Thermal-cum kinetic behavior of Thermites

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Abstract

Aluminum and metal oxide react with each other in a thermite reaction to produce a large amount of heat. In this paper various thermite compositions were synthesized and the ignition temperatures of these thermites were measured using Differential Thermal Analysis/Thermo Gravimetric Analysis. First is the discussion of the behavior, applications, benefits and characteristics of thermite mixture as a subclass of energetic materials. Secondly, five different thermite compositions Aluminothermite, Copper thermite, Chromium thermite, Zinc thermite and lead thermite were synthesized by mixing fuel and the oxidizer in stoichiometric ratios. Aluminothermite was synthesized by two different ways i.e. by simple physical mixing and by using n-Hexane as solvent. Finally, the ignition temperatures of these thermite systems were investigated by using Differential Thermal Analysis/Thermo Gravimetric Analysis at different scan rates in Nitrogen atmosphere. It was found that ignition temperatures of these systems range between 800 to 1250°C. Thermite reactions are difficult to start as they require very high temperatures for ignition, e.g. for Al–Fe2O3 thermite is ca. 1220 °C. Also, the influence of heating rates on the Differential Thermal Analysis behavior of the mixtures was verified. The results showed that as the heating rate was decreased, ignition temperatures of the mixtures were also decreased. Ignition temperature of Aluminothermite was reduced from 1220 to 1130°C when the heating rate was lowered from 10 - 5 °C /min. It was also observed that the ignition temperature is significantly reduced when the binary Si–Bi2O3 system is added as sensitizer in Copper thermite system. The ignition temperature of the system was 1020 °C which was reduced to 890 °C after using sensitizer.

Keywords: Thermites, Kinetic, TGA, Ignition temperature

Introduction

Thermite is one of the major subclass of pyrotechnic compositions which is composed of metal powder as fuel and metal oxide as oxidizer with the release of huge amount of heat [1-3]. German scientist Hans Goldschmidt in 1895 patented this redox reaction between a metal and a metal oxide and was referred as thermite [4]. Thermite reactions are characterized by oxidation- reduction reaction between a metal and metal oxide. Mostly Aluminum is used as a fuel and hematite (Fe_2O_3) as oxidizer.

Thermite compositions generally consist of finely divided powerfully reducible metal oxides, mostly ferrous oxide and finely divided strong reducing agent acting as fuel like Aluminum. Other Thermite compositions containing metals and the oxides of metals are known.

The metal oxides include FeO, PbO_2, CuO, Cr_2O_3, Fe_2O_3, MoO_2, CoO, NiO_2, Cu_2O, Sb_2O_3, WO2, WO_3 and others. The oxidizable metals include Al, Si, Zr, Be, Mg, Ba, Ti B and others [5]. Thermite reactions can be ignited by a combustion wave from a chemical reaction, an electric current, and radiation energy from a laser beam or by mechanical impact [6]. Generally thermite reactions are quite difficult to start because they need very high temperature for their ignition. K. Ilunga et al. [1] measured the ignition temperature of the Copper-thermite (Al–CuO) system by using DTA at a scan rate of 50 °C min−1 in a nitrogen atmosphere. Thermal initiation of various thermite systems generally involves heating of one of the constituents above its melting point, mostly the metal. The reaction will start by this method and liberate heat and causes the reaction to speed up. Ignition occurs when the reaction becomes self-sustaining and propagates [7-10]. Thermite compositions have number of applications and advantages both in military and commercial fields. In defense sector thermite is used in the synthesis of composites, generating agents for automobile airbags, exploding-on-contact missiles, in propellants and explosives, and combine sometimes with conventional explosives such as TNT, RDX etc resulting in rapid release of heat and energy. Vindhya Narayanan *et. al*. [11] firstly described the use of thermite based materials in the preparation of ceramic lining in metal pipes. The thermite reaction is an environmental-friendly energy source, and it can be utilized as a fuel in oxygen-free environments such as underwater due to the inherent zero oxygen balance of the thermite reaction [12]. In the binary oxidizer - fuel system such as a thermite reaction, the initial reactions are assumed to be diffusion-limited solid-solid reactions. The reaction rate and the combustion velocity can be enhanced by increasing particle contacts and decreasing the particle size [13].

Thermite reactions have been used widely for many applications in both military and commercial sectors. Energetic thermites having Aluminum as a fuel and metal oxide as oxidizer, because of their high energy densities and capability for self-sustained reaction, they are exceptionally energy efficient, and have a wide range of applications in thermal batteries, propulsion, waste discarding, and power production for micro systems [14, 15].

An effort has been made in this dissertation to synthesize new thermite compositions having best fuel-oxidizer balance. Optimum stoichiometry was determined by varying the fuel and oxidizer ratios to attain the fastest combustion wave speed of these various compositions. The overall objective of this study was the synthesis of various thermite compositions with

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their specific stoichiometric calculations and to find out the thermal-cum kinetic behavior of these thermite mixtures. The specific aim of the research presented in this paper was to investigate different synthesis methods for thermite compositions and their effect on thermal behavior of the material and investigation of the effect of heating rate on the decomposition of thermites. It will also help to investigate the effect of using sensitizer on the thermal properties of these thermites.

Experimental

Various thermite compositions are prepared in this work by using aluminum as fuel for all the compositions and varying oxidizers. These compositions were prepared by mixing stoichiometric quantities of fuel and oxidizers shown in the table 1 below. Two synthesis methods were used. First by simple physical mixing of fuel and oxidizer and the other one in which a suitable organic solvent is used to achieve a uniform mixing. In Copper thermite a sensitizer is used to analyze its effect on thermal properties of thermites. The ratio of the sensitizer and thermite is 20 % to 80% respectively.

In order to carry out the thermal and kinetic studies of different Thermite samples, the Diamond Differential Thermal Analysis/ Thermo Gravimetric Analysis (DTA/TGA) module has been used. This instrument has been so designed that it precisely records the thermo gravimetric as well as the differential thermal analytic measurements of a single sample simultaneously and it produces TG curve along with DTA curve at the same time. Mostly inorganic materials like ceramics and metals are analyzed by using this instrument. Furthermore, it is also used for high polymer organic materials. This thermal analyzer operates from room temperature to the temperature as high as 1600°C.

With an aim to achieve above mentioned objectives Simultaneous Thermal Analysis of thermite samples was carried out using the Diamond TGA/DTA by Perkin Elmer. The samples were subjected to TG and DTA analysis and experiments were carried out at different sample masses and heating rates under inert atmosphere. The weight loss patters of both the samples were observed on TG curves as well as the exothermic and endothermic events including phase transformations, melting and decomposition were observed with the help of DTA curves.

Table 1: Tabular form of Thermite System synthesis

S/No	Composition	Oxidizer	Fuel	Ratios Oxidizer/Fuel	Organic Solvent	Sensitizer
1	FeA1	Fe_2O_3	Al	2.296 : 1	-	-
2	FeA2	Fe_2O_3	Al	2.96 : 1	-	-
3	nFeA3	Fe_2O_3	Al	2.96 : 1	n-Hexane	-
4	CrA1	Cr_2O_3	Al	2.81 : 1	-	-
5	CrA2	Cr_2O_3	Al	2.81 : 1	-	-
6	ZnA1	ZnO	Al	81.9 : 18.1	-	-
7	ZnA2	ZnO	Al	81.9 : 18.1	-	-
8	PbA1	Pb_3O_4	Al	3 : 1	-	-
9	PbA2	Pb_3O_4	Al	3 : 1	-	-
10	CA1	CuO	Al	4.42:1	-	-
11	CA2	CuO	Al	4.42:1	-	Si- Bi_2O_3

Results and Discussion

Composition- FeA1

Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TG) were carried out on Composition-FeA1 containing the powder mixture of Fe_2O_3 and Al. A heating rate of 10°C/min was used and the experiment was carried out under Nitrogen atmosphere with a flow rate of 20 ml/min as shown in table 2.

Table 2: Experimental conditions for FeA1

Conditions	DTA
Sample Mass	7.7 mg
Temperature Range	30°C to 1250°C
Heating Rate	10°C/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

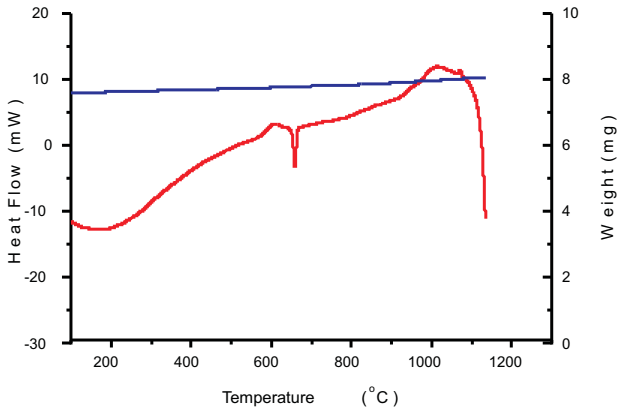


Fig 1: DTA/TGA curve of FeA1

DTA curve of composition-FeA1 exhibits endothermic and exothermic peaks at different temperatures within the programmed temperature range as shown in Figure 1. The first endothermic peak was observed at 660 °C which corresponds to the melting of the aluminium metal. Then first exothermic peak was observed at 1020 °C which may be the formation of intermediates $FeAl_2O_4$ and immediately after that another very low intensity exothermic peak was observed 1070 °C. This peak signifies thermal decomposition of these intermediates. There was no other exotherm observed which can confirm the decomposition of the mixture or the ignition of thermite. This means that because the ingredients of the mixture were not in proper ratio therefore, thermite mixture was not ignited.

Composition- FeA2

10.5 mg of the composition-FeA2 was taken and heated up to 1300°C with the heating rate of 10°C/min as shown in table 3.

Table 3: Experimental conditions for FeA2

Conditions	DTA
Sample Mass	10.5 mg
Temperature Range	25°C to 1300°C
Heating Rate	10°C/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

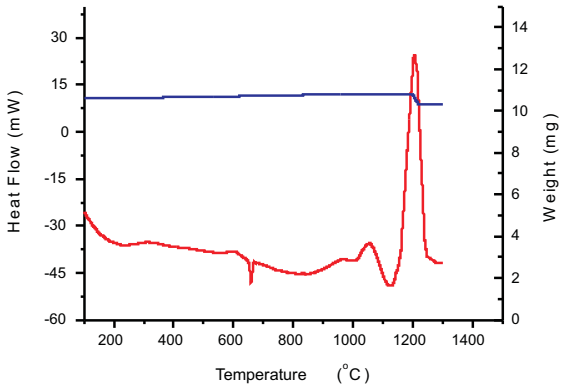


Fig 2: DTA/TGA curve of FeA2

Figure 2 shows first endothermic peak at 660 °C which corresponds to the melting point of aluminum. The first exothermic peak was observed at 990 °C which may be the formation of intermediate hercynite $FeAl_2O_4$. Immediately after an endothermic peak is present representing the decomposition temperature of hercynite and then another exothermic peak was obtained at temperature 1070 °C which is again the formation of other intermediates like Fe_3O_4. Then these intermediates immediately decomposed and a sharp and intense exothermic peak at 1220 °C was obtained which is the ignition point of thermite mixture. A very slight change in the weight of the mixture is observed.

Composition- nFeA3

The experimental conditions applied for Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TG) of the composition-nFeA3 are shown in table 4.

Table 4: Experimental conditions for nFeA3

Conditions	DTA
Sample Mass	13.3 mg
Temperature Range	25°C to 1300°C
Heating Rate	5°C/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

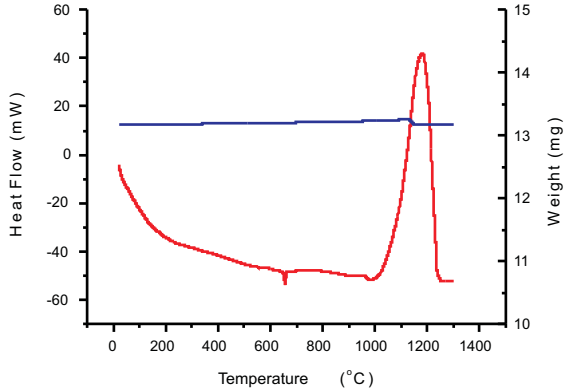


Fig 3: DTA/TGA curve of nFeA3

First endotherm has an onset temperature of 660 °C and corresponds to the melting of the aluminium metal shown in figure 3. Then a very low exothermic peak was obtained at 970 °C which may be the formation of hercynite. This was followed by a fast exotherm. The ignition temperature of the composition under these conditions can be taken as the corresponding onset temperature, i.e. ca.1130°C in this case. These results show that decrease in the heating rate lowers the ignition temperature of thermite mixture. Also uniform mixing was done by the addition of a suitable solvent n-Hexane which also helped in lowering the ignition temperature of thermite.

Composition- CrA1

Sample mass of 4.5 mg of Composition-CrA1 was taken for DTA/TG analysis. Heating rate of 10°C/min was kept constant and the sample was heated up to 1250°C as shown in table 5 below.

Table 5: Experimental conditions for CrA1

Conditions	DTA
Sample Mass	4.5 mg
Temperature Range	25°C to 1250°C
Heating Rate	10°C/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

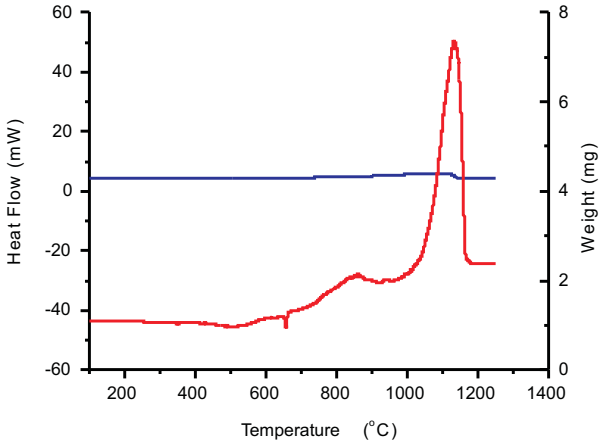


Fig 4: DTA/TGA curve of CrA1

As shown in figure 4, first endothermic peak was observed at 660 °C which corresponds to the melting point of aluminum. After that at temperature 840 °C there is an exothermic peak which shows that there may be formation of intermediates. Then this intermediate decomposed and at 1030 °C an exothermic peak starts which indicates the decomposition of thermite mixture into its products. At temperature 1120 °C the mixture completely decompose and this is the ignition point of chromium thermite. Like compositions FeA1, FeA2 and nFeA3 this thermite also shows a slight weight loss during the decomposition of the mixture

Composition- ZnA1

Table 6 represents experimental conditions applied for DTA/TGA for the composition ZnA1.15 mg sample was heated upto 1300 °C with heating rate of 10°C/min.

Table 6: Experimental conditions for ZnA1

Conditions	DTA
Sample Mass	15.0 mg
Temperature Range	25°C to 1300°C
Heating Rate	10°C/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

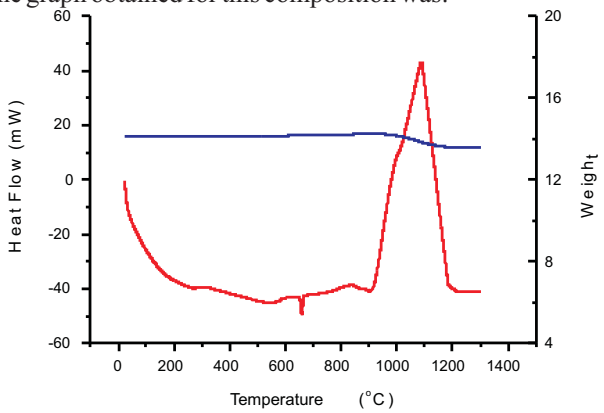


Fig 5: DTA/TGA curve of ZnA1

First endothermic peak is observed at 660 °C shown in Figure 5 which indicates the melting of aluminum. Then at temperature 905 °C there is an exothermic peak which shows that the heat is evolved due to the decomposition of the mixture. The decomposition completes at temperature 1070 °C which means that thermite mixture is ignited completely. TG curve shows the weight loss of the mixture during this whole process.

Composition- PbA1

Experimental conditions applied for Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) are shown in table 7. Sample was heated with constant heating rate of 10°C/min up to 1000°C.

Table 7: Experimental conditions for PbA1

Conditions	DTA
Sample Mass	7.8 mg
Temperature Range	25oC to 1000oC
Heating Rate	10oC/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

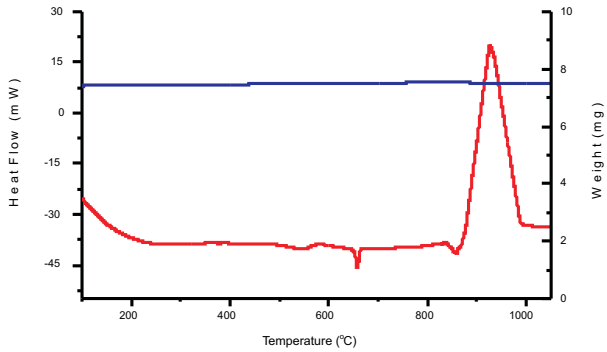


Fig 6: DTA/TGA curve of PbA1

DTA curve of composition-PbA1 in Figure 6 represents first endothermic peak at 660 °C which corresponds to the melting point of the aluminium metal. There is an endothermic peak observed at 860 °C which may be the decomposition of ingredients. Then immediately after that at 920 °C a sharp exothermic peak is observed with minor weight loss which is the ignition temperature of Lead thermite. As lead thermite is generally graded as weak thermite composition so no intense peak was observed. There is a very slight change in the weight loss shown in TG curve.

Composition- Ca1

Sample mass 0f 11 mg was heated up to 1250°C with 10 °C /min constant heating rate as shown in table 8.

Table 8: Experimental conditions for CA1

Conditions	DTA
Sample Mass	11.0 mg
Temperature Range	25°C to 1250 °C
Heating Rate	10°C/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

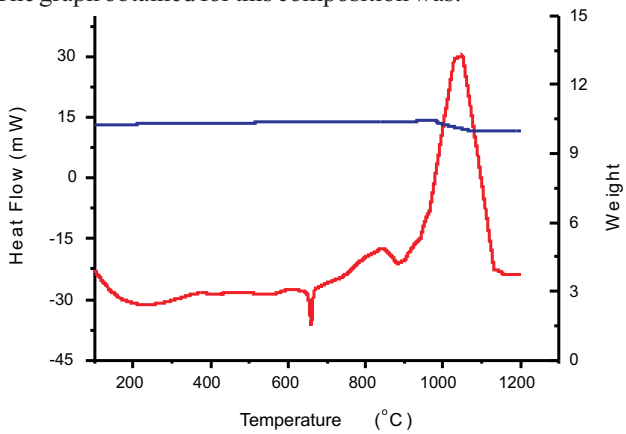


Fig 7: DTA/TGA curve of CA1

Figure 7 shows the DTA response for a stoichiometric copper thermite mixture comprising aluminum as fuel and copper oxide as oxidizer. The first endotherm has an onset temperature of 660 °C and corresponds to the melting of the aluminium metal. There is another endothermic peak observed at temperature 880 °C probably corresponds to the melting and dissolution of the CuO in the aluminium melt. This peak is followed by a sharp exothermic peak at 1020 °C which is the ignition temperature of the composition under these conditions.TG curve shows weight loss which confirms the ignition of thermite system.

Composition- Ca2

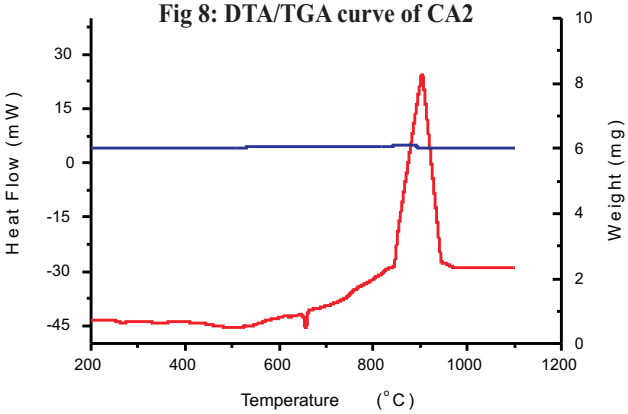
Differential Thermal Analysis (DTA) was carried out on Composition-CA2 containing the mixed powder of CuO and Al. Sensitizer containing Si and Bi_2O_3 was also used to lower the ignition temperature of this thermite system. Table 9 shows experimental conditions of Ca2.

Table 9: Experimental conditions for CA2

Conditions	DTA
Sample Mass	6.0 mg
Temperature Range	25°C to 1250°C
Heating Rate	10°C/min
Atmosphere	Nitrogen
Flow Rate	20 ml/min
Pan Material	Alumina Crucibles

The graph obtained for this composition was:

Fig 8: DTA/TGA curve of CA2



First endothermic peak in this case is observed at 660 °C which corresponds to the melting of aluminum metal as shown in Figure 8. This peak is followed by a sharp exothermic peak at 890 °C which is the ignition temperature of the composition under these conditions. The use of Si + Bi_2O_3 (mass ratio 1:4) as sensitizer for the Al+ CuO plus thermite reaction, lowers the ignition temperature of the system from 1020 to 890 °C.

Conclusion

There are many such thermite systems which are not completely characterized and not much work has been carried out for practical application feasibility. Many experiments have shown that these thermites can be superior replacements for current energetic materials in certain applications. In this work various thermite compositions were prepared by simple physical mixing and with simple physical solvent mixing. The thermal events taking place within the samples when exposed to non-isothermal DTA analysis were observed carefully. The experiments show that various thermite compositions have ignition temperature ranging between 800 °C to 1220 °C. It was observed that heating rate is an important factor in the thermal decomposition of thermite systems. With increase in the heating rate of the sample, the melting points and ignition temperatures of mixtures was also enhanced. The ignition temperature of Aluminothermite was reduced from 1220 °C to 1130 °C when the heating rate of the composition was lowered from 10°C/min to 5°C/min. Use of sensitizer also affects the ignition temperature of thermite mixture. (Si + Bi_2O_3) was used as sensitizer in copper thermite. The ignition temperature of copper thermite was found 1020 °C and when a (Si + Bi_2O_3) sensitizer was used then the ignition temperature was lowered. The ignition temperature of this composition was lowered from 1020 °C to 890 °C by the use of sensitizer.

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