Materials and Design 155 (2018) 396–403

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Controllable synthesis of $NiCo_2O_4$/Al core-shell nanowires thermite film with excellent heat release and short ignition time

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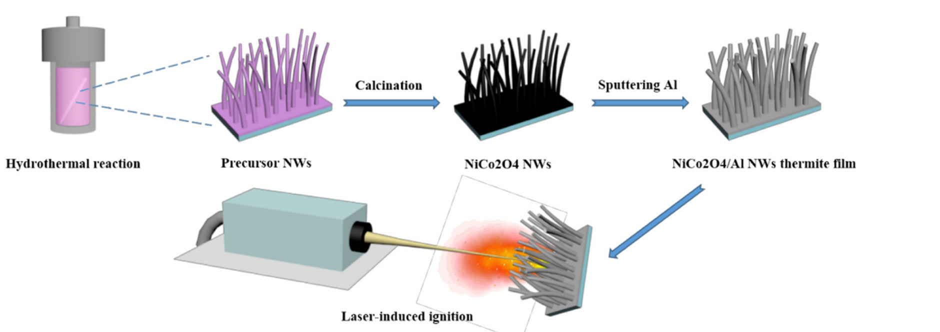
HIGHLIGHTS

- $NiCo_2O_4$ has been selected as an oxidizer of the nanothermite film for the first time.
- The morphology and heat release of the obtained nanowires thermite films can be controlled by the aluminizing thicknesses.
- The nanothermite film exhibits excellent heat release and short ignition time.
- The $NiCo_2O_4$/Al core-shell nanowires thermite film has the greatly potential prospect in the field of ignition materials.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 April 2018
Received in revised form 31 May 2018
Accepted 15 June 2018
Available online 18 June 2018

Keywords:
$NiCo_2O_4$/Al
Core-shell nanowires structure
Nanothermite film
Heat release
Magnetron sputtering

ABSTRACT

$NiCo_2O_4$ has been selected as an oxidizer to realize the nanothermite film for the first time in this study. The $NiCo_2O_4$/Al core-shell nanowires (NWs) thermite film has been fabricated using a facile hydrothermal-annealing synthesis method and a controllable magnetron sputtering process. The as-obtained $NiCo_2O_4$/Al NWs thermite film shows a uniform structure and distribution on the substrate, with a favorable interfacial contact between the bimetallic oxide and the fuel at the nanoscale. It is found that the quantity of Al plays a key role in the total heat release magnitude. The maximal heat release of the $NiCo_2O_4$/Al nanothermite film has reached 2076.0 J/g at the optimal Al deposited thickness of 450 nm with the obtained optimum Al/$NiCo_2O_4$ molar ratio of 4.9. Moreover, this design strategy is highly compatible with microelectromechanical systems (MEMs) and it can be applied to realize other nanothermites composed by bimetallic oxide and fuel.

1. Introduction

Energetic materials (EMs), as a class of substance storing chemical energy, can independently undergo intense redox reactions and energy release by combustion or detonation when stimulated by a certain amount of an external energy. Generally, EMs are composed of propellants, explosives and pyrotechnics [1]. In recent years, nanoenergetic materials (NEMs) have attached a lot of interests in energy academic community, because they are of faster energy release rate and higher heat release than traditional EMs. Nanothermite, as an important subgroup of NEMs, often consists of nano reactive metal (e.g. Mg [2, 3] or Al [4]) and nano metal oxides (e.g. CuO [4–7] or Co_3O_4 [8, 9]). In general, thermites can be ignited by laser or heating to undergo a redox reaction between the reactive metal and oxidizer, thus undoubtedly emitting a large amount of heat. Nanothermites have displayed more excellent properties compared with traditional thermites, such as shorter ignition time, larger energy release and higher reaction rate, due to their much

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https://doi.org/10.1016/j.matdes.2018.06.025

higher interfacial contact and shorter diffusion distance at the nanoscale. Moreover, the performances of nanothermites can be adjusted by careful controls in their morphology and interfacial contacts, and the molar ratio between the two components of nanothermites. Thus, it has been reported in the past two decades that nanothermites will have broad potential applications in micro-initiators [7, 10], micro-heaters [11], micro-thrusters [12], thermal batteries and gas generators [13, 14] etc.

As the research goes on, a variety of the preparation methods for nanothermites have been proposed already in the past, mainly including physical mixing [15, 16], self-assemble [17, 18], sol-gel [19], arrested reactive milling [20], electrophoretic deposition [21, 22], atomic layer deposition [23], thermal evaporation [24] and magnetron sputtering [8, 25, 26]. Each method has its merits based upon the needs in an individual application. Blobaum et al. prepared a reactive CuO_x/Al multilayer foil using the sputtering deposition method for the first time, and investigated the self-propagating reactions, the thermodynamics and kinetics of the CuO_x/Al thermite reaction [27]. Since then, many researchers have obtained multilayer nanothermite film of different metal oxides [28, 29]. To the best of our knowledge, owing to its shorter preparation period, uniform film formation, less impurity and more compatibility with MEMS technology than other methods, magnetron sputtering method has been employed more widely to fabricate thermite film.

Through the comparison of the reaction performance of different nanothermite structures, it is found that the nanothermite morphology can greatly affect their performance. Hence, it is important to control the formation of a homogenous morphology. Recently, one-dimensional NWs have always been used as a suitable carrier to fabricate thermites film with a core-shell structure as a result of the improvements in their mixing uniformity and contacting intimacy between the metal oxidizer and reactive Al, such as CuO/Al [30] and Co_3O_4/Al [8]. In general, one-dimensional metal oxide NWs can grow in the same size approximately vertically on the substrate to form an array structure, which can afford a largely accessible surface to ensure the sufficient contact with the fuel Al. According to the reported literature [9], the nanothermite film based on one-dimensional NWs structure has successfully led to an enhancement in the heat release and an improvement of ignition performance.

Meanwhile, numerous researches in metal oxides are concentrated on Bi_2O_3 [31], CuO [4, 7, 30], Co_3O_4 [8, 9], Fe_2O_3 [17, 19, 22], NiO [32, 33], MoO_3 [16, 20] and WO_3 [34], all of which are single and transition metal oxides. However, there are little studies on the bimetal oxides to be applied for nanothermites. It has been indicated that the binary or ternary composite metal oxides possess some special properties due to the combined features of simple metal oxides, such as catalytic property, synergistic effects and electronic properties [35], which can bring some excellent performances in the application of energetic materials [36]. For example, due to adding the nanometer-sized composite metal oxides, the thermal decomposition and combustion characteristics of ammonium perchlorate can be improved [35]. Through the integration of two or three metals in one oxide matrix, the composite system can produce novel nano-structured materials. Due to the superior electronic characteristic in the composite system, the desired energetic property can be readily achieved by the combination the oxides and fuel Al on a nanoscale. Among various composite metal oxides, spinel $NiCo_2O_4$, a magnetic bimetal oxide, is deem as a promising material in many fields because of its unique superiorities such as low-cost, high stability, relatively richness and eco-friendliness [37, 38]. More importantly, $NiCo_2O_4$ possesses a higher electrochemical activity and better electrical conductivity compared with monometallic nickel or cobalt oxides. The prominent performance is ascribed to sufficient redox reactions from both cobalt and nickel ions [38]. These fascinating features are greatly beneficial to its application in the field of NEMs. As far as we know, in the reported literature, $NiCo_2O_4$ has been mainly studied and applied in the supercapacitors [37–39], electrocatalytic application [40, 41], Li-ion batteries [42], Na-ion storage [43] and catalytic degradation of organic dye [44].

In this study, the $NiCo_2O_4$ NWs film has been selected as an oxidizer to prepare nanothermite film. A $NiCo_2O_4$/Al core-shell NWs thermite film was formed on the $NiCo_2O_4$ NWs template, which was fabricated by a conventional hydrothermal-annealing synthesis with the deposition of Al using magnetron sputtering. In order to study the $NiCo_2O_4$/Al molar ratio effects on the morphology, energy release and ignition performance, the $NiCo_2O_4$/Al core-shell NWs thermite films were designed with four different deposition thicknesses of Al. After the thermo-chemical properties of all the obtained samples were studied, the maximum value of the heat release of the optimized nanothermite film is 2076.0 J/g, which accounts for 52.7% of a theoretical value.

2. Experimental section

2.1. Materials

Nickel nitrate hexahydrate ($Ni(NO_3)_2\cdot 6H_2O$, 99%), cobalt nitrate hexahydrate ($Co(NO_3)_2\cdot 6H_2O$, 99%), urea ($CO(NH_2)_2$, 99.5%), ammonium fluoride (NH_4F, 96%) and absolute ethanol (C_2H_5OH, 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the chemical reagents were of analytical grade and they were used without any further purification. Al-NPs (99.9%) with an average diameter of 50 nm were supplied by Aladdin Industrial Corporation. Microslides (Nantong Flod Thai Experimental Instrumental Co., Ltd.) were used as substrates. Deionized water were used throughout all experiments.

2.2. Synthesis of $NiCo_2O_4$ NWs film

$NiCo_2O_4$ NWs film was synthesized using a typical hydrothermal-annealing synthesis method [45]. First, a microslide ($2 \times 4 \times 0.1$ cm) was ultrasonically cleaned by sulfuric acid, absolute ethanol and deionized water. Second, 0.194 g $Ni(NO_3)_2\cdot 6H_2O$, 0.388 g $Co(NO_3)_2\cdot 6H_2O$, 0.148 g NH_4F and 0.6 g $CO(NH_2)_2$ were dissolved in 50 mL deionized water under vigorous stirring to form a homogeneous solution. Then, this homogeneous solution and the cleaned microslide were sealed in a 50 mL Teflon-lined autoclave and maintained at 120 °C for 5 h. After the autoclave cooled down to room temperature naturally, the microslide was taken out and rinsed with deionized water and absolute ethanol to wash off reagent residues. Finally, the $NiCo_2O_4$ NWs precursor, which was deposited on the microslide, was calcined at 400 °C for 5 h in a muffle roaster to obtain the $NiCo_2O_4$ NWs film.

2.3. Preparation of $NiCo_2O_4$/Al NWs thermite film

The $NiCo_2O_4$/Al NWs thermite film with a core-shell structure was prepared using a magnetron sputtering in order to form a layer of Al film on the surface of as-obtained $NiCo_2O_4$ NWs film. During the whole sputtering process, ultrahigh purity Ar with a flow of 30 sccm worked as a functional gas. Simultaneously, the vacuum pressure in the working chamber and the substrate temperature were maintained at 5×10^{-3} Pa and ca. 30 °C, respectively. In order to explore the optimal molar ratio of Al to $NiCo_2O_4$ and obtain the optimal heat release and ignition characteristics of the $NiCo_2O_4$/Al NWs thermite film, the deposition thickness of Al layer was set to 150, 300, 450 and 600 nm.

For comparison, the $NiCo_2O_4$-NWs/Al-NPs thermite was fabricated by a traditional ultrasonic mixing [46]. The mixture of the fuel and oxidizer was prepared ultrasonically in the solvent of cyclohexane at a stoichiometric ratio for 30 min. Then, after the suspension was dried in a vacuum oven at 65 °C for 5 h, the $NiCo_2O_4$-NWs/Al-NPs thermite was formed.