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Reactions leading to ignition in fully dense nanocomposite Al-oxide systems

Alexandre Ermoline [a], Mirko Schoenitz [a], Edward L. Dreizin [b,*]

[a] Reactive Metals, Inc., Newark, NJ 0102, United States
[b] New Jersey Institute of Technology, Newark, NJ 07102, United States

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ABSTRACT

Aluminum-metal oxide energetic compositions with components mixed on the nano-scale are substantially more reactive than conventional thermites and are of interest as potential additives to propellants, explosives, and pyrotechnics. For such nanocomposite materials prepared by Arrested Reactive Milling (ARM), the exothermic reactions leading to ignition were detected to begin at relatively low temperatures. These materials are prepared by mechanical processing at room temperature, and the nature of the interface present between aluminum and the oxidizer (metal oxide, e.g., CuO, MoO_3, Bi_2O_3, etc.) is unknown. Experiments using a Thermal Activity Monitor (TAM III) quantify the reaction rates between aluminum and CuO at temperatures between 303 and 373 K. Results of the present TAM III measurements and results of earlier measurements using differential scanning calorimetry for the same 2Al·3CuO nanocomposite are interpreted considering two different reaction models. The rate-limiting step is described either as a conventional thermally activated diffusion, or using the Cabrera–Mott model developed originally for oxidation of fresh metal surfaces. It is shown that the thermally activated diffusion model is inadequate for description of the low-temperature reactions observed in nanocomposite thermites prepared by ARM. The Cabrera–Mott model provides a description qualitatively matching the experimental results; achieving the quantitative match is expected to be possible by adjusting the model parameters.

1. Introduction

Multiple reactive compositions and energetic compounds include powders and, more recently, nanopowders of aluminum [1–3]. Aluminum particles can be mixed with various oxidizers, including ammonium perchlorate, ammonium nitrate, sodium nitrate, metal oxides, etc. In all such mixtures, the initial reactions leading to aluminum ignition are rate limited by relatively slow diffusion of the reacting species through the protective aluminum oxide layer, which is always present on the Al surface naturally passivated by exposure to an oxidizing gas environment [4–7]. However, most of the reactive interfaces existing in the Al-containing nanocomposite materials prepared by Arrested Reactive Milling (ARM) [8] are not directly exposed to gaseous oxidizer during the material preparation, storage, or handling. Indeed, for the thermite compositions mechanically milled under inert environment, when a fresh aluminum surface is produced, it is immediately pressed against that of a solid oxidizer, e.g., CuO, MoO_3, etc. As a result, fully dense, nanocomposite structures are formed, as that shown in Fig. 1. Most of the reactive interfaces between Al and oxidizer are therefore located inside such structures so that respective Al surface is not exposed to air after the material is recovered from the ball mill, stored, and handled. It is unclear whether a passivating amorphous Al_2O_3 layer, similar to that present on any aluminum surface exposed to air, also exists between inclusions or layers of metallic Al and solid oxidizer pressed against one another, void-free, within each powder particle prepared by ARM. If such an oxide layer is present, the kinetics of both the initial exothermic reactions leading to ignition and low-temperature reactions resulting in the material aging are expected to be similar to those in the composite materials comprising blends of aluminum powders with respective oxidizers. However, if the alumina layer is not formed, or if the structure and morphology of the layer separating metallic aluminum and oxidizer in the materials prepared by ARM are different from those of the "naturally grown" amorphous alumina, it is reasonable to expect that both the ignition and aging kinetics for the ARM-prepared materials are qualitatively different from those of the mixed powders or nanopowders with the same bulk composition. The objective of this effort is to establish whether initial exothermic reactions in the ARM-prepared nanocomposite thermites can be described using conventional, thermally activated diffusion or whether a different reaction mechanism should be introduced.

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* Corresponding author. Fax: +1 973 596 5855.
E-mail address: dreizin@njit.edu (E.L. Dreizin).

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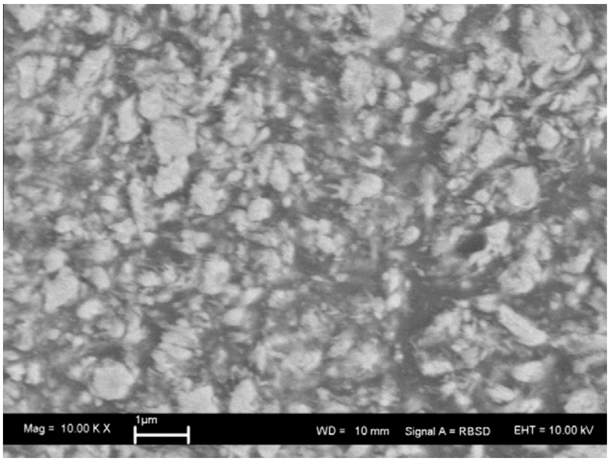

Fig. 1. A portion of the cross-sectioned fully dense particle of a nanocomposite Al–CuO material prepared by ARM. Light-colored CuO inclusions are embedded into a dark-colored aluminum matrix.

The manuscript first presents the experimental results, including a very brief overview of the previously published DSC measurements [9–17] and new measurements using microcalorimetry. Both data sets are processed to estimate the thickness of the aluminum oxide layer grown based on the measured reaction enthalpy. Further, the measured reaction enthalpies and estimated rates of oxide growth are compared to those expected based on different reaction mechanisms and their respective mathematical descriptions [18–20].

2. Onset temperatures for exothermic reactions measured by thermal analysis for nanocomposite thermites

Multiple literature reports are available on onset temperatures and reaction kinetics for exothermic reactions in thermite-type composite and nanocomposite materials prepared by mixing of nanopowders [9–11]. In addition, reactions were studied for the composite nanofoils produced by layered deposition [12,13]. The deposition was performed at elevated temperatures initiating a reaction between the deposited layers.

For a variety of aluminum based thermites, including Al–MoO_3 [9], Al–Fe_2O_3 [10], Al–I_2O_5 [11] and other systems, the onset of exothermic redox reactions was detected between 730 and 850 K, with lower temperatures observed for finer powders and nanopowders. Similarly, the onset of exothermic reactions in the same temperature range was observed for Al–CuO nanofoils [12,13]. This temperature range effectively coincides with the temperatures at which the first oxidation step for aluminum powders and nanopowders is observed in gaseous oxidizers [4–7]. For the latter case, the oxidation step was assigned to a polymorphic transformation occurring in the naturally formed amorphous alumina surface layer, resulting in the formation of crystalline γ-Al_2O_3.

Detailed studies of exothermic reactions in the ARM-prepared nanocomposite thermites [14–17] showed that the reaction onset is observed at much lower temperatures, between 400 and 500 K. This significant difference in the onset temperature for the exothermic reaction suggests that the reaction mechanism and respective rate-limiting processes might be different for the ARM-prepared thermites as compared to the nanocomposites thermites containing naturally passivated aluminum particles.

3. Low-temperature reactions characterized by microcalorimetry

Focusing on low temperature processes, expected to be critical in causing ignition at high heating rates, in this work the heat release during isothermal reactions in a material with bulk composition of 2Al·3CuO prepared by ARM was studied using a microcalorimeter TAM III by TA Instruments. This particular composition was selected for the present initial experiments somewhat arbitrarily among many available nanocomposite thermites prepared by ARM. One advantage of the Al–CuO thermites is that their cross-sections examined under SEM show good contrast between fuel (Al) and oxidizer (CuO), so that measuring dimensions of the CuO inclusions is relatively straightforward.

All samples were prepared by milling starting powders of Al and CuO in Ar atmosphere using hexane as a process control agent. Immediately after milling, the prepared powders were placed in an Ar-filled glovebox for about 18 h to remove hexane. The preparation details and phase composition analysis of the produced nanocomposites performed using electron microscopy and X-ray diffraction (XRD) were reported elsewhere [14]. Prepared materials contain starting components, Al and CuO with traces of additional phases formed during ball milling. In particular, trace amounts of intermetallic alloys $CuAl_2$ and Cu_9Al_4, as well as Cu and γ-Al_2O_3, were detected. Overall, the composition of the produced samples does not differ significantly from the stoichiometric 2Al·3CuO. Prepared powders were uniform chemically and morphologically, as implied by repeated XRD and electron microscopy analyses of different material batches. In addition, repeated DSC and TAM III measurements produced well reproducible results, further confirming uniformity of the prepared powders.

Experiments with 2Al·3CuO in the TAM III were conducted under isothermal conditions at three different temperatures: 303 K (30 °C), 323 K (50 °C), and 373 K (100 °C). The sample analyzed at 303 K was used as prepared; the samples analyzed at 323 and 373 K prior to the measurements were stored in air during 1 and 5 days, respectively.

When a sample stored at room temperature is introduced into the calorimeter furnace, the temperature difference between the sample and the calorimeter creates a heat flow to the sample until the temperatures equilibrate. After that, the sample is lowered into the sample holder, which creates another disturbance in the heat flow signal, mainly due to friction between the sample holder and the walls of the ampoule in which the sample is placed. According to the TAM III measurement protocol, the overall time required for the signal to become free of disturbances caused by introduction of the sample into the calorimeter is not less than

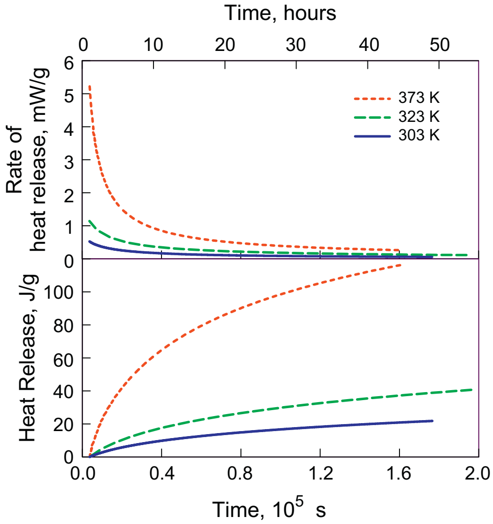

Fig. 2. Integral heat release and rate of heat release for reaction in 2Al·3CuO ARM nanocomposites at various temperatures obtained from TAM III measurements.