Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 451 (2006) 34–43
thermochimica acta
www.elsevier.com/locate/tca

Exothermic reactions in Al–CuO nanocomposites

Swati M. Umbrajkar, Mirko Schoenitz, Edward L. Dreizin *
New Jersey Institute of Technology, Newark, NJ 07102, USA

Received 28 June 2006; received in revised form 1 September 2006; accepted 7 September 2006

Abstract

Heterogeneous reactions in the Al–CuO system were investigated using differential scanning calorimetry combined with structural and phase analyses of partially reacted samples. The dense nanocomposite 2Al + 3CuO powders used in this study were prepared by arrested reactive milling. Ignition experiments with the powders heated at different rates were also performed and compared to the results of thermal analysis. The results of thermal analysis measurements were processed using isoconversion techniques and a multistep reaction mechanism was proposed to describe the experiments. The reaction between Al and CuO started at ∼400 K and was well described by four parallel reaction steps. The kinetic descriptions of individual steps depend on the frequency factors specific for the powders used in this study and activation energies that should remain valid for any Al–CuO composite materials. The values of the frequency factors and activation energies were determined as well as the specific reaction mechanisms describing each reaction step. The identified reaction steps were tentatively assigned to specific processes of CuO decomposition followed by diffusion of reacting species through amorphous and then crystalline Al_2O_3 polymorphs. Ignition of the nanocomposite Al–CuO materials was shown to be driven primarily by the lower-temperature oxidation processes. It was shown that ignition of Al–CuO nanocomposite powders can be described reasonably well using the proposed kinetics of Al–CuO heterogeneous reactions.

Keywords: Kinetic parameters; Thermites; Nanocomposites; Modeling; Ignition

---

1. Introduction

Unique nanostructured materials, including reactive nanocomposite powders based on exothermic thermite reactions, have attracted a great deal of interest. Different types of reactive nanocomposites have been synthesized, such as mixed nanopowders (also called metastable intermolecular composites, or MIC) [1–3], porous nanocomposites produced by sol–gel synthesis [4,5], multilayer nanofoils [6,7], and dense nanocomposite powders produced by arrested reactive milling (ARM) [8–10]. Despite different synthesis techniques and material types, the common approach has been to increase the interface area available for heterogeneous reaction between solid fuel and oxidizer components. The ARM technique used in this work to prepare nanocomposite powders is derived from mechanical milling of starting components capable of highly exothermic reaction [11]. For such components, the reaction can be mechanically triggered during the milling and become self-sustained [12]. In ARM, the milling is stopped just before the reaction is initiated [8]. The products are micron-sized powders, which contain reactive components mixed on a nanoscale. The nanocomposites are nearly 100% dense, and their external surface is relatively small, unlike that of the nanocomposites produced from mixed nanopowders. Therefore, only a small fraction of metal oxidizes upon exposure to air producing a thin external passivating oxide layer while bulk of the metal remains reactive. ARM synthesis is a “top-down” process, that is, the synthesis of nanocomposites by continuous refinement of micron-scale starting materials and is readily scalable. Thus, the ARM nanocomposites can be less expensive than similar compositions produced using alternative, “bottom-up” approaches, where nanoparticles or composites are grown from molecular precursors [1–5].

Among several types of reactive nanocomposites synthesized by ARM [8–10], Al–CuO thermites are of particular interest. The reaction is highly exothermic and its temperature can be adjusted to produce either molten or vapor-phase copper. Thus, a broad range of potential applications is possible including joining compounds and energetic compositions enabling transient gas generation. Recently, Al–CuO_x multilayer nanofoils were produced and characterized [6,7]. Differential thermal analysis

---

* Corresponding author. Tel.: +1 973 596 3327; fax: +1 973 642 4282.
E-mail address: dreizin@njit.edu (E.L. Dreizin).

doi:10.1016/j.tca.2006.09.002

traces of these nanofoils when heated from ambient conditions to 1673 K indicated that the reaction proceeded via two separate exotherms occurring around 850–950 and 975–1275 K. These events were interpreted as reactions controlled by lateral growth of Al_2O_3 nuclei and then by diffusion of oxygen through growing Al_2O_3 layers, respectively. It was suggested that the oxygen diffusion through CuO_x layers was not a rate-limiting process for the observed reactions [7]. However, in our initial experiments with Al–CuO dense nanocomposite powders produced by ARM, exothermic events were observed to occur at much lower temperatures, staring from about 400 K [13]. Thus, the reaction mechanisms proposed in refs. [6,7] need to be expanded and verified in order to be applied to a broader range of Al–CuO nanocomposites. The present study is aimed to develop a more adequate description of Al–CuO thermite reactions. Furthermore, the correlation of different processes occurring during such reactions and ignition of Al–CuO nanocomposites occurring at high heating rates was of interest. Differential scanning calorimetry (DSC), X-ray diffraction (XRD) and heated filament ignition experiments [14] were used to quantify the ignition kinetics and related reaction mechanisms.

2. Experimental

2.1. Preparation of nanocomposite powders

A shaker mill (8000 series by Spex CertiPrep) was employed in this research. Flat-ended steel vials were used along with 5 mm steel balls. Starting blends were prepared in stoichiometric proportions from powders of elemental aluminum (99% pure, −325 mesh by Atlantic Equipment Engineers) and cupric oxide CuO (99% pure, 1–5 μm, by Atlantic Equipment Engineers). Synthesis was carried out in argon environment. A small amount of hexane (C_6H_{14}) was added as a process control agent (PCA) to hinder the cold welding during milling. The process temperature was monitored using thermistors attached to the sides of the milling vials and connected to a digital data logger. The instant of reaction was marked by a sharp rise in the vial temperature.

Table 1
Nanocomposite powder samples prepared and used in this research (batch mass 3 g; ball to powder mass ratio 5; 5 mm steel balls)

Sample ID	Hexane (ml)	Milling time (min)
1	0	2
2	1	16
3	8	60

Highly metastable energetic nano-composites were prepared by arresting the milling before the spontaneous exothermic reaction. When the amount of PCA added to the mixture was varied, the milling times required to initiate the reaction changed. Three different samples were prepared by varying both the amount of PCA and the milling times, as shown in Table 1. When the materials were milled without any PCA, the reaction occurred within 2 min. When 1 ml of hexane was added, the reaction was triggered after 16 min of milling. When 8 ml of hexane was added, the reaction did not initiate even after an hour of milling and the metastable samples were prepared by stopping milling after 60 min. For each sample, several 3 g batches were prepared using a ball to powder mass ratio of 5.

2.2. Sample characterization

Morphology and composition of the composites were examined on a LEO 1530 field emission scanning electron microscope (SEM) operated at 10 kV. The samples were embedded in epoxy and cross-sectioned for examination. The phase composition was determined for each sample by X-ray diffraction (XRD). The XRD was performed on a Phillips X'pert MRD powder diffractometer operated at 45 kV and 40 mA using Cu Kα radiation (λ = 1.5438 Å). Temperature-dependent structural transformations were determined by differential scanning calorimetry (DSC) using a Netzsch Simultaneous Thermal Analyzer STA409 PC. Alumina pans were used and the furnace was flushed with argon at approximately 10 ml/min. DSC traces were recorded between room temperature and 1013 K with heating

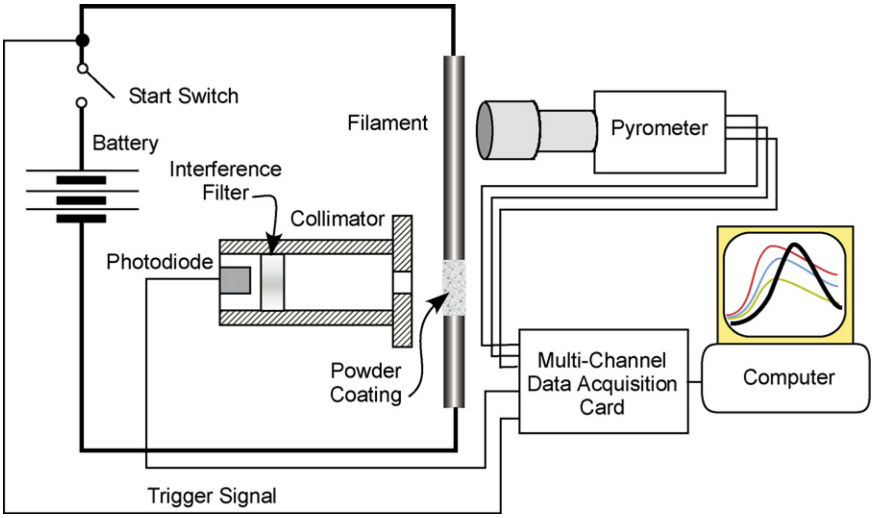

Fig. 1. Heated filament setup used for powder ignition experiments.