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Kinetics study in Ti–Fe_2O_3 system by electro-thermal explosion method

Ya-Cheng Lin [a], Alexander S. Shteinberg [b], Paul J. McGinn [a], Alexander S. Mukasyan [a], *

[a] Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA
[b] ALOFT Corporation, 61 Fairlawn Dr., Berkeley, CA 94708, USA

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ABSTRACT

High-temperature (1300–1600 K) kinetics of titanium (Ti) and iron (III) oxide (Fe_2O_3) heterogeneous thermites were investigated using electro-thermal analysis (ETA) technique. Three different grades of Fe_2O_3 powder precursors were mixed separately with Ti powder ($Ti:Fe_2O_3 = 13.34$ M ratio) and were subjected to ETA experiments. For the first time a high-speed infrared thermal imaging system was also applied simultaneously with ETA to explore temperature-time history of the reaction process. Obtained ETA results show that $Ti + Fe_2O_3$ thermite reaction systems exhibit apparent activation energies in the range of 60–100 kJ/mol. The reaction mechanism for Ti/Fe_2O_3 thermites is also discussed. The Ti–Fe_2O_3 thermite reaction involves several steps such as reduction of Fe_2O_3 by Ti with formation of Fe and TiO_2 phases, followed by formation of the Ti_2Fe intermetallic metastable phase. Statistical treatment of experimental data shows that ETA is a sensitive and accurate technique for kinetics study of high-temperature heterogeneous thermite reactions.

1. Introduction

Thermites are commonly referred to as highly exothermic reactive mixtures of metal powder fuels (i.e., aluminum, magnesium, titanium, zinc) and metal/non-metal oxides (i.e., boron oxide, silicon dioxide, chromium oxide, iron (II, III) oxide, copper (II) oxide). Once initiated the exothermic reduction-oxidation (redox) reaction proceeds rapidly and releases substantial heat, which is sufficient to boost the combustion temperatures up to ~4000 K. Such thermite systems hold great promise for a variety of applications, including extracting pure metals from ores [1], joining of materials (Goldschmidt et al. utilized thermites for railway welding applications in the 1900s [2]), synthesis of advanced refractory ceramics coatings [3] and ceramic reinforced metal–matrix composites [4]. Recently, a new class of thermite reactions, known as super-thermites, attracted great attention for preparation of energetic nano-composites [5,6].

To gain better control of thermite processes, it is critical to evaluate the kinetics of the corresponding redox reactions. However, due to the extremely high exothermicity of such systems, which leads to high reaction temperatures and short characteristic reaction times (≥1 msec), it is essentially impossible to measure high-temperature kinetics of such reactions using conventional isothermal methods as well as TGA/DTA/DSC-based approaches. One of the few unique methods that allows measuring rapid high-temperature kinetics for such heterogeneous reactions is called electro-thermal analysis (ETA) [7–9]. ETA is based on the phenomenon of electro-thermal explosion (ETE), i.e., the ability of a reaction to self-initiate along the bulk of the sample under the conditions of rapid preheating by passing electric current through the reactive media, which causes heat to build up due to the electrical resistance of the material (i.e., Joule heating). In ETA experiments Joule heating by an external power supply is used only in the initial stage of reaction initiation, after which the electric current is turned off and further temperature change occurs solely due to the heat release by a self-sustained exothermic reaction. Also, there is no experimental evidence that such brief Joule preheating may influence the kinetics of chemical interaction in investigated systems. Moreover, high heating rates ($>10^4$ K/s) that can be achieved by ETE allow one to uniformly heat the sample and neglect heat losses, so that the whole process can be considered as an adiabatic thermal explosion. More detailed description of ETA principals and methodology of kinetics measurement can be found in Ref. [7]. These key features make the ETE approach convenient for studies of high-temperature thermite reactions.

The fundamental basis of ETE was developed many years ago [8,10]. However, only recently a new generation of ETA apparatus

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* Corresponding author. Tel.: +1 574 631 9825; fax: +1 574 631 8366.
E-mail addresses: amoukasi@nd.edu, yachenglintw@gmail.com, zekelin2008@gmail.com (A.S. Mukasyan).

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was built and applied to investigate high-temperature reactions, specifically in the Ni–Al system [7]. It was proven that ETA is a robust technique to study kinetics of rapid (~seconds), high-temperature (>1000 K), gasless heterogeneous reactions.

In this work, the ETA method was used in combination with a rapid thermal vision device to extract kinetics parameters, primarily focusing on calculating the apparent activation energy of Ti/Fe_2O_3 thermite mixtures. Particularly, three types of Fe_2O_3 powder precursors, which have distinctive morphologies, were mixed with Ti powder and then subjected to ETA experimentation. The reaction mechanisms for reactions in Ti/Fe_2O_3 thermite system are also discussed.

2. Material and methods

2.1. Sample preparation

Titanium powders (−325 mesh, 99.5%, Alfa Aesar, MA, USA) and three commercial grades of iron (III) oxide powders, denoted as mFe_2O_3 (99.5%, Alfa Aesar, MA, USA), MFe_2O_3 (99.7%, Atlantic Equipment Engineers, NJ, USA), and nFe_2O_3 (99.9%, Rockwood Pigments, MD, USA), were used in the experiments. The characteristic morphologies of the iron (III) oxide powders are presented in Fig. 1. The Brunauer–Emmett–Teller (BET) specific surface area (SSA) measurements were carried out on a Coulter SA3100 analyzer at 77 K, with nitrogen as the adsorbent gas. These three iron (III) oxides were vacuum outgassed at 298 K for 6 h before the SSA measurement. Specifics of the microstructures and morphologies for the three investigated Fe_2O_3 powders are summarized in Table 1.

Table 1
Specifics of iron (III) oxide powders.

	mFe_2O_3	MFe_2O_3	nFe_2O_3
Specific surface area (m^2/g)	14 ± 2	11 ± 1	119 ± 1
Morphology	Irregular	Irregular	Needle-shaped
Particle size (nm)	100–300	50–200	~100

The initial Ti + Fe_2O_3 mixtures with desired compositions were prepared by 6 h wet mixing in a 200 ml ethanol bath in rotary ball (5 mm ZrO_2 milling ball) milling device with a 5:1 ball to powder ratio and rotation speed 100 rpm, followed by filtration and dried in a vacuum oven at 343 K overnight. The mixtures were then cold-pressed using an automatic press (Carver Inc., IN, USA) into cylindrical (typically $Ø = 5$ mm × $l = 12$ mm) samples with a relative density of 75–80% under the following conditions: maximum load 80 MPa, dwelling time 2 min. The cold-pressed cylindrical sample was placed into the ETA reaction chamber and clamped between the electrodes by a pneumatic system (Fig. 2a), for further experimentation.

2.2. Infrared thermal imaging measurement

A high-speed infrared thermal imaging system (SC6000, FLIR Systems, MA, USA) was used to explore the ignition characteristics of the process. With FLIR's ThermaCAM Researcher software, thermal images and videos can be captured over several different temperature ranges up to 2300 K. Depending on the frame size and temperature range of the investigation, frame rate upwards of 15,000 fps is achievable. The use of a high-speed IR camera allows obtaining temperature distributions on the sample surface during the heating process, making it convenient for monitoring ignition process.

2.3. Electro-thermal explosion analysis

Kinetics experiments were conducted in the ETA-100 apparatus (ALOFT Corporation, CA, USA) under pure argon atmosphere (99.995%, Praxair Inc., CT, USA). To obtain additional information on temperature-time (T–t) maps during thermal explosion, the infrared thermal imaging system was set and aligned with the ETA-100. Fig. 2b depicts the schematic diagram of the reaction chamber assembly with the optical system and the infrared camera. Fig. 2c shows a more detailed illustration of cylindrical sample position and the corresponding photo-diode array. It can be seen that the optical system, which consists of lenses, narrow band filter, sapphire windows and 16 photodiodes (Fig. 2b), allows for measuring temperature-time profiles along the sample height in 16 specific points located 2 mm apart (Fig. 2c) (see Ref. [7] for more details).

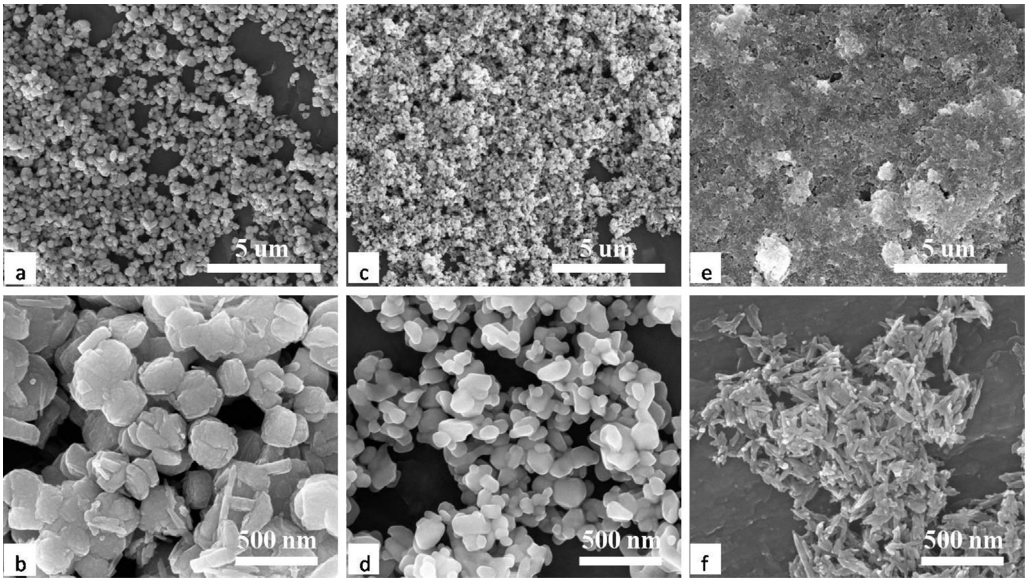

Fig. 1. Typical SEM microstructure images of initial mixtures: Ti/mFe_2O_3 (a, b), Ti/MFe_2O_3 (c, d) and Ti/nFe_2O_3 (e, f). Note that (b, d, f) display higher-magnification of mFe_2O_3, MFe_2O_3 and needle-shaped nFe_2O_3.