



Review

Correlating ignition mechanisms of aluminum-based reactive materials with thermoanalytical measurements



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ABSTRACT

A class of non-detonating materials capable of highly exothermic reactions, referred to as reactive materials (RMs), has been subjected to extensive recent studies. Examples include pure reactive metals, intermetallic, metal-metalloid composites, and thermites; the latter two types of materials include nano-composite and nanostructured compositions. Most of the studied RMs are based on aluminum. Potential applications for RMs include additives to conventional energetics (propellants, explosives, and pyrotechnics) and reactive structural components. Design of energetic systems including RM's requires reliable prediction of their ignition kinetics, including ignition delays as a function of involved heating rates, pressures, and oxidizing environments. Direct measurements of such ignition delays are often impossible because of hostile surroundings RMs are exposed to. Research has been active in quantifying ignition temperatures and kinetics using simplified configurations and low heating rates, relatively easily achieved in laboratory conditions. Alternatively, multiple ignition studies focused on a specific stimuli, e.g., electric current, spark, heat pulse, etc. However, correlation between laboratory studies and ignition observed in practical situation is tentative at best. Substantial discrepancies exist between different experiments and, respectively, proposed ignition models. More recently, thermo-analytical (TA) measurements performed isothermally or at well-controlled heating rates and in well-characterized environments were used to identify and describe quantitatively reactions leading to ignition. In this review, TA measurements aimed to develop models for ignition of pure aluminum, aluminum-based reactive intermetallics, and thermites are considered using specific examples for each type of material. The focus is on relatively recent studies. Results and interpretations of the TA measurements are discussed in terms of their relevance to describing ignition for each specific type of material. The examples included are selected because substantial progress in characterization of their ignition mechanisms was made recently using TA measurements. Individual exothermic steps were identified and assigned to particular reactions or phase transformations in each specific material system. Kinetics of some of the identified steps were reported and applicability of such kinetics is discussed for modeling ignition, involving much higher heating rates than thermo-analytical measurements. Different ignition stimuli are considered, and ignition models involving detailed analysis of heat transfer affected by identified chemical reactions are discussed briefly. Both benefits and limitations of applying the TA based reaction mechanisms for ignition models are considered. Some common caveats in interpreting TA measurements for reactive materials are also reviewed. Despite substantial progress, there are no comprehensive and universally accepted ignition models for the materials systems. A common theme observed here for all reactive materials is that ignition is caused by more than one reaction and/or phase change. Many, but not all such reactions and phase changes can be characterized based on thermo-analytical measurements.

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1. Introduction

Equipment for thermoanalytical (TA) measurements and relevant methods of data processing to recover reaction kinetics developed rapidly starting from the middle of the 20th century making thermal analysis today one of the most common and widely used laboratory techniques. Not surprisingly, combustion researchers have exploited TA measurements to characterize both stability and ignition of many heterogeneously reacting materials, e.g. [1–6], (many more examples are available in the literature). However, despite the precision and high level of automation for state of the art TA equipment, the interpretation of results may be difficult when the goal is to characterize ignition.

Ignition is commonly described by classic Semenov or Frank–Kamenetskii models [7,8]. Both models assume a single Arrhenius type exothermic reaction and neglect the reaction progress function, describing how evolution of the reacting system affects the reaction rate. They also assume that the transport of reagents is fast compared to their consumption in the reaction. It is a good assumption for slow, kinetically controlled gas-phase reactions; however, it is not sustained for most heterogeneous combustion reactions, even for “simple” systems comprising pure metal particles, when condensed phase diffusion may determine the reaction rate. It has been recognized long ago that for many condensed fuels, the ignition models need to be altered by accounting for consumption of reactants, e.g., by introducing a basic reaction progress function, e.g., [9].

The situation involving ignition of reactive materials may be somewhat more complex. Even if consumption of reactants prior to ignition is negligible, low-temperature, slow pre-ignition reactions may affect significantly material properties controlling diffusion of reacting species. For example a protective oxide layer may become thicker, introducing an additional diffusion barrier. Initial components might produce new compounds and/or structures, especially in the vicinity of the reaction interface, altering the reaction mechanism. Phase changes, such as melting of material near the reaction interface, change transport processes in the reacting systems dramatically. Such processes may occur when only a very small amount of reactants was consumed, but they can have pronounced effect on further reactions. Thus, such processes must be accounted for in the ignition model.

A useful model must describe self-heating leading to combustion. It should also describe how the temperature ramp affected the material and, especially, the reaction interface, even if consumption

of reactants was relatively small. Often, there are multiple exothermic reaction steps, which become important at different stages of reaction progress, and neglecting this may critically bias ignition models for reactive materials.

TA measurements enable one to identify and characterize quantitatively the effect of material evolution on its reaction rate. Advantages of such measurements, which are often combined with product analysis, include their capability to distinguish multiple individual reaction steps, assign specific reactions and/or phase changes to the measured heat effects or mass changes, and quantify kinetics of the identified reactions.

There are, however, important limitations. The rates of TA measurements are necessarily much lower than the heating rates occurring in most practical situations involving ignition of reactive materials. Therefore, translating any processes detected in TA to a practical situation requires a well-justified kinetic model. For example, if aluminum nano-powder begins oxidizing at ~720 K when heated at 5–20 K/min in thermo-gravimetric (TG) experiments [10], oxidation of aluminum nanoparticles in a propellant or explosive, where it is heated much faster, is likely to begin at a higher temperature. In addition to using kinetic calculations, translating the reactions observed in TA experiments to practical scenarios assumes that no other process, undetectable in TA experiments, would occur. It is also assumed that the reactions observed in TA experiments remain fundamentally unchanged at higher heating rates, which may not necessarily be the case. For example, some reactions occurring at low heating rates may require an intermediate product generated in preceding reaction steps. At higher heating rate, such reaction steps may be abbreviated, so that no intermediate product required for subsequent reaction steps is produced. As a rule, these latter assumptions are difficult to validate.

To be useful, TA measurements should be well designed. Typically, such measurements include differential thermal analysis (DTA), DSC, and TG analysis [11]. Simultaneous DTA and TG or DSC and TG are often used. Commonly for all TA methods, the sample temperature is controlled and a characteristic parameter quantifying the sample reaction at a given temperature is measured. Methods of temperature control and the actual accuracy with which the sample temperature is defined vary depending on the type of the instrument. In a power compensated DSC, the sample temperature is strictly controlled, while in a heat flow DSC or DTA, a small temperature difference between sample and reference is

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