

Ignition Behavior of Al/Fe₂O₃ Metastable Intermolecular Composites

S K Sahoo^{1*}, S M. Danali², P. R. Arya³

High Energy Materials Research Laboratory, Pune-411021, INDIA

Abstract— Nano size Al/Fe₂O₃ thermite system has been reported in the literature as metastable intermolecular composites (MIC). Nano Al/nano Fe₂O₃ MIC has been prepared in various proportions by ultrasonic method. A comparative study on heat output and thermal behavior has been made on MIC using DTA (Differential Thermal Analysis), STA (Simultaneous Thermal Analyzer) and bomb calorimeter. It has been observed that nano-size ingredients produce more heat output compared to micron size ingredients. The ignition temperature also reduces in case of MIC indicating faster release of energy at lower temperature. The impact of ignition of nano-thermite has been reported based on ignition DTA experiment. DTA analysis also shows complete reaction in case of MIC where as micron size thermite showed an endothermic peak of Al melting indicating incomplete reaction. The PXRD (Powder X-Ray Diffraction) data of combustion products has been used to establish the combustion mechanism of MIC. The activation energy of MIC has been calculated using Kissinger, Ozawa and Starink kinetic equations and compared with literature reported values.

Keywords— MIC, combustion kinetics, heat output, STA, DTA.

Abbreviations used

ΔH = heat of combustion (cal/g)

E_a = activation energy (kJ/mol)

T_m = maximum peak temperature of DTA (K)

α = heating rate (K/min)

M = slope of the linear line

C_1 = intercept of the linear line and constant of Kissinger equation

C_2 = intercept of the linear line and constant of Ozawa equation

Z_1 and Z_2 = pre-exponential factor (frequency factor)

R = universal gas constant (8.314 J/K mol)

I. INTRODUCTION

The thermite systems give very high-temperature output and are preferred as heat source for several applications. The Al/Fe₂O₃ thermite system is a classical thermite system and can be used for welding of railway tracks (since 1898), cutting and perforation of materials, to produce alumina liners *insitu* for pipes, a portable heat source, a high-temperature igniter, a pyrotechnic heat producer as an additive to explosives [1] propellants [2], gas generating compositions [3], nanoenergetic microelectromechanical systems (MEMS) platform for micro-propulsion system [4] and incendiary grenade [5]. This system has also been investigated in environmental protection processes [6], namely for the treatment and recycling of zinc hydrometallurgical wastes [7, 8] and for the treatment of by-products of steel industry [9]. Other recent applications of this reactive system are the synthesis of ceramic reinforced metal-matrix composites [10, 11], of magnetic granular films [12], of iron aluminides [13-15], of transition metal carbide/ nitrides [16], alloying/welding [17] and energetic nanocomposites [18-20]. Al/Fe₂O₃ has been used for catalytic application of combustion of AP/HTPB system [21]. Recently fabrication of hybrid nano-composite from Al/Fe₂O₃ system has been reported in the literature [22].

Recent developments in the preparation and production of nanomaterials have created a new kind of energetic materials commonly known as nanoscale composite energetic materials, metastable intermolecular composites (MIC) or simply

nanoenergetics. MIC's are also known as superthermites. In these materials, nanosized particles of ingredients are used to produce dramatic changes in combustion behavior. Nanosized metals and metal oxides in the MICs have replaced the micron sized constituents which are used in conventional thermites. The reduction of particle size with increased surface area effectively enhances homogeneity of the mixture [23]. This change in particle size produces significant changes in the kinetics and reaction propagation characteristics of the thermite. Generally, nano-particles on approaching towards molecular size and intermixing at this level increase the characteristics of the thermite over micron size thermite mixtures [24, 25]. It is considered that ignition is generally a melting of one of the two components followed by a diffusion-controlled reaction. The melting point of aluminum is 660 °C whereas Fe₂O₃ begins to melt at 1565 °C. Nano-scale particles have been considered highly reactive and melting point independent wherein the solid-solid physical contact may be sufficient for ignition [26].

A number of studies have been carried out on Al/Fe₂O₃ thermite for its reaction mechanism and kinetics. Sarangi et al [27] investigated this system using different Al percent and studied its reaction kinetics. Duraes et al [28] studied the reaction intermediate and final product characterization of Al/Fe₂O₃ system taking various molar ratio of both the constituents. Mei et al [29] made an interesting investigation for the kinetics and combustion mechanism of the reaction as given in Eq. 1 below. Fan et al also studied the kinetics and combustion mechanism of the thermite reaction [30]. Bullian et al [31] investigated the reaction kinetics of 38.6% Al and 61.4% Fe₂O₃ thermite system. Weiser et al [32] investigated ignition of different stoichiometric proportion of Al/Fe₂O₃ system for their product under pressure. Cheng et al [33] studied the kinetics of thermally initiated reaction of Al/Fe₂O₃ nanothermite. Wang et al reported Al/Fe₂O₃ thermite reaction mechanism based on residue collected from DSC experiments at different temperature [34]. In this paper we have reported the reaction mechanism based on combustion product analysis obtained from bomb calorimeter experiments for different thermites.

Heat of reaction of the thermite system described by Eq. 1 is sufficient to raise its temperature to very high values (~3000 K), above the melting points or even the boiling points of reactants, intermediate and final products for the following reaction:



However, the ignition behavior of MIC's based on nano Al and nano Fe₂O₃ has not been reported yet in the literature. An attempt has been made to study the ignition behavior of MIC using DTA, STA and bomb calorimeter. The PXRD has been used to study thermite reaction mechanism by the combustion product analysis.

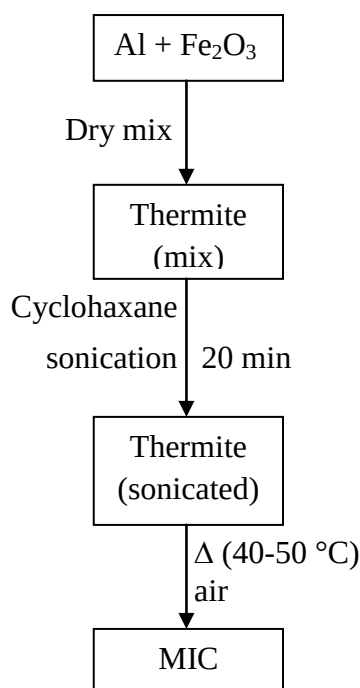
II. EXPERIMENTAL

Nano sized α -Fe₂O₃ (70nm) was prepared through emulsion route as described in literature [35]. Nano Al (100nm) was obtained from SIBTERMOCHIM Ltd, Russia. Other chemicals used for this work were: micron size (1.6 μ) α -Fe₂O₃ (Cyanide & Pigment Ltd, Kolkota, India), and cyclohexane (Thomas Baker, India). The scheme for preparation of thermite is described in Fig.1. Nano Al and Fe₂O₃ powder were mixed thoroughly with various weight ratio as given in Table-1. A composition was prepared by adding 5g dry mix of nano Fe₂O₃ and Al into 100ml cyclohexane. The contents were ultrasonicated for 20 min. to break the agglomerates. The contents were then poured into a watch glass and slightly heated to allow evaporation of cyclohexane.

TABLE-1
COMPOSITION DETAIL.

Composition Code	Al (100nm) %	Fe ₂ O ₃ (70nm) %	Fe ₂ O ₃ (1.6 μ) %
T1	25	-	75
T2	15	85	-
T3	25	75	-
T4	35	65	-

* Batch size = 5 g

**FIG. 1. SCHEME FOR MIC PREPARATION**

Heat output (calorimetric value) of the MICs was measured using LECO AC-350 Bomb Calorimeter (USA make) in argon medium at a pressure of 5 atm. Ignition temperature was measured using a DTA instrument (Stanton Redcroft, UK make) at a heating rate of 40 °C/min at ambient condition. For kinetic study, thermal analysis experiments were carried out at different heating rates of 20, 30 and 40 °C/min. Simultaneous thermal analysis (STA) experiments were carried out by purging nitrogen at a flow rate of 100 mL/h using TA instruments (model SDTQ600 of USA make). Powder X-ray diffraction (X'Pert pro, Panalytical, The Netherlands) studies of the combustion products (residue obtained from bomb calorimeter experiments) were carried out using Cu K α radiation of wave length 1.5405 Å.

III. RESULTS AND DISCUSSION

3.1 Heat output

The heat output values of MIC obtained from bomb calorimeter experiment have been given in Table-2. The value for MIC of 25:75 ratio of Al/Fe₂O₃ (T3) was 665 cal/g. The thermite composition with same percentage of Al & Fe₂O₃ (T1) produced 515 cal/g heat output. This indicated that MICs provided efficient combustion compared to thermite. The heat output value with 35% aluminium increased to 689 cal/g and with 15% Al heat output decreased to 210 cal/g. The decreasing trend in heat output result with decreasing fuel percentage has also been reported in literature [36]. The variation in heat output result in all the MIC was due to incomplete reaction which could be due to non availability of adequate oxidizer or fuel in the composition. According to Eq. 1, for the stoichiometric reaction, 25:75 weight ratio is required for Al/Fe₂O₃ thermite system. According to the result reported by Sarangi et al, [27] a complete reaction takes place for Al/Fe₂O₃ thermite system for the ratio of 8:1. Bullian et al [31] studied Al/Fe₂O₃ thermite system with ratio of 38.6: 61.4.

TABLE-2
CALORIMETRIC VALUES OF THERMITE COMPOSITIONS.

Composition	T1	T2	T3	T4
Cal val (cal/g)	515	210	665	689

3.2 Ignition of thermite and MIC using DTA

The ignition behavior of T1 and T3 mixture was measured with the help of DTA at a heating rate of 40 °C/min (Fig. 2). In case of thermite mixture T1 (micron size Fe₂O₃), a very smooth and broad exothermic peak at 615 °C was observed. Whereas a strong and sharp ignition peak at 605 °C could be seen for the MIC T3 (with nano Fe₂O₃). However, T4 mixture showed similar ignition behavior. The DTA data indicated that T3 and T4 mixture provided faster heat release as compared to thermite mixture T1.

Sarang et al [27] reported that the reduction reaction in air always took place at 890 °C and could not be ignited in inert atmosphere. Mei et al [27] has mentioned that the combustion reaction takes place in two stages, Fe_2O_3 first completely decomposes to Fe_3O_4 and O_2 at 960 °C, and then Al reacts with Fe_3O_4 to produce Al_2O_3 at 1060 °C. Wang et al [37] reported that first exothermic peak appears at 853 °C at a heating rate of 10 °C. They also observed an endothermic peak near 660 °C for the melting point of Al. Cheng et al [33] reported the ignition temperature of different Al/ Fe_2O_3 nano thermite system in the range of 686-1036 °C.

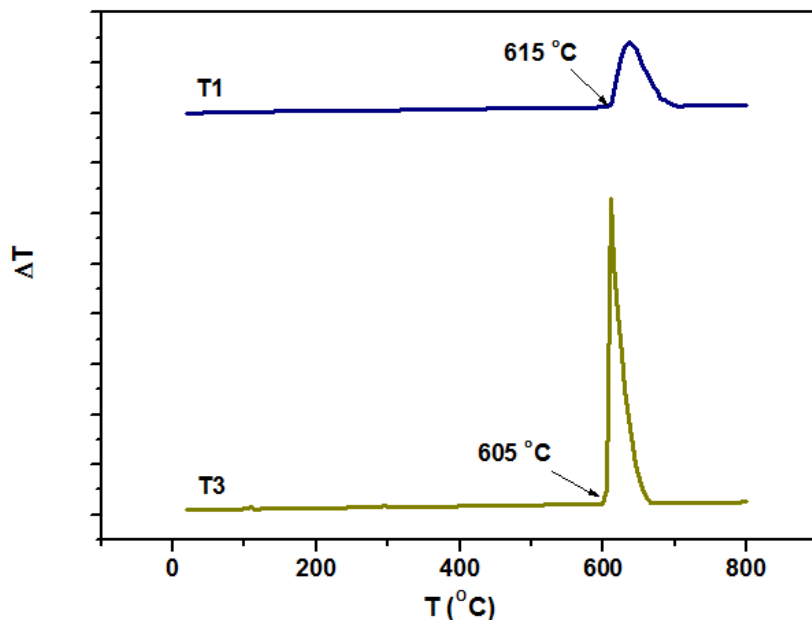


FIG. 2. DTA GRAPH AT 40 °C/MIN FOR MIC.

However, it has been observed the ignition behavior of MIC T3 with a strong and sharp exotherm at 605 °C (Fig. 2), which is lower than the earlier reported values. The alumina crucibles after the DTA experiments are shown in this Fig. 3. The crucible remained intact after experiment in case of sample T1 (Fig. 3a and 3b). However, it has been observed that crucibles were broken after experiments (Fig. 3c and 3d). The vigorous exothermic reaction for nano sized MIC seems to be of high impact with much faster release of heat energy. Due to this very high impact upon ignition the crucible got broken.

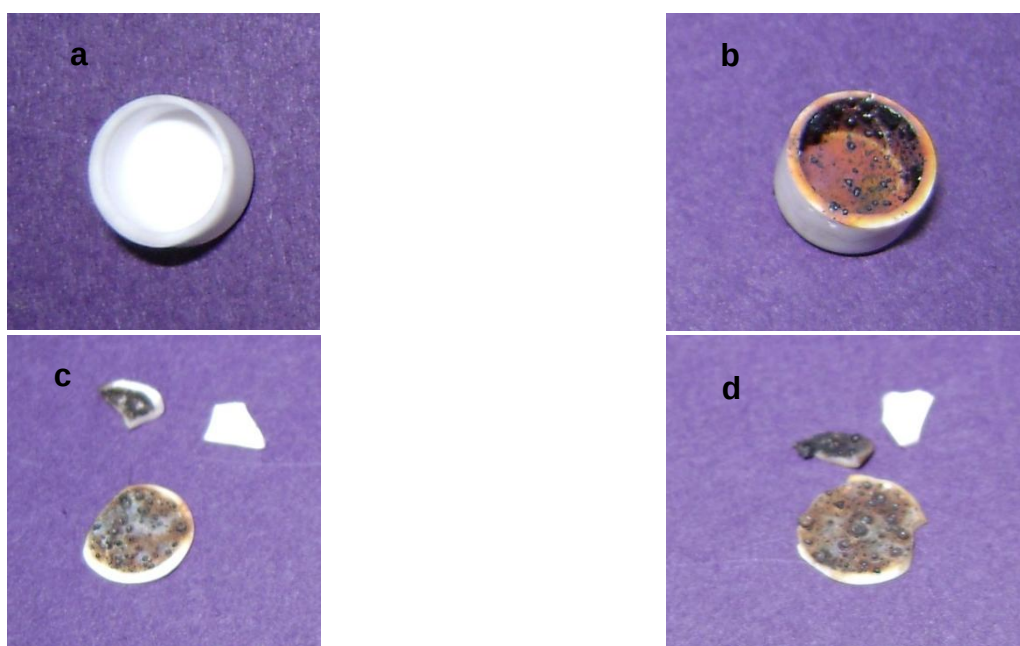


FIG. 3. CRUCIBLES USED BEFORE (A) AND AFTER DTA EXPERIMENTS. (B) FOR THERMITE T1 AND (C) AND (D) FOR MIC T3.

In the present study, no any endothermic peak was observed in MIC and thermite composition. However, a sharp exothermic peak was obtained at nearly 605 °C before ignition. It may be due to the melting of nano Al. Soon after melting, reaction of nano Al with nano Fe₂O₃ continues followed by fast combustion reaction. Due to nano-sized particles, the distance between fuel and oxidizer particles is reduced. The sharper ignition peak of MIC than for micron size thermite (T1) may be understood based on the explanation given by Plantier [26]. Thermite reactions are diffusion controlled and hence decrease in the diffusion distance causes reduction in ignition time and increased reaction rate of the mixture. Because of the contact distance of both the constituents (fuel and oxidizer) is reduced almost to the molecular dimension, these reactions are capable of producing higher rates of energy release and resulting in enhanced reactivity [38-40]

3.3 Thermogravimetric and Differential Thermal Analysis

STA measurements were carried out at a heating rate of 20 °C/min (Fig. 4 and Fig. 5). The details of STA results have been given in Table-3. DSC curve showed the exothermic peak between 616-621 °C for all the three samples (T1, T3 and T4). The peak intensity/area under the curve was found maximum in case of T4 as compared to T1 and T3. The peak area under the curve is proportional to enthalpy change (ΔH) of the material. Hence from the graph and Table-3, the values of ΔH was higher in case of T4 (906 J/g) and T3 (821 J/g) as compared to T1 (597 J/g). Along with exothermic peak, there was an endothermic peak at 654 °C in the DSC curve of T1, which was due to the melting of unreacted Al remained after ignition. This peak was not observed in case of T3 and T4. XRD data confirmed that No unreacted residual Al was left in case of T3 and T4.

The TGA experiment was carried out at a heating rate of 20 °C/min. Continuous weight gain was observed at a true onset temperature of 550 °C (Fig. 5a). Similar behavior has been reported for nano Alex by Jones et al. [41]. They have explained that the weight gain is due to nitridation on the surface of nano Al or of the un-reacted Al core [42] which is described as follows (Eq. 2)

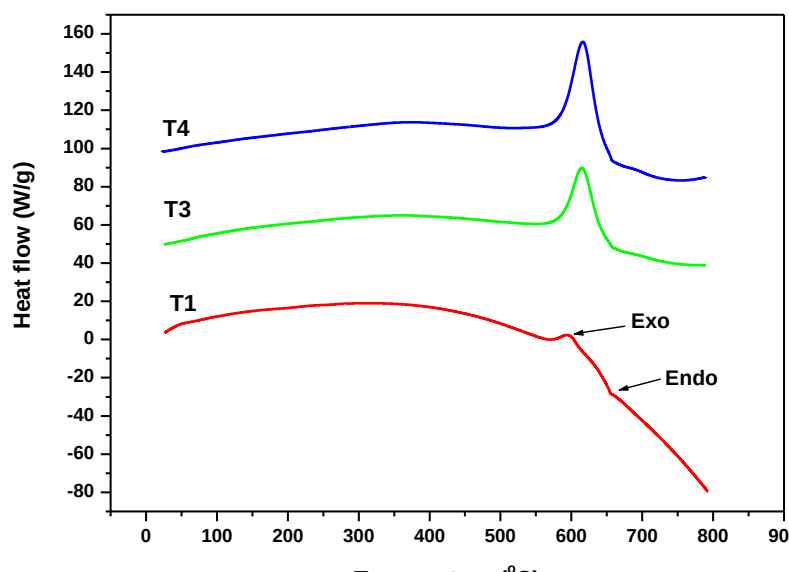


FIG. 4. DSC CURVES FOR MIC T1, T3 AND T4 AT A HEATING RATE OF 20 °C/min. INSERT IS THE ENLARGEMENT OF ENDOTHERMIC PEAK FOR T1

TABLE-3
DATA OBTAINED FROM STA ANALYSIS.

Sample	DSC peak position (°C)	ΔH (J/g)	Wt. gain (%)
T1	621 ↑ 654 ↓	597	4.01
T3	616 ↑	821	4.71
T4	620 ↑	906	8.53

↑- exo, ↓-endo

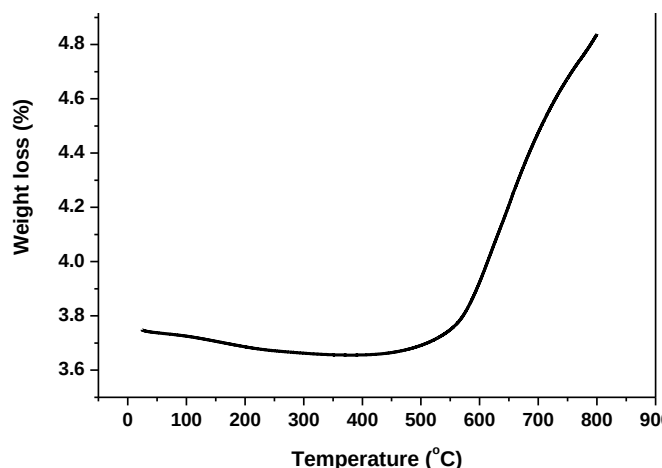


FIG. 5. (A) TG PLOTS FOR NANO AL AT A HEATING RATE OF 20 °C/MIN.

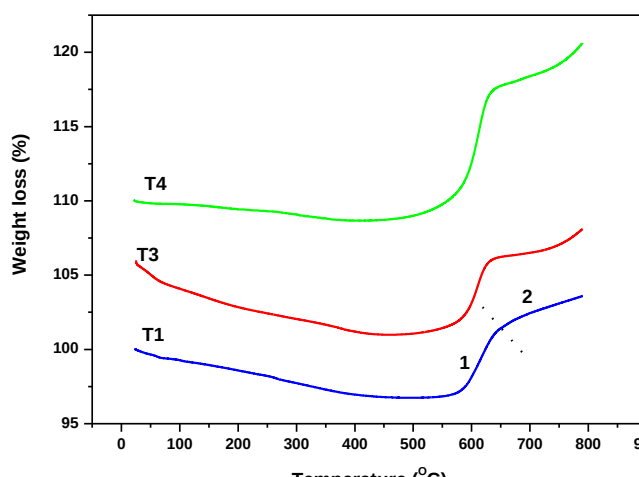


FIG. 5. (B) TG PLOTS FOR T1, T3 AND T4 AT A HEATING RATE OF 20 °C/MIN

Nitridation leads to exotherm in DTA graph. But due to lower peak temperature and higher heating rate it did not appear on corresponding DTA graph. The DTA peak at around 660 °C was due to melting of un-reacted core Al. In TG graph of MIC T1, T3 and T4 (Fig. 5b) weight gain was observed in two steps for sample T1. Step 1 (weight gain =4.01%) was due to nitridation along with thermite reaction and step 2 was due to melting of un-reacted Al. In case of T3 and T4 sharp weight gain was observed. This is due to the much faster ignition reaction of nano size MIC than micron size. This result is in agreement with DSC and ignition DTA peaks. More weight gain, observed in case of T4 (8.53%) as compared to T3 (4.71%), was due to the presence of more amount of Al undergone nitridation.

3.4 Combustion Kinetics

Based on DTA plot at a heating rate of 20, 30 and 40 °C/min, kinetics of the combustion parameters were studied. Three different methods have been applied for the calculation of activation energy (E_a) for comparison. Those are (a) Kissinger method, (b) Ozawa method and (c) Starink method.

3.4.1 Kissinger Method

According to Kissinger “during the rise in temperature the reaction passes by a maximum before decreasing”[43]. It is based on the equation below

$$\ln\left(\frac{\alpha}{T_m^2}\right) = -\frac{E_a}{RT} + C_1 \quad (3)$$

$$C_1 = \ln\left(\frac{E_a}{RZ_1}\right) \quad (4)$$

The plot of $1000/T_m$ and $\ln(\alpha/T_m^2)$ gives a straight line (Fig. 6) and from the slope M activation energy can be calculated as

$$E_a = -RM \quad (5)$$

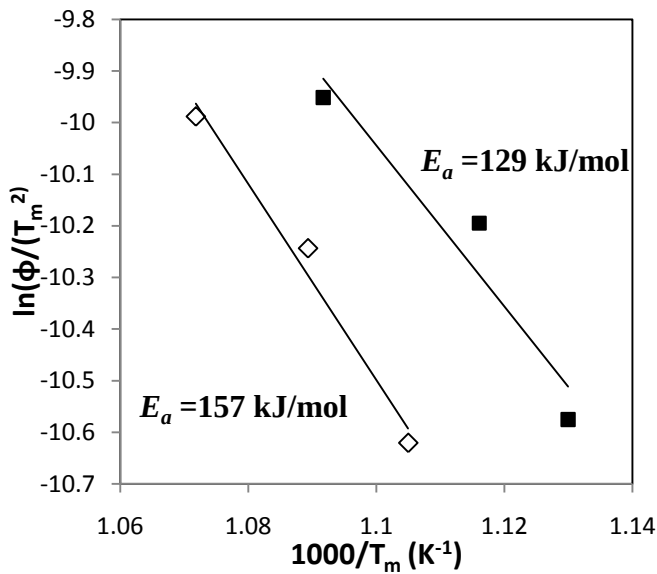


FIG. 6. PLOT OF $1000/T_m$ and $\ln(\alpha/T_m^2)$ USING KISSINGER'S METHOD

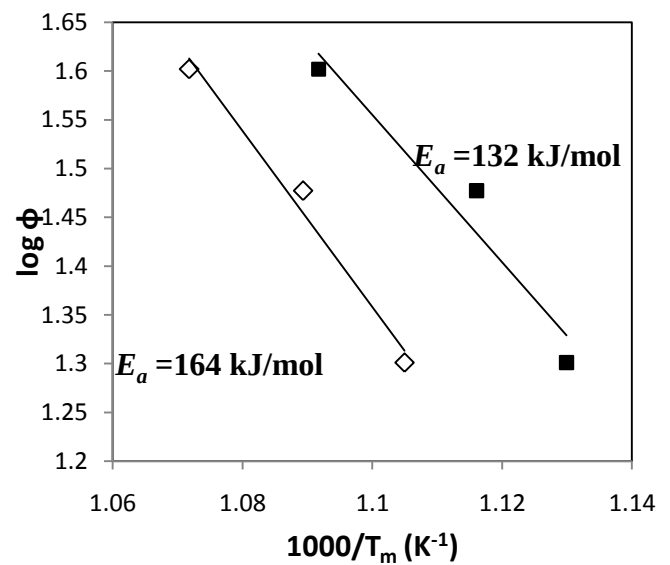


FIG. 7. PLOT OF $1000/T_m$ and $\log \alpha$ USING OZAWA'S METHOD

3.4.2 Ozawa Method

Ozawa proposed the following kinetic equation for the determination of activation energy [44]

$$\ln \alpha = -\frac{E_a}{RT} + C_2 \quad (6)$$

The plot of $1000/T_m$ and $\log \alpha$ gives a straight line (Fig. 7) and from the slope M activation energy can be calculated as

$$E_a = -2.19R.M \quad (7)$$

3.4.3 Starink Method

A new method for the derivation of activation energies is proposed by Starink [45]. According to him

$$\ln \left(\frac{T_m^{1.8}}{\alpha} \right) = Z_2 \frac{E_a}{RT_m} + C_3 \quad (8)$$

$$Z_2 = 1.0070 - 1.2 \times 10^{-5} E_a \quad (9)$$

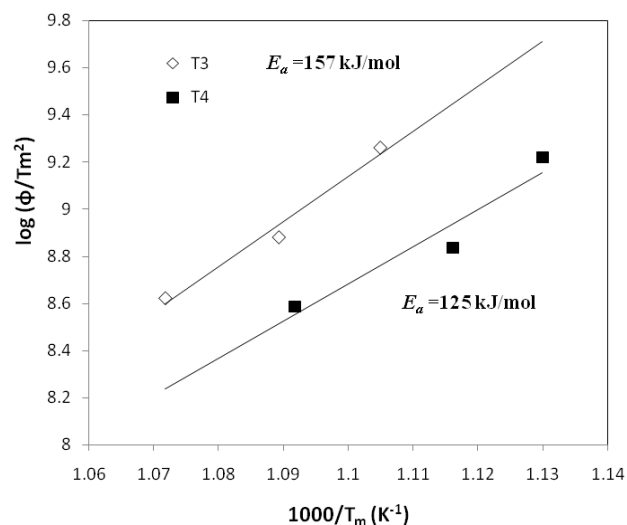


FIG. 8. PLOT OF $1000/T_m$ and $\ln(T_m^{1.8}/\alpha)$ USING STARINK METHOD

The plot of $1000/T_m$ and $\ln(T_m^{1.8}/\alpha)$ produces a straight line (Fig. 8). From the slope M and A , activation energy can be calculated as

$$E_a = \frac{RM}{A} \quad (10)$$

TABLE-4
ACTIVATION ENERGY (E_a) of MIC in kJ/mol.

MIC	Kissinger method	Ozawa method	Starink method
T3	157	164	157
T4	129	132	125
Ref 28	-	-	145
Ref 29	-	248	-

Activation energies estimated by Kissinger, Ozawa and Starink methods are tabulated in Table-4. E_a is found to be 157, 164 and 158 kJ/mol for MIC T3 and that of 129, 132 and 126 kJ/mol for MIC T4 respectively. Fan et al [28] reported that the value of E_a by Starink method was 145 kJ/mol for the thermite reaction. Bulian et al [31]. found the nearest value of 247.76 kJ/mol for the similar nano thermite reaction applying Ozawa method.

3.5 Combustion Mechanism

The thermite compositions and the products obtained after heat of combustion experiments of the compositions were analyzed by powder XRD. The XRD patterns of compositions and the combustion products have been shown in Fig. 9 and 10. The phases present in the products after combustion have been presented in Table-5. The corresponding Miller planes have been shown against their peaks of both Al and α -Fe₂O₃.

In case of thermite (T1), as shown in Fig. 10, the products obtained were cubic-Al₂O₃, cubic-Fe and cubic-Fe₃Al. The later one Fe₃Al, an intermetallic phase, was detected with higher intensity in the products of sample. The intermetallic phase peak coincided with Fe phase. As from DSC graph (Fig-4), the presence of Fe₃Al phase was confirmed by the observation of endothermic peak for Al melting. In case of MIC's T2 and T3, hercynite (cubic-Al₂FeO₄ which is Fe+2Al₂O₄) was widely identified as an intermediate product of the thermite reaction [24]. In case of T2, other than hercynite, cubic-FeO phase was found. Along with hercynite, rhombohedral- α -Al₂O₃ and cubic-Fe phases were found in MIC T3. Formation of Fe phase in this case may be due to reduction of FeO to Fe. Fig-10 revealed the presence of rhombohedral α -Al₂O₃ phase along with low intensity peak of cubic-Fe for the combustion of T4. No other products were found in this case.

TABLE-5
FINAL COMBUSTION PRODUCT OF MICs (BASED ON XRD ANALYSIS).

Composition	Products
T1	Al ₂ O ₃ , Fe, Fe ₃ Al
T2	Al ₂ FeO ₄ (i.e. Fe+2Al ₂ O ₄), FeO
T3	Al ₂ O ₃ , Fe, Al ₂ FeO ₄
T4	Al ₂ O ₃ , Fe

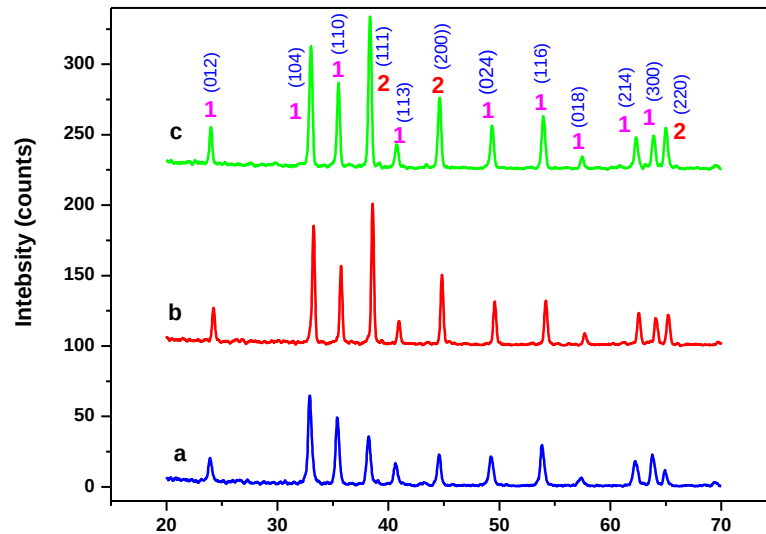


FIG. 9. XRD PATTERNS MICs (a) T1, (b) T3 and (c) T4. THE PHASES INDICATED IN THE PATTERNS ARE 1- Fe_2O_3 (Rhombohedral), 2-Al (Cubic) WITH THEIR CORRESPONDING PLANES.

The probable mechanism for the micron size thermite reaction (for T1) can be discussed on the basis of the above results and literature review. Fe–Al intermetallic phases produce when Fe phase obtained product is in contact with melted aluminum [11, 13-14]. Due to the presence of nano Al, the reaction proceeds in case of T1 as nitridation followed by melting of Al and then reaction with Fe_2O_3 to form Al_2O_3 and FeAl_3 . Micron size iron oxide could not get reduced completely, But in case of MIC's, a violent reaction (also recognized by DTA) occurs among the nano reactants as the ignition point reached and energy release is much faster than thermite. In case of T2, excess of oxidizer turned out to be FeO . Sample T3 showed intermediate product hercynite. Similar products have been reported in the literature also [34]. The difference in reaction mechanism for thermite and MICs can be explained as reduction of thermite fuel and oxidizer particle size from the micron regime to nano-scale dimensions has been shown to produce more favorable combustion behavior. Such fine-sized particles make greater intermixing and reduced diffusion distance between fuel and oxidizer. As discussed earlier, because of diffusion controlled molecular level reactions, decrease in the contact distance among the fuel and oxidizer could decrease ignition time and higher energy release rate.

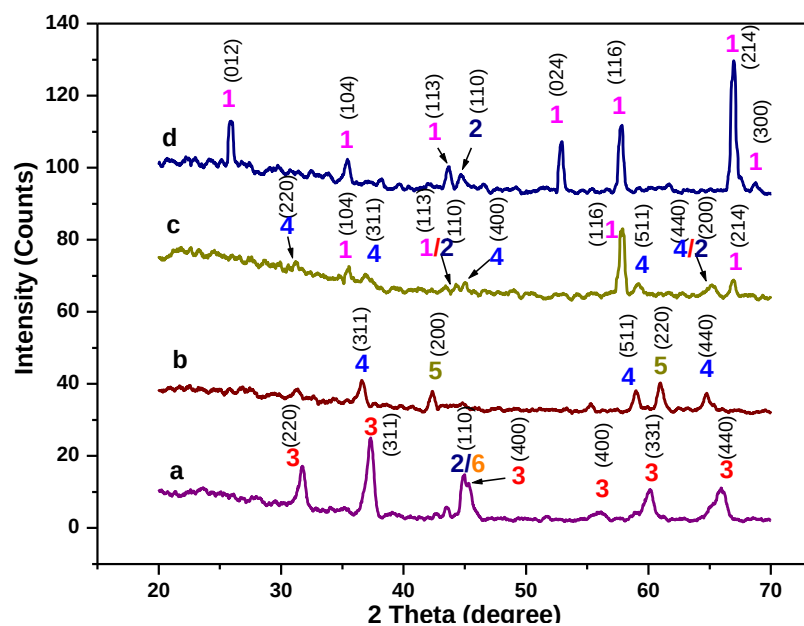


FIG. 10. XRD PATTERNS FOR COMBUSTION PRODUCTS OF (a) T1, (b) T2, (c) T3 and (d) T4 THE PHASES INDICATED IN THE PATTERNS ARE 1- Al_2O_3 (Rhombohedral), 2-Fe (Cubic), 3- Al_2O_3 (Cubic), 4- Al_2FeO_4 (Cubic i.e. $\text{Fe}+2\text{Al}_2\text{O}_4$) 5- FeO (Cubic), 6- Fe_3Al (Cubic)

IV. CONCLUSION

Nano thermite compositions (MICs) were prepared by ultrasonic method using nano Al and nano iron oxide of different weight percentage which were found to be more efficient than micron size thermite composition. Heat of combustion obtained by bomb calorimeter increased upon increasing Al content. Ignition temperature measured by DTA of MICs was lower than micron size thermite composition and combustion reaction was very fast with faster release of thermal energy. In the thermo-gravimetric analysis, two transitions were observed, one for nitridation ignition with exo followed by melting of Al with endo peak for thermite. MIC showed only one nitridation ignition with exo peak. The activation energy was calculated using Kissinger, Ozawa and Starink kinetic equation and found to be 164, 157 and 158 kJ/mol. MIC's are more efficient in energy release than micron size thermite composition. The mechanism of the combustion reaction was investigated by XRD of combustion products. Micron size thermite composition produced byproducts such as Al_2O_3 and FeAl_3 , whereas in case of MIC's, hercynite was the intermediate product along with FeO and with increasing Al content in MIC, formation of Fe phase took place along with Al_2O_3 .

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REFERENCES

- [1] Fisher SH, Grubelich MC, Theoretical energy release of thermites, intermetallics and combustible metals, Proceedings of the 24th International Pyrotechnics Seminar, IIT Research Institute Chicago, July 1998;27-31:231-286.
- [2] Bezmelnitsyn A, Thiruvengadathan R, Barizuddin S, Tappmeyer D, Apperson S, Gangopadhyay K, Gangopadhyay S, Modified nanoenergetic composites with tunable combustion characteristics for propellant applications, Propellants Explos. Pyrotech. 2010;35:384 – 394.
- [3] Martirosyan KS, Wang L, Luss D, Development of Nanoenergetic Gas-Generators, NANO '08, 8th IEEE Conference on Nanotechnology, 2008; 817-818.
- [4] Martirosyan KS, Hobosyan M, Lyshevsk SE, Enabling nanoenergetic materials with integrated microelectronics and MEMS platforms (2012) 12th IEEE International Conference on Nanotechnology (IEEE-NANO) The International Conference Centre Birmingham, Birmingham, United Kingdom August 2012; 20-23, .
- [5] Song E, Tracy GV, Enhanced incendiary grenade, Proceedings of the 27th International Pyrotechnics Seminar, IIT Research Institute Chicago, July 16-21, 2000;393-411.
- [6] Cao G, Orr`u R, Self-propagating reactions for environmental protection: state of the art and future directions, Chem. Eng. J. 2002;87: 239-249.
- [7] Sannia M, Orr`u R, Concas A, Cao G, Self-propagating reactions for environmental protection: remarks on the treatment and recycling of zinc hydrometallurgical wastes, Ind. Eng. Chem. Res. 2001;40:801-807.
- [8] Porcu M, Orr`u R, Cao G On the use of industrial scraps for the treatment of zinc hydrometallurgical wastes by self-propagating reactions, Chem. Eng. J. 2004;99:247-256.
- [9] Kallio M, Ruuskanen P, M`aki J, P`oyli`o E, L`ahteenm`aki S, Use of the aluminothermic reaction in the treatment of steel industry by-products, J. Mater. Synth. Process. 2000;8(2): 87-92.
- [10] Travitzky N, Kumar P, Sandhage KH, Janssen R, Claussen N, Rapid synthesis of Al_2O_3 reinforced Fe-Cr-Ni composites, Mater. Sci. Eng. A 2003;344: 245-252.
- [11] Dong Y, Yan D, He J, Li X, Feng W, Liu H, Studies on composite coatings prepared by plasma spraying Fe_2O_3 -Al self-reaction composite powders, Surf. Coat. Technol. 2004;179:223-228.
- [12] Miagkov VG, Polyakova KP, Bondarenko GN, Polyakov VV, Granular Fe- Al_2O_3 films prepared by self-propagating high temperature synthesis, J. Magn. Magn. Mater. 2003;258-259: 358-360.
- [13] Yang J, La P, Liu W, Hao Y, Microstructure and properties of Fe_3Al - $\text{Fe}_3\text{AlC}_{0.5}$ composites prepared by self-propagating high temperature synthesis casting, Mater. Sci. Eng. A 2004;382: 8-14.
- [14] Deevi SC, Sikka VK, Swindeman CJ, Seals RD, Application of reaction synthesis principles to thermal spray coatings, J. Mater. Sci. 1997;32: 3315-3325.
- [15] Chakraborty SP, Sharma IG, Suri AK, Bose DK, Studies on preparation, characterisation and evaluation of properties of Fe_3Al -based intermetallic alloy of composition Fe-16Al-5.44Cr-1Nb-0.5C, J. Mater. Process. Technol. 2001;115: 413-422.
- [16] Jin S, Shen P, Zhou D, Jiang Q, A common regularity of stoichiometry-induced morphology evolution of transition metal carbides, nitrides, and diborides during self-propagating high-temperature synthesis, Cryst. Growth Des. 2012;12: 2814 – 2824.
- [17] Collins ES, Pantoya ML, Daniels MA, Prentice DJ, Steffler ED, Arche SPD, Heat flux analysis of a reacting thermite spray impinging on a substrate, Energy Fuels 2012;26: 1621 – 1628.

- [18] Schoenitz M, Dreizin EL Consolidated energetic nanocomposites: mechanical and reactive properties“, Proceedings Of Thirty-Sixth Annual Conference of I.C.T. and Thirty-Second International Pyrotechnics Seminar, 28 June-1 July 2005, Karlsruhe, Federal Republic of Germany, Poster 133.
- [19] Tillotson TM, Gash AE, Simpson RL, Hrubesh LW, Satcher Jr JH., Poco JF, Nanostructured energetic materials using sol-gel methodologies, *J. Non-Cryst. Solids* 2001;285: 338–345.
- [20] Menon L, Patibandla S, Bhargava Ram K, Shkuratov SI, Aurongzeb D, Holtz M, Berg, J Yun J, Temkin H, Ignition studies of Al/Fe₂O₃ energetic nanocomposites, *Appl. Phys. Lett.* 2004; 84(23): 4735–4737.
- [21] Zhao N, He C, Liu J, Gong H, Zhang J, Dependence of catalytic properties of Al/Fe₂O₃ thermites on morphology of Fe₂O₃ particles in combustion reactions *Journal of Solid State Chemistry*, 2014;219: 67-73
- [22] Roen GA, Bozorg SFK, Nosko M, Švec P, Reactive mechanism and mechanical properties of in-situ hybrid nano-composites fabricated from an Al-Fe₂O₃ system by friction stir processing, *Mater Character*, 2017;127: 279-287
- [23] Sanders VE, Asay BW, Foley TJ, Tappan BC, Pacheco AN, Son SF, Reaction propagation of four nanoscale energetic composites (Al/MoO₃, Al/WO₃, Al/CuO, and B₁₂O₃), *J Propul. Power* 2007;23(4): 707-714.
- [24] Aumarm CE, Skofronick GL, Martin JA, Oxidation behaviors of aluminum nanopowders, *J. Vac. Sci. Technol. B* 1995; 13(2): 1178-1183.
- [25] Yong Lde, Park B, Valenta F, A study of the radiant ignition of a range of pyrotechnic materials using a CO₂ Laser, MRL Technical Report, MRL-TR- 1990; 90,20.
- [26] Plantier K, Combustion behavior of Nano composite Al/Fe₂O₃, MSc Thesis, Texas Tech University (USA), May 2004.
- [27] Sarangi B, Sarangi A, Ray HS, Kinetics of aluminothermic reduction of MnO₂ and Fe₂O₃ : A thermoanalytical investigation, *SIJ Int.* 1996; 36(9): 1135-1141.
- [28] Duraes L, Costa BPO, Santos R, Correia A, Camposd J, Portugal A, Fe₂O₃/aluminum thermite reaction intermediate and final products, *Mater. Sci. Eng. A* 2007;465: 199–210.
- [29] Mei J, Halldearn RD, Xiao P, Mechanisms of the aluminium-iron oxide thermite reaction, *Scripta Mater.* 1999; 41(5): 541–548.
- [30] Fan RH, Lu HL, Suna KL, Wang WX, Yi XB, Kinetics of thermite reaction in Al-Fe₂O₃ system, *Thermochim. Acta* 2006; 440: 129–131.
- [31] Bullian CJ, Swiatkiewicz JJ, Puszyński JA, Investigation of reaction mechanisms and combustion characteristics of nanothermites, Particle Technology Forum-03, AIChE Annual Meeting, Oct-Nov-2005, No-511d.
- [32] Weiser V, Roth E, Raab A, Mar M del, Lorenzo J, Kelzenberg S, Eisenreich N, Thermite type reactions of different metals with iron-oxide and the influence of pressure, *Propellants Explos. Pyrotech.* 2010;35 :240 – 247.
- [33] Cheng JL, Hng HH, Lee YW, Du SW, Thadhani NN, Kinetic study of thermal- and impact- initiated reactions in Al-Fe₂O₃ nanothermite. *Comb.Flame* 2010;157:2241-2249.
- [34] Wang Y, Song XL, Jiang W., Deng GD., Guo XD, Liu HY, Li FC, Mechanism for thermite reactions of aluminum/iron-oxide nanocomposites based on residue analysis *Trans. Nonferrous Met. Soc. China* 2014;24: 263-270
- [35] Sahoo SK, Agarwal K, Singh AK, Polke BG, Raha KC, Characterization of γ- and α-Fe₂O₃ nano powders synthesized by emulsion precipitation-calcination route and rheological behaviour of α-Fe₂O₃, *Int J Eng. Sci Technol.*, 2010; 2(8): 118-126.
- [36] Berger B, Parameters influencing the pyrotechnic reaction, *Propellants Explos. Pyrotech.* 2005;30: 27-35.
- [37] Wang SX, Liang KM, Zhang XH Wang GL, Influence of heating rate on DTA curve on aluminothermic reaction, *J. Mater. Sci. Lett.* 2003;22: 855-856.
- [38] Jian G, Chowdhury S, Sullivan K, Zachariah MR, Nanothermite reactions: Is gas phase oxygen generation from the oxygen carrier an essential prerequisite to ignition?, *Comb. Flame* 2013;160: 432–437.
- [39] Asay BW, Son SF, Busse JR, Oschwald DM, Ignition characteristics of metastable intermolecular composites, *Propellants, Explos., Pyrotech.* 2004;29: 216-219.
- [40] Bockmon BS, Pantoya ML, Son SF, Asay BW, Mang JT, Combustion velocities and propagation mechanisms of metastable interstitial composites, *J. Appl. Phys.* 2005;98: 064903.
- [41] Jones DEG, Fouchard RC, Turcotte AM, Kwok QSM, Brousseau P, Thermal characterization of passivated nanometer size aluminium powders, 27th International Pyrotechnics Seminar, IIT Research Institute Chicago, July 16-21, 2000; 821-830.
- [42] Kwok QSM, Fouchard RC, Turcotte AM, Lightfoot PD, Bowes R, Jones DEG, Characterization of aluminum nanopowder compositions, *Propellants Explos., Pyrotech.* 2002;27: 229 - 240.
- [43] Bensouyad H, Hamana D, Analysis methods for the determination of energies activation and the study of the precipitation reactions in Al-4.5% weight Cu alloys, *J Eng Appl Sci*, 2008;3(7): 583-586,
- [44] Heireche L, Belhadji M, The methods Matusita, Kissinger and Ozawa in the study of the crystallization of glasses, the case of Ge-Sb-Te alloys, *Chalcogenide Lett.* February 2007;4(2): 23 – 33.
- [45] Starink MJ, The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods, *Thermochim. Acta* 2003; 404:163.