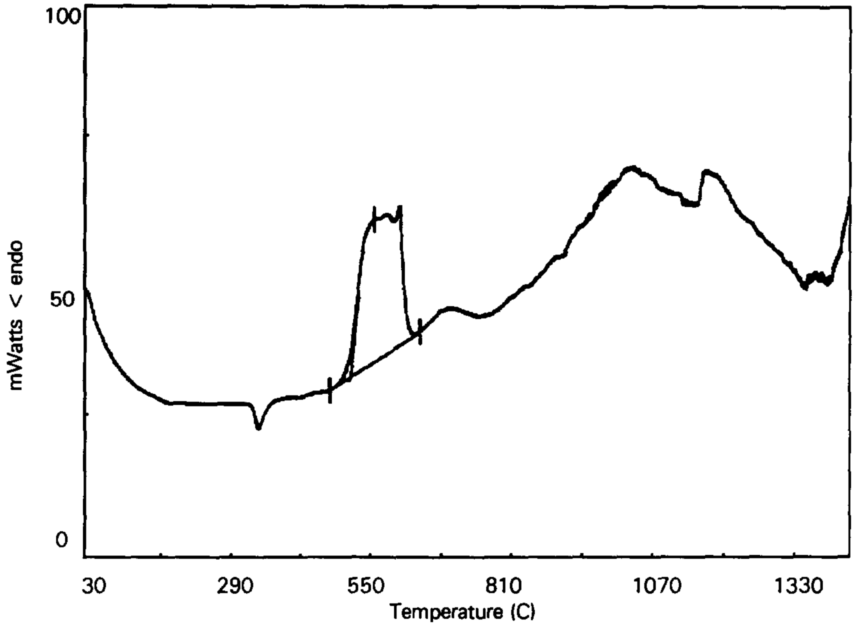

Fig. 2. Thermogram (DSC) of Teflon under air. Weight: 6.77 mg; scan rate: 20°C min^{-1}; atmosphere: air, 40 cm^3 min^{-1}. Peak from: 475.1-643.5°C; onset: 513.9°C; J g^{-1}: −1271.65; peak: 559°C.

metals, nickel and aluminum, are present in the Pyronol composition. Both a Teflon/Al composition and a Teflon/Ni composition were prepared in stoichiometries representative of the Pyronol composition. Figures 5 and 6 illustrate the calorimetry findings with the first of these two compositions. Figure 5 shows that aluminum influences the Teflon decomposition mode (exothermic doublet) and alters Teflon pyrolysis in argon from an endothermic to an exothermic event. Figure 5 also shows multiple metal fluorinations commencing at 845.1°C. These fluorination reactions are energetic with respect to a calculated thermitic heat of reaction of 4015.68 J g^{-1}. The composition generates in excess of 4580 J g^{-1} under an argon atmosphere. Under an air atmosphere (Fig. 6) the Teflon/Al reaction yields increased energy in at least two highly exothermic events. The first exothermic region (peak at 978.4°C), probably fluorination, generates more than 5131 J g^{-1}, followed by an additional exothermic region, probably due to combustion, yielding in excess of 10000 J g^{-1}. This reaction in an air atmosphere displays combustive effects due to both $(CF_x)_nO$ and atmospheric oxygen. Assignment of the first exothermic peak in Fig. 6 to a fluorination reaction is based upon a similar location for an exothermic peak found in Fig. 5. The energetics associated with both peaks assigned to fluorination reactions are also similar.

The Teflon/Ni reaction, in argon, shows similar exothermic behavior (Fig. 7) after Teflon pyrolysis, and additionally shows a gas phase reaction

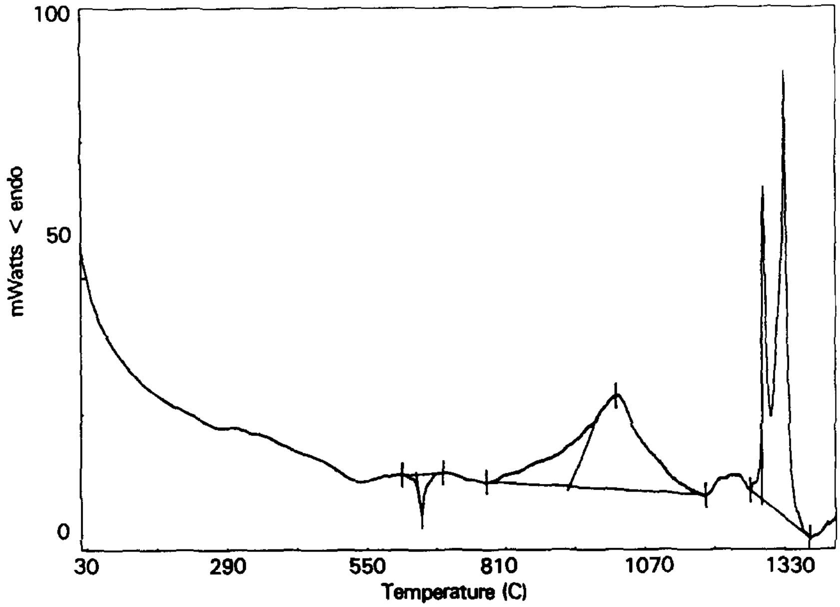

Fig. 3. Thermogram (DSC) of stoichiometric Fe_2O_3/Al under argon. Weight: 4.63 mg; scan rate: 20°C min^{-1}; atmosphere: argon, 18 cm^3 min^{-1}.
Peak from: 615.1–692.2°C; onset: 643°C; J g^{-1}: 113.81; peak: 649.9.
Peak from: 773.4–1181.5°C; onset: 925.8°C; J g^{-1}: −2349.29; peak: 1014.9°C.
Peak from: 1264.8–1373°C; onset: 1285.5°C; J g^{-1}: −1909.75°C; peak: 1330.9°C.

between Teflon decomposition products and nickel. The same reaction run in air reflects an altered thermogram (Fig. 8) displaying both combustive and fluorination effects. The additional shoulder located at 1146°C is due to combustion.

A second thermitic reaction is of course possible between ferric oxide and nickel. This stoichiometric thermitic composition was studied under both an argon and an air atmosphere. Little difference was observed between atmospheres. Figure 9 shows the thermogram obtained in the argon atmosphere. Conkling [5] reports 0.96 kcal g^{-1} as the heat of reaction for elemental reduction of ferric oxide to iron. This equates to 4015.68 J g^{-1}, a value with which the Fe_2O_3/Al reaction studied here agrees with well (to within 3.2%). There was poorer agreement (8.8%) when nickel was employed as the reducing agent. We suspect that the high temperature doublet seen in the Fe_2O_3/Al reaction also appears in the Fe_2O_3/Ni reaction, but is beyond the temperature range of the Perkin-Elmer furnace (1500°C), and that additional heats of reaction associated with the doublet would in fact further improve comparisons.

Comparison of the DSC data (Figs. 2–9) with calorimetric data obtained in air and argon atmospheres for the Pyronol composition (Figs. 10 and 11) leads to unexpected conclusions. Under either atmosphere, neither the

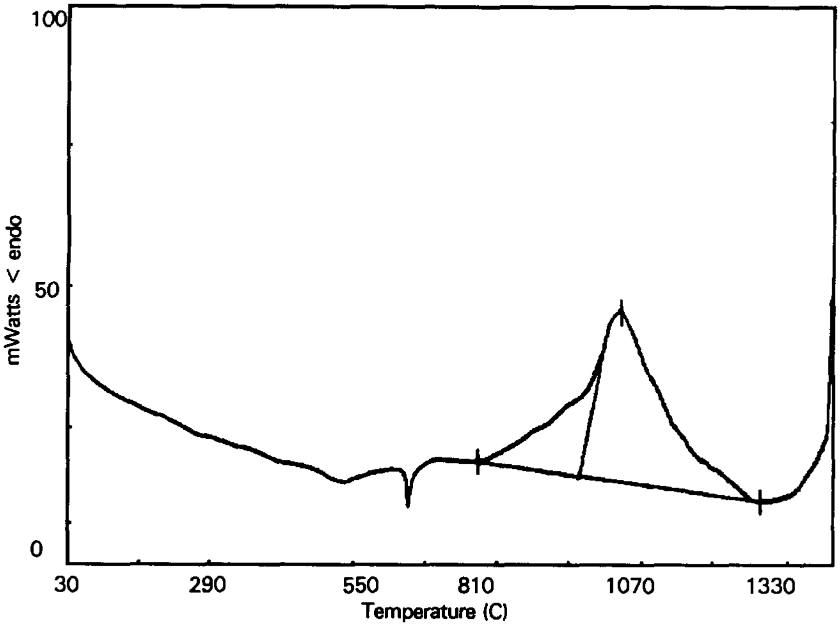

Fig. 4. Thermogram (DSC) of Al_2Ni under argon. Weight: 2.54 mg; scan rate: 20°C min^{-1}; atmosphere: argon, 18 cm^3 min^{-1}. Peak from: 775.1–1279.6°C; onset: 955.5°C; J g^{-1}: −9072.79; peak: 1032.3.

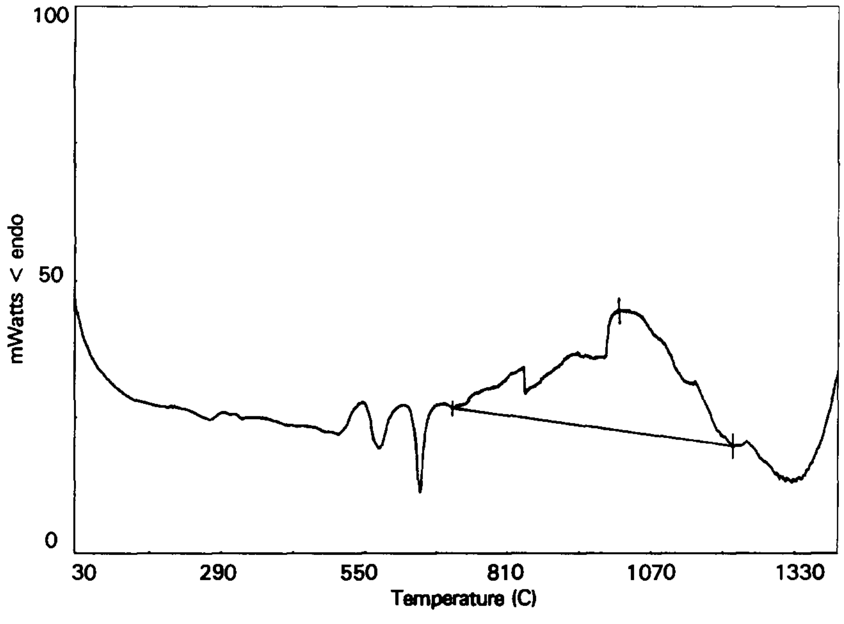

Fig. 5. Thermogram (DSC) of Teflon/Al under argon. Weight: 4.77 mg; scan rate: 20°C min^{-1}; atmosphere: argon, 18 cm^3 min^{-1}. Peak from: 710.9–1218.6°C; onset: 845.1°C; J g^{-1}: −4583.03; peak: 1013.6°C.

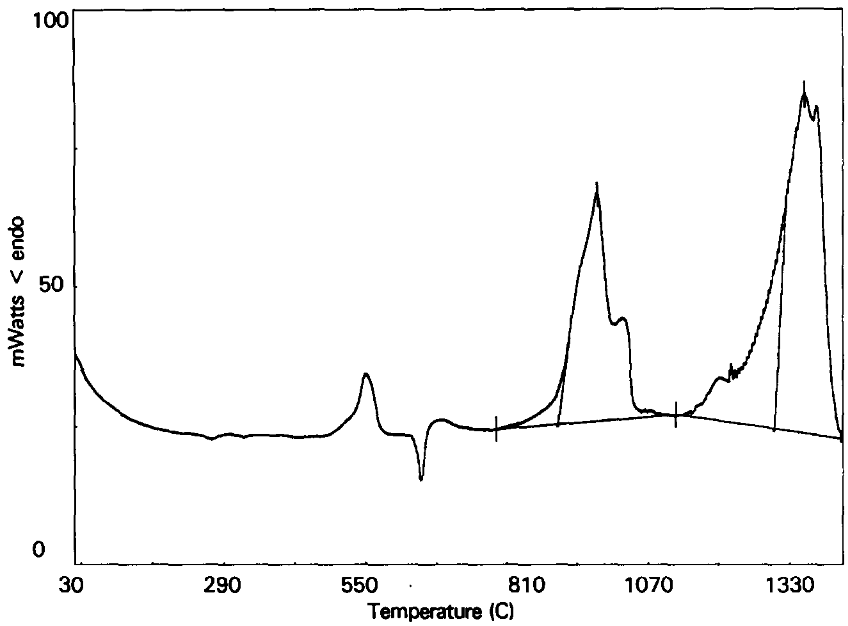

Fig. 6. Thermogram (DSC) of Teflon/Al under air. Weight: 5.38 mg; scan rate 20°C min^{-1}; atmosphere: air, 40 cm^3 min^{-1}; peak from: 791.1–1121.9°C; onset: 904.4°C; J g^{-1}: −5131.77; peak: 978.4°C. Peak from: 1121.9–1427.6°C; onset: 1302.4°C; J g^{-1}: −10391.05; peak: 1359.2°C.

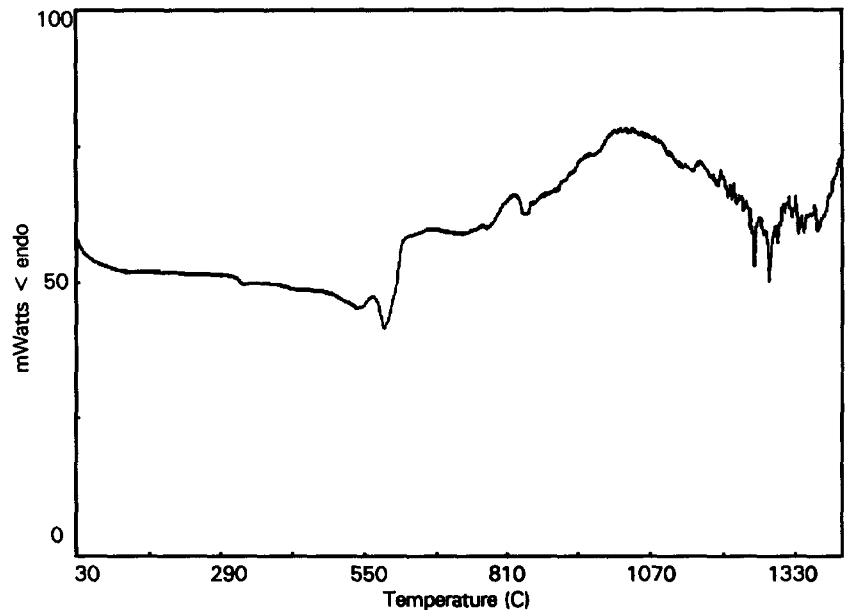

Fig. 7. Thermogram (DSC) of Teflon/Ni under argon. Weight: 5.35 mg; scan rate: 20°C min^{-1}; atmosphere: argon, 18 cm^3 min^{-1}.

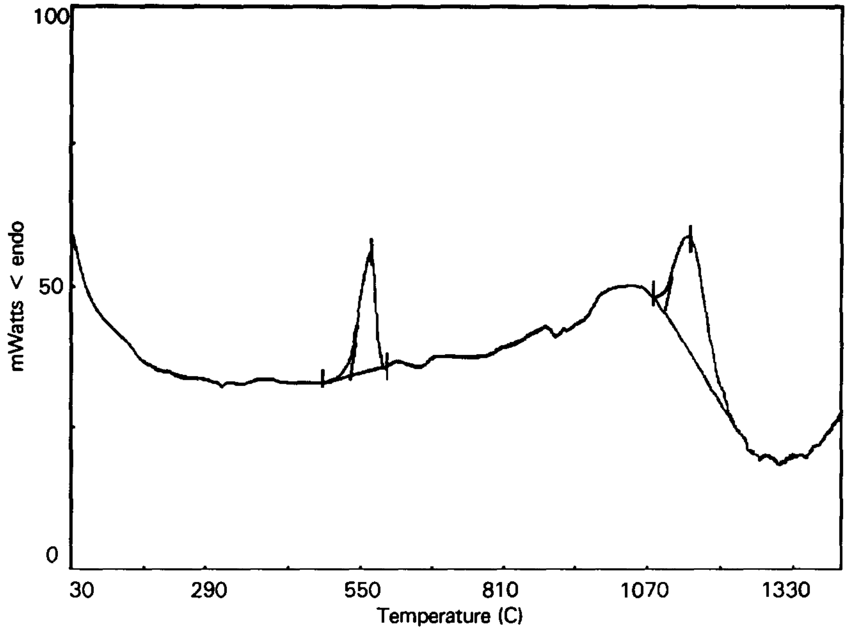

Fig. 8. Thermogram (DSC) of Teflon/Ni under air. Weight: 7.54 mg; scan rate: 20°C min^{-1}; atmosphere: air, 40 cm^3 min^{-1}. Peak from: 482.2-660.6°C; onset: 531.6°C; J g^{-1}: −372.73; peak: 569.8°C. Peak from: 1080.3-1250.6°C; onset: 1096.8°C; J g^{-1}: −753.25; peak: 1146.4°C.

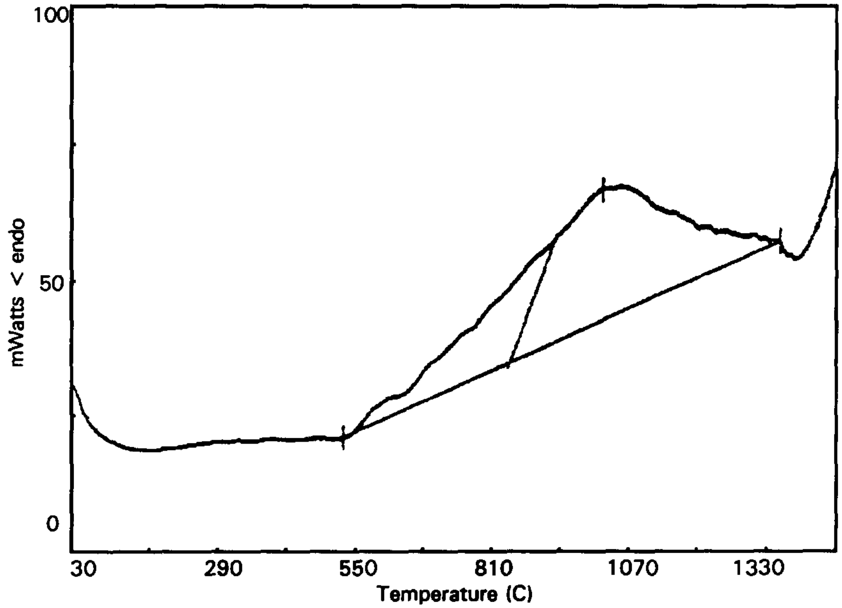

Fig. 9. Thermogram (DSC) of stoichiometric Fe_2O_3/Ni under argon. Weight: 10.81 mg; scan rate: 20°C min^{-1}; atmosphere: argon, 18 cm^3 min^{-1}. Peak from: 527-1341.8°C; onset: 838.1°C; J g^{-1}: −3534.59; peak: 1016.7°C.

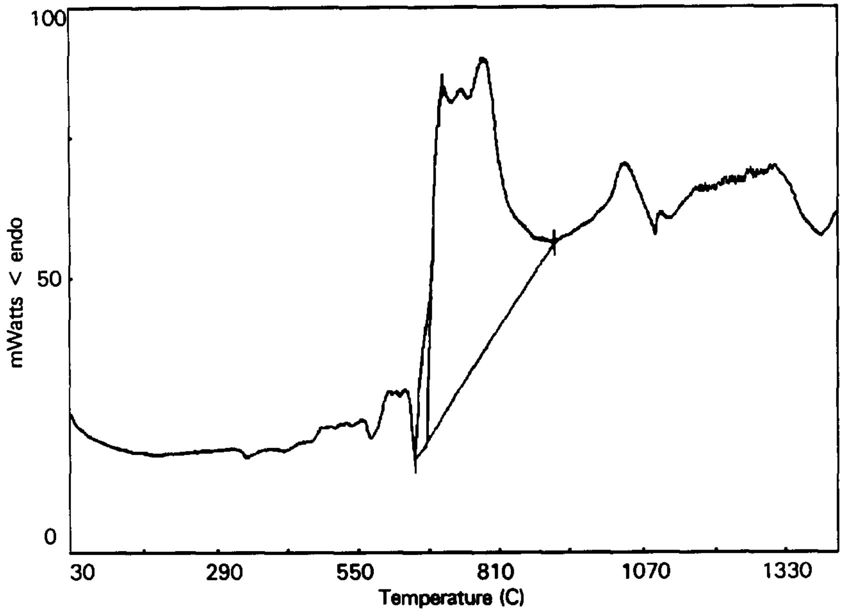

Fig. 10. Thermogram (DSC) of Pyronol under argon; weight: 11.93 mg; scan rate: 20°C min^{-1}; atmosphere: argon, 18 cm^3 min^{-1}. Peak from: 652.1–905.7°C; onset: 672.6°C; J g^{-1}: −2730.45; peak: 697°C.

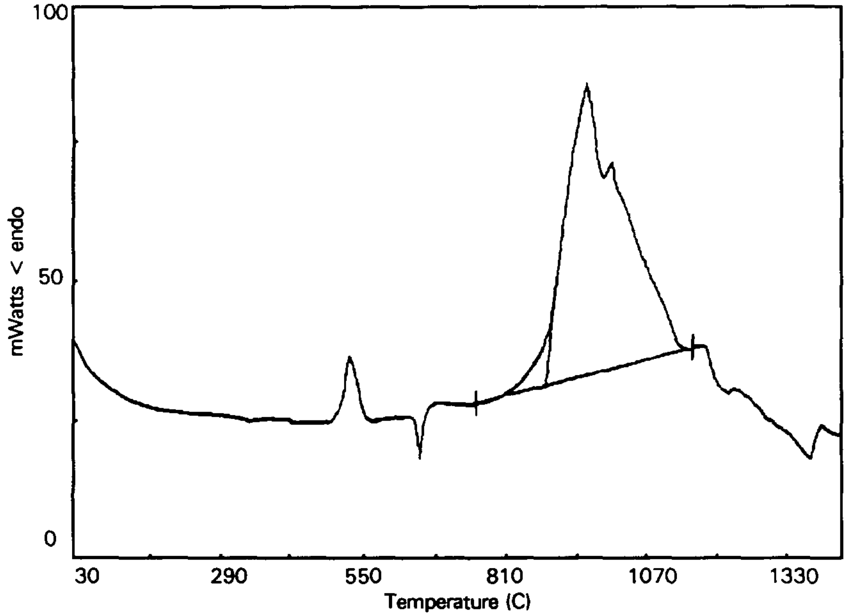

Fig. 11. Thermogram (DSC) of Pyronol under air. Weight: 14.04 mg; scan rate 20°C min^{-1}; atmosphere: air, 40 cm^3 min^{-1}. Peak from: 755.3–1155°C; onset: 881.3°C; J g^{-1}: −3907.5; peak: 961.1°C.

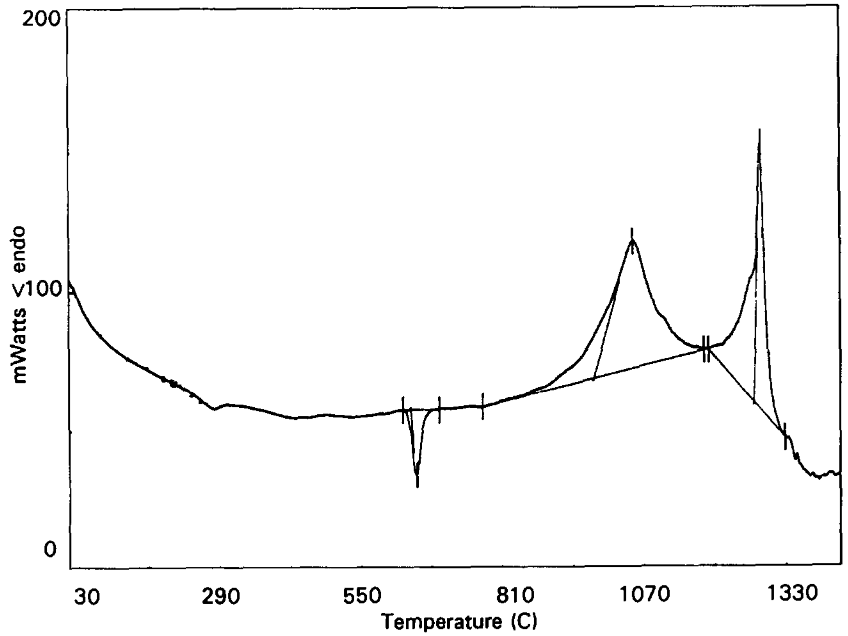

Fig. 12. Thermogram (DSC) of Pyronol without Teflon under argon. Weight: 25.91 mg; scan rate: 20°C $\min^{-1}$; atmosphere: argon, 18 $cm^3 \min^{-1}$. Peak from: 628.3–695.4°C; onset: 642°C; J g^{-1}: 68.8; peak 651.4°C. Peak from: 775.1–1181.8°C; onset: 979.3°C; J g^{-1}: −750.61; peak: 1052.8°C. Peak from: 1190.2–1328.6°C; onset: 1271.5°C; J g^{-1}: −519.62; peak: 1287°C.

Fe_2O_3/Al nor the Fe_2O_3/Ni thermitic reaction takes place in the Pyronol composition. In argon, immediately following Teflon decomposition, a complex exotherm (triplet) appears which is not attributable to the Teflon/Al, Teflon/Ni or the intermetallic reaction. Under air as atmosphere, an exotherm resembling a combination of both the Teflon/Al and Teflon/Ni reactions (conducted in air) occurs. Finally, an inspection of the thermogram for a Pyronol composition synthesized without Teflon (Fig. 12) shows an exothermic peak at 1052°C followed by a second exotherm located at 1287°C. These peaks have locations and contours similar to those found in Figs. 3 and 4, the thermograms representing intermetallic and thermitic reactions.

CONCLUSIONS

In summary, the energetics of the Pyronol composition do not depend on thermitic or intermetallic reaction chemistry. Pyronol energetics are related to combustive and fluorination reactions directly attributable to the decomposition of Teflon. Teflon decomposition is influenced by the nature of the metal present in the composition. Teflon/metal compositions are highly energetic, particularly in the presence of oxygen. Because Teflon/metal reactions dominate, active metal reducing agents are depleted and therefore cannot participate in thermitic and intermetallic reactions.

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