Reactive Nano-Composites: Structure-Reactivity Relationship

Research Objectives

The primary goal of the work is to investigate the effect of ***short-term*** (<15 min) **high energy ball milling** (HEBM) on the microstructure and the reactivity of ***variety*** of nanostructured reactive composite materials, such as **Ni-Al, Ti-C, Ti-Si, Ta-C, Si-C, .**

Approach:

- ✓ Reactive composites are produced by ***short term HEBM***.
- ✓ The structures of the produced reactive nano-composites are characterized on ***micro-, nano-*** and ***atomic levels*** by high resolution electron microscopy.
- ✓ ***Ignition and combustion characteristics*** for the composites are determined relative to their structural parameters.

Experimental Methods

Preparation of Reactive Composites: short term high energy ball milling

Table 1. Milling Conditions

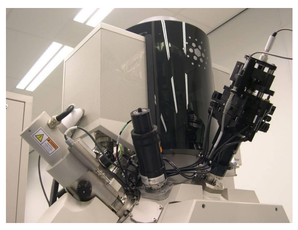
Milling Parameter	Value
Crash Ratio	40 : 1
Speed rpm	650
Milling Media	440 CSS, Ø 2 mm
Dry Milling (DM) Time	0-30 min
Wet Grinding (WG) Time (5 ml hexane)	0 - 15 min
Critical Milling Time (DM)	4-17 min

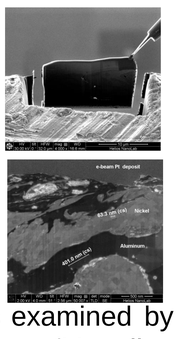
Planetary Ball Mill: Retsch PM100

Characterization :

I. Micro-, nano- and atomic structures

- BET specific surface area measurements (at 77K) for reactive composite particles are performed on a Coulter SA3100 analyzer;
- The phase composition of materials is determined by X-ray diffraction (XRD, D8 Advance, Bruker).

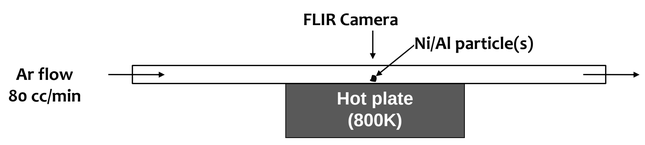




- *Micro- and nano-* structures of materials is examined by field emission scanning electron microscopy (Magellan 400, FEI) with resolution 0.6 nm, which is also equipped with a Bruker energy dispersive X-ray spectroscopy (EDS) analyzer;
- A Helios NanoLab600 system (FEI) with dual electron/ion beam is used to produce cross-sections of ball milled particles by ion milling with a gallium-ion beam.
- *Atomic level* structure analysis is performed by a FEI-Titan 80-300 transmission electron microscope (TEM) with information limit 0.1 nm.

II. Reactivity

The self-ignition temperature (T_{ig}), ignition delay time (τ_d) and velocity (U_c) of combustion front propagation for reactive composites are measured using a setup which includes a hot plate, a quartz tube and a high-speed infrared camera (FLIR SC6000; temperature range -10 – 2000ºC; recording rate up to 10^3 frames/s) to visualize the reaction process.
A particle or pressed compact of material is placed into a preheated (up to 800 K) quartz tube (300mm in length, 15 mm inner diameter and 1 mm wall thickness).



Before the experiment pure argon (99.9998%) is purged (80 cc/min) through the tube for 10 min to eliminate air. A high-speed infrared camera positioned above the opening allows measurement (spatial resolution of 2 mm, temperature resolution of 5 K and recording speed of 1000 frame/s) of the temperature-time history of the reaction process.

A Metter-Toledo Thermo gravimetric Analyzer and Differential Scanning Calorimeter (TGA/DSC) is also used to study the reaction onset temperature of milled materials. Apparent activation energies of investigated systems were estimated according to the Kissinger method [Anal Chem 1957 (29) 1702].

Results

General: several binary reactive systems have been investigated, including ***metal-metal*** (Ni-Al); ***metal – non metal*** (Ti-C; Ti-Si; Ta-C) and ***non metal – non metal*** (Si-C). These systems are characterized by different ductility/brittleness of the elements, as well as by the specific heats of the combustion reactions. It is demonstrated that, in all cases, short-term (4-15 min) HEBM significantly modifies the microstructure of the initial powder mixtures. More specifically such mechanical treatment leads to the formation of the ***composite particles***, which consist of both elements. In the bulk of the composite particles reagents have very high contact area with boundaries free of oxide layers. It is more important that micro volumes exist where reagent are ***mixed on nano/atomic level***. All above features lead to the ***significant decrease of self-ignition temperature*** for each system and ***increase velocity*** of the combustion wave propagation. It is worth noting that HEBM allows one to ***precisely control these combustion parameters***. For all above systems one can find conditions when ignition temperature ***is well below of melting point of any elements*** and intermediate products, thus ***solely solid state reaction*** govern the process. Finally, in some system (e.g. Si-C) it allows ***self-sustained mode*** of reaction, which ***cannot be accomplished*** in the initial mixture by any other means.

Ti-C System

- it is shown that after the first 2 minutes of dry milling (DM) in an inert (argon) atmosphere the initially crystalline graphite flakes were almost completely amorphized and uniformly distributed on the surface of the deformed titanium particles. A subsequent “cold-welding” leads to formation of Ti-(C-rich/Ti)-Ti agglomerates. TEM studies (Fig.1) reveal that the (C-rich/Ti) composite layers consist of nano-size (20 nm) Ti particles distributed in the matrix of the amorphous carbon and thus are characterized by extremely high surface area contacts between the reagents. A rapid self-ignition of the material during DM occurs just after 9.5 min of mechanical treatment, resulting in formation of pure cubic TiC.
- It was found that the ignition temperature in Ti-C structural energetic material prepared under optimized HEBM conditions is 600 K (Fig.2), which is more than three times lower than that of the initial reaction mixture (Tig 1900 K). A significant decrease of the effective activation energy for interaction in the Ti-C system is observed (from 95 kcal/mol to 56 kcal/mol). ***J. Appl. Phys*. 113 (2), 024302-024302-10 (2013).**

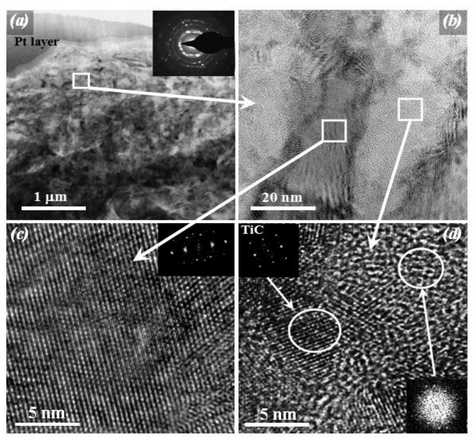


Fig. 1 TEM analysis of Ti/C particles obtained *after 7.5 min of DM: STEM image and a SAD pattern (a), HRTEM image of selected area (b) and enlarged images Ti (c) and TiC_x nano-crystallites (d)*

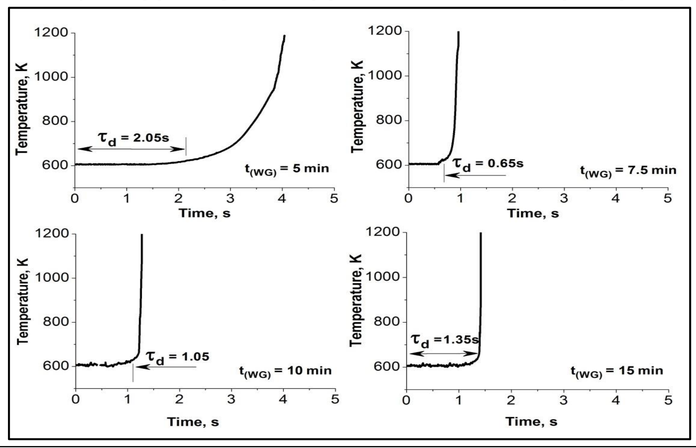


Fig. 2 Temperature - time profiles for dry milled materials with different milling times

Ni-Al System

Varying the ball-milling conditions allows control of the volume fraction of two distinct milling-induced micro structures, that is, coarse and nanolaminated (Fig.3). It is found that increasing the fraction of nanolaminated structure present in the composite particles leads to a decrease in their ignition temperature (Tig) from 700 and 500 K (Fig.4). Material with nanolaminated microstructure is also found to be more sensitive to impact ignition when compared with particles with a coarse microstructure. It is shown that the minimum kinetic energy thresholds for impact ignition, obtained for an optimized nanolaminated microstructure, is only 100 J. High-speed imaging showed that the impact-induced ignition occurs through formation of hot spots caused by impact, thus having thermal nature ***Phys. Chem. C*., 116 (39), 21027-21038 (2012);**

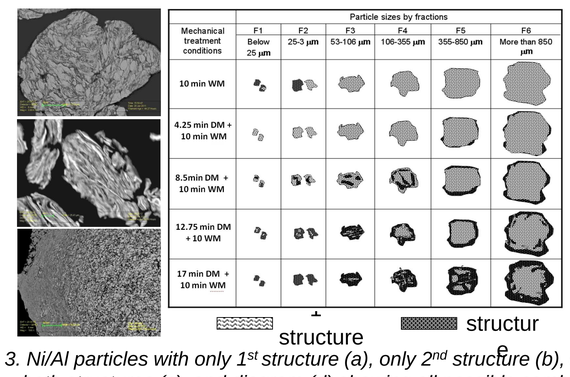


Fig. 3. Ni/Al particles with only 1st structure (a), only 2nd structure (b), combination of both structures (c), and diagram (d) showing all possible combinations.

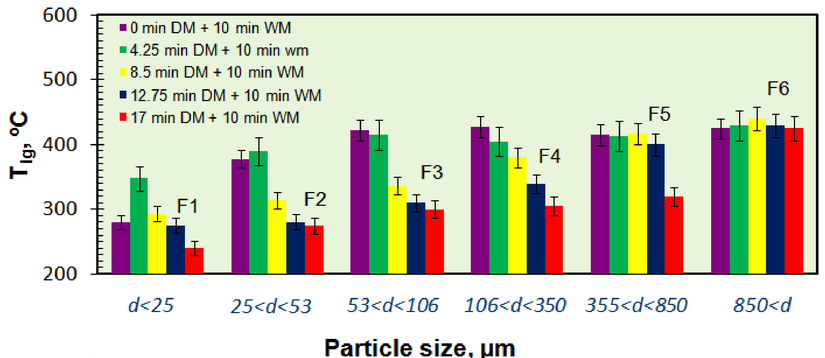


Fig. 4. Ignition temperature for Ni/Al materials obtained at various milling conditions as a function of particle size.

Si-C System

It was shown that influence of HEBM on the combustibility of the Si/C mixture (Fig.5) possesses a critical character: the self-sustained reaction (Fig.6) becomes feasible only after a critical time of ball milling (i.e., 10 min for 90G; 30 min for 17G). Comparison of the microstructures for as-milled and as-synthesized powders reveals that for all investigated conditions the morphologies of the as-milled reactive Si/C media are essentially the same as that for SiC combustion products (Fig.7). Thus for the first time direct synthesis of silicon carbide (SiC) nanopowders (size 50–200 nm, BET~20 m2/g) in Si–C system is conducted in an inert atmosphere (argon) using a self-propagating high-temperature. synthesis approach.
***J. Am. Ceram. Soc*., 96 (1), 111-117 (2013).**

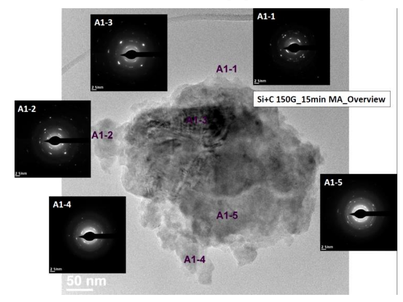


Fig. 5 . Nano-structure of the composite Si/C particle.

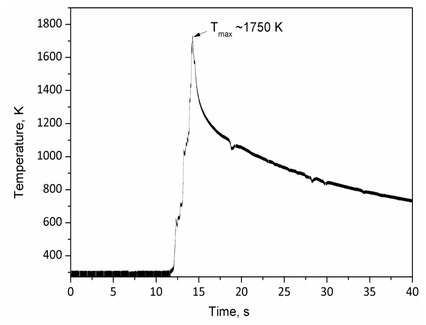


Fig. 6. Time-temperature profile of combustion wave for the sample subjected to 15 min of HEBM at 90G conditions.

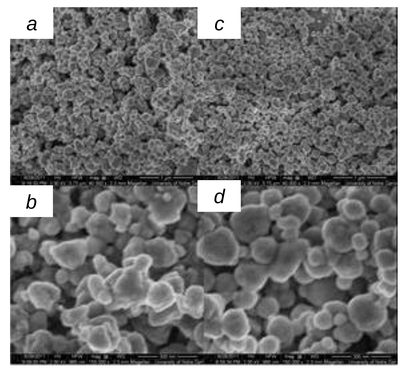


Fig. 7 . Microstructures of as milled (a,b) and as-synthesized () particles

Future Research Plans: Experimental

- Defining of the micro- and nano- structural parameters for composite reactive particles, which can be used for modeling of the ignition and combustion processes in such systems
- Finding the correlations between these parameters and the impact ignition thresholds.
- Validation of the theoretical predictions.

Acknowledgement

Funding from the Defense Threat Reduction Agency (DTRA), Grant Number HDTRA1-10-1-0119. Counter-WMD basic research program, Dr. Su M. Peiris, program director.

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