Ignitable reactive Al-Ni-Me_xO_y composite products by ball milling and ultrasonic powder consolidation

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Abstract

Hybrid, ignitable reactive composites of aluminium with nickel and metal oxides (Fe_2O_3, CuO) were fabricated by low-energy ball milling/mechanical alloying (BMA) and preheated ultrasonic powder consolidation (UPC). In BMA, lamellar particulates were produced and consolidated into pellets by cold-pressing, into sandwich sheets between thin aluminium foils, and loose admixtures with additional Al powders or coatings. In UPC, full-density consolidates of hybrid bimetallic-thermite systems were consolidated at various compositions. The resulting composites are ignitable by low-voltage electric discharge to high-temperature/high heat output self-propagating exothermic reactions (SPER). These were studied by differential scanning calorimetry (DSC) and infrared pyrometry, and the ignition temperature, exotherm enthalpy, adiabatic temperature and SPER front velocity were found to depend on initial composition, processing conditions, product particle/lamella distribution, and thermal impedance of the final material. BMA and UPC are shown to provide fast, robust, affordable and scalable routes for manufacturing of high value-added thermal composite products of aluminium for structural welding, electronic bonding and rapid thermal processing, self-sintering and self-heating materials, and tools for biomedical cauterization.

Keywords: Nickel; thermite; reactive nanoheater; ball milling; ultrasonic powder consolidation.

1. Introduction

Reactive bimetallic and metal-oxide (thermite) nanostructures (nanoheaters) based on aluminium have recently found renewed interest in applications such as microelectronics rapid thermal processing, welding and soldering; microcoating and microjoining; self-sintering powders, self-curing composites and self-heating materials; biomedical assay microchips and cauterization catheters etc [1]. This is owed to their demonstrated electrical or thermal ignitability to react and release highly-localized, instantaneous, precise amounts of heat through self-propagating exothermic reactions (SPER). To achieve desirable SPER performance (ignition level, adiabatic temperature, front velocity etc), the form and dimension distribution of such hybrid structures needs to be engineered via proper material and process engineering.

Recent developments in facile synthesis of ignitable, exothermically reactive nanostructures, has introduced the ultrasonic powder consolidation (UPC) process [3]. Reactive composites of compositions 2Al-Fe_2O_3-x(Al-Ni) and 2Al-3CuO-x(Al-Ni) (x = 1 - 4) were fabricated from nano-thick Al and Ni flakes and Fe_2O_3 and CuO nanoparticles by UPC. Application of in-plane ultrasonic vibration for 1 s at 573 K under a uniaxial pressure of 100 MPa produced full-density consolidates. In addition, bimetallic Al-Ni nanostructures [4], have renewed interest in the ball milling / mechanical alloying (BMA) process. Actively-cooled high-energy BMA has been attractive for continuous production, while low-energy BMA has been better suited to batch fabrication under experimentally controllable and observable conditions in the laboratory [5].

Both solid-state processes are presented in this paper for material particles including metal and oxide powders. The resulting consolidate structures consisting of globular and/or lamellar formations from the micro- to nano-scale are also studied through metallurgical and thermal analysis, assessing their SPER characteristics.

2. Ultrasonic power consolidation

2.1. Material preparation

For the UPC process, thermal plasma-synthesized Fe_2O_3 and CuO nanoparticles (20-40 nm and 30-50 nm in size, respectively) all purchased from Alfa Aesar and Al and Ni nanoflakes with sub-micron thicknesses (100-300 nm) produced by a proprietary ball-milling technique at Fukuda Metal Foil & Powder Co., Ltd. were used as the raw materials. Figure 1 shows SEM pictures of the as-received particles. The Fe_2O_3 and CuO nanoparticles were agglomerated. The Al and Ni flakes came coated with stearic acid to prevent pyrophoric reactions during commercial shipping and storage. Therefore, the flakes were first rinsed in agitated ethanol for 2 minutes and dried in air. Removing the acid did not cause pyrophoric oxidation as they were still protected by their pre-existing surface oxide.

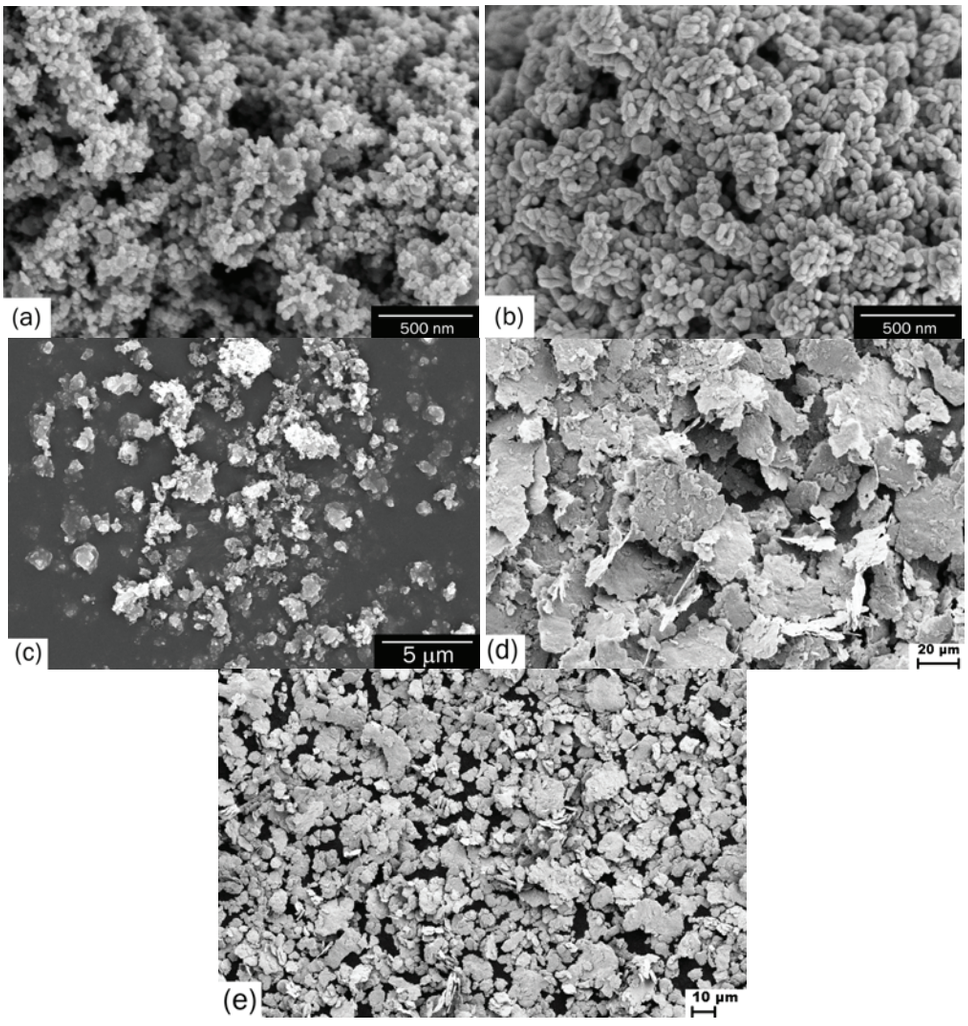


Figure 1. SEM pictures of as-received (a) Fe_2O_3 nanoparticles, (b) CuO nanoparticles, (c) Al_2O_3 particles , (d)Al flakes and (e) Ni flakes.

The Al and Ni flakes were then blended with metal oxide particles (Fe_2O_3 or CuO) in the molar ratios represented by 2Al-Fe_2O_3-*x*(Al-Ni) and 2Al-3CuO-*x*(Al-Ni) where *x* was varied from 1 to 4. The blended powders were dry-mixed in a cylindrical container 40 mm in diameter and 38 mm in depth rotating horizontally at 750 rpm for one hour with no mixing aid medium. No pyrophoric oxidation or reaction occurred. Then, the particles were further rotary-mixed for an additional hour in ethanol. This was followed by ultrasonic sonication in ethanol for 2.5 hours in order to reduce the agglomeration of Fe_2O_3 and CuO nanoparticles, and finally by an hour of additional rotary-mixing and 2.5 hours sonication, before drying in air and final pulverizing and dry-mixing for 20 minutes.

2.2. Fabrication

The powder mixtures were ultrasonically consolidated as shown schematically in Figure 2. The UPC setup employed a STAPLA Condor® ultrasonic welder which operated at 3 kW, a fixed frequency of 20 kHz and an adjustable vibration amplitude at the sonotrode tip of up to 9 μm. The UPC set up was also equipped with a heater plate to perform UPC experiments at elevated temperatures. The UPC experiments employed a die - punch arrangement, also depicted in Figure 2. The die and the punch were made of 2 mm and 3.5 mm thick stainless steel sheets, respectively, both of which had a matching diameter of 4.1 mm. The die was first placed on the heater plate kept at the desired consolidation temperature (which was optimized at 573 K in the present work). Then, about 0.1 g of powder mixture was placed in the die and held under a normal pressure of 100 MPa applied through the sonotrode and the punch. This heated the powder mixture to the set consolidation temperature typically in about 60 s. As soon as the powder compact reached the consolidation temperature, 20 kHz in-plane ultrasonic vibration was applied to the powder compact for 1 s at an amplitude of 9 μm through the sonotrode and the punch while keeping the compact under a normal pressure of 100 MPa. The consolidated specimen, 4.0 mm in diameter and 0.5 - 0.7 mm in thickness, and about 0.03 g in mass, was removed from the die immediately after the vibration was turned off.

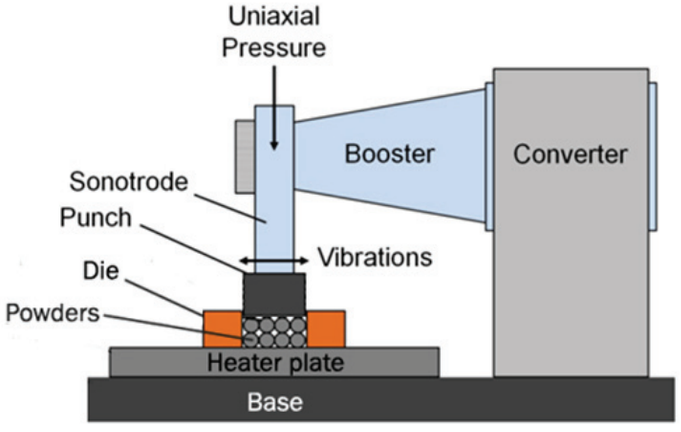


Figure 2. Schematic of the ultrasonic powder consolidation setup.

2.3. Metallurgical characterization

The as-consolidated nanoheater specimens were characterized by scanning electron microscopy (SEM) using a JEOL JSM-6360 SEM. The phases in the reacted specimens were identified by X-ray diffraction (XRD) using a Rigaku RU-300 rotating anode X-ray diffractometer with Cr Kα radiation and a Bruker AXS D8 Discover X-ray diffractometer with Cu Kα radiation.

2.4. Microstructure Results

Figure 3 shows SEM images of consolidated specimens of 2Al-Fe_2O_3-3(Al-Ni) and 2Al-3CuO-1(Al-Ni) composites in their cross sections. The–two composites exhibit microstructure consisting Ni flakes (light) and oxide particles (dark) distributed evenly in a fully densified and metallurgically bonded Al matrix (gray). The oxide particles are located both at the interface of Al and Ni flakes and within the Al matrix. Despite the long procedure of premixing and sonication used, the prior agglomeration of Fe_2O_3 and CuO nanoparticles, Figure 1, persisted in the consolidated hybrid composites, forming elongated clusters of Fe_2O_3 and CuO nanoparticles along the Al-Ni interface (arrows).

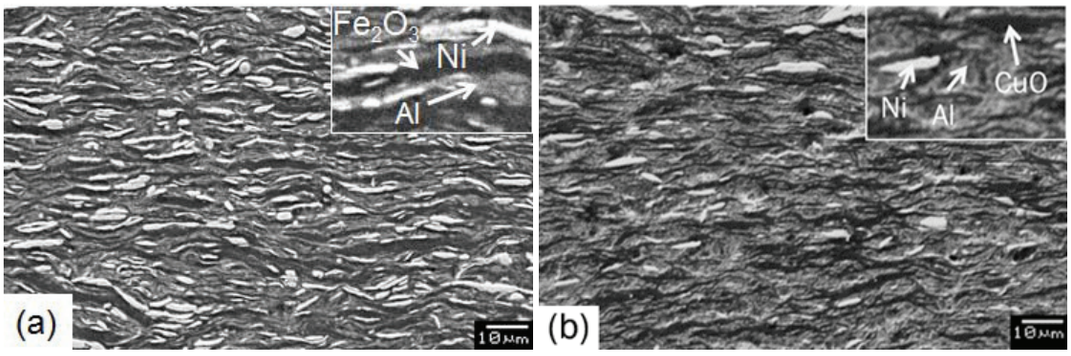
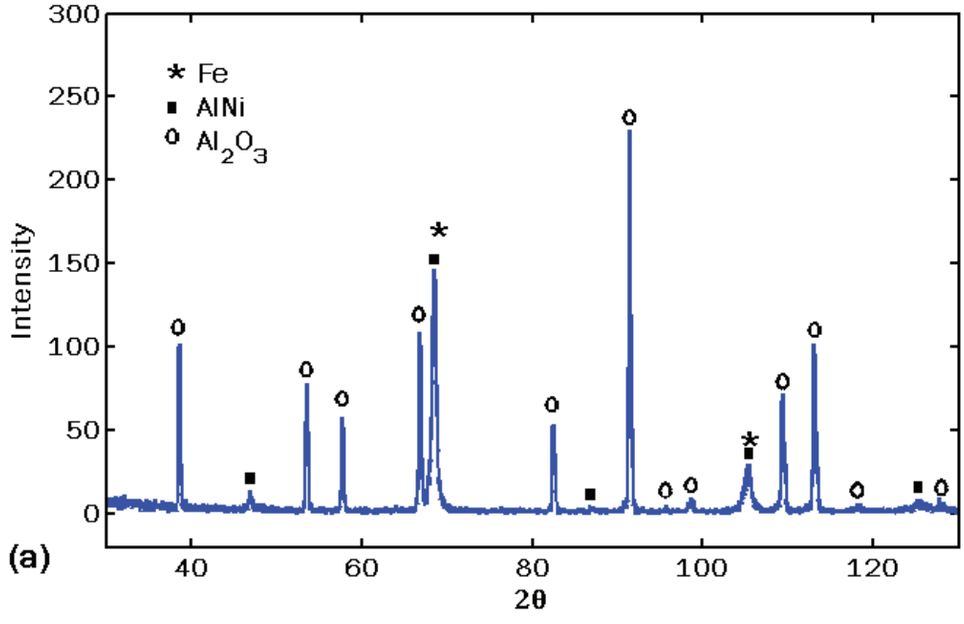


Figure 3: SEM images of (a) 2Al-Fe_2O_3-3(Al-Ni) and (b) 2Al-3CuO-1(Al-Ni) reactive composites, consolidated by subjecting premixed compacts to ultrasonic vibration for 1 s at 573 K under 100 MPa uniaxial pressure.

The consolidated composites all ignited when subjected to continuous heating at a rate of 2.08 K/s (125 K/min) in Ar atmosphere. The final reaction products in the 2Al-Fe_2O_3-3(Al-Ni) specimens were identified by XRD as Al_2O_3, Fe and AlNi in the 2Al-Fe_2O_3-3(Al-Ni), and Al_2O_3, AlNi and Cu in the 2Al-3CuO-*x*(Al-Ni) specimens, Figure 4.



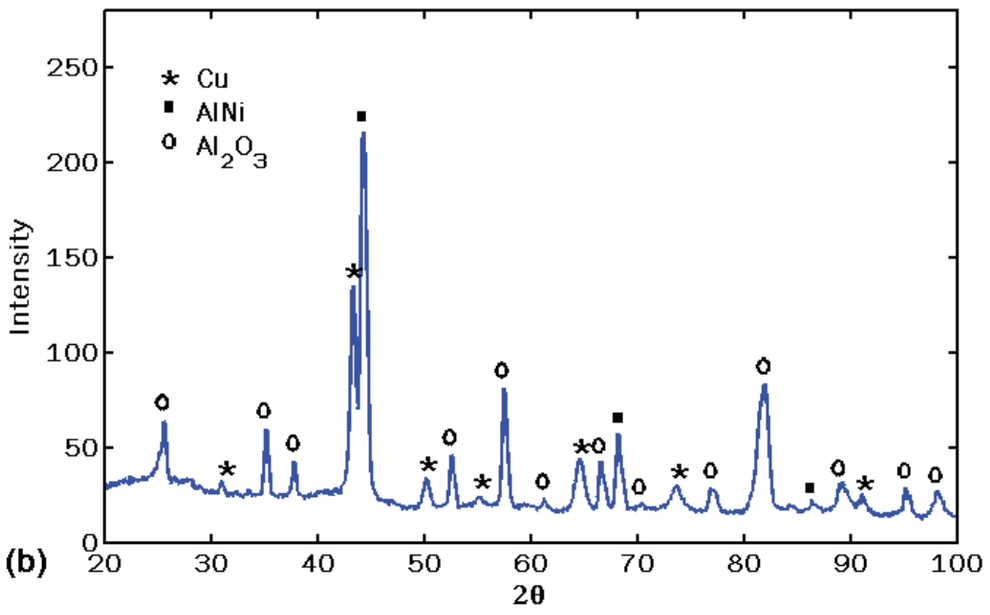


Figure 4. XRD patterns of ignited hybrid composites. (a) 2Al-Fe_2O_3-3(Al-Ni) and (b) 2Al-3CuO-3(Al-Ni).

3. Mechanical Alloying

Alternatively, ball milling (BMA) was carried out at room temperature in nitrogen atmosphere, in a low-energy planetary mill. Al (99.5 % purity) and Ni (99.95 %) powders of 325 mesh size, molar ratio of 1:3 and total mass of 32 g were processed by BMA. The laboratory setting used a cylindrical 80 ml vial, with five stainless steel balls of 20mm diameter, at rotation speed 300 rpm. The process was interrupted for sample removal and characterization. Figure 5 shows typical experimental scanning electron micrographs of ball-milled Al-Ni particulates after 2, 4, 6 and 8 hours of processing respectively. The sections show initially coarse globular packs of the harder Ni particles with intermediate softer Al particle "glue", gradually evolving into lamellar globules and finer planar lamellae of the two metals with increasing BMA time.

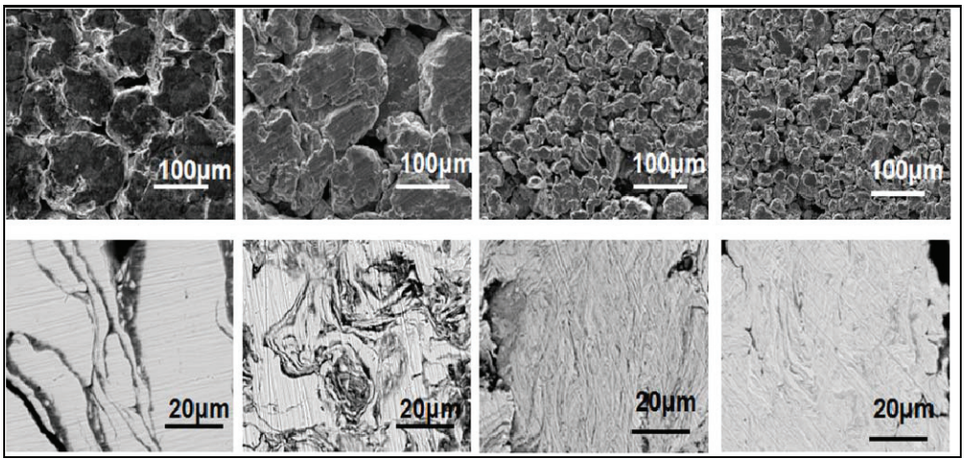


Figure 5. SEM micrographs (SE top row, BSE bottom row) of ball-milled Al (dark phase)-Ni (bright) particulates after 2, 4, 6 and 8 hours (respective columns).

3.1. Structural Characterization

In the SEM microstructures of the ball-milled consolidates, stiffer Ni particles (bright) tend to spheronize and disperse within Al (dark), while softer Al particles tend to flatten, planarize, bend and fill the gaps among Ni phase. Al-Al and Ni-Ni interfaces gradually smear into single domains, leaving Al-Ni bilayers visible. Initial spheronization (perimeter rounding) of clusters results from their omnidirectional impact and assembly orientations, because of plastic compression or frictional shear of powder asperities of high curvature yielding high local loads. Flattening of the particulates into lamellae results because of normal impacts in the direction of their shorter dimension, in which the smaller surface curvature makes it flatter and increases the probability for a collision due to the larger solid angle subtended. Moreover, further planarization of the BMA particulates into lamellae is due to frictional shearing, and their distortion occurs because of multi-point bending over stiffer spheroidal neighbor clusters.

3.2. Thermal Analysis

Figure 6 illustrates the continuous DSC scans of the samples up to1773 K (1500 ^{o}C) and the phases identified at various interruption temperatures [5]. All samples exhibited numerous exothermic peaks, followed by endothermic peaks starting at around 1653 K (1380 ^{o}C), corresponding to the melting of the remaining phases. Early samples showed a slight exothermic peak around 900 K, which is the eutectic temperature between Al and Al_3Ni, indicative of enhanced reaction due to the melting of the remaining Al (the endothermic peak is masked by the exothermic reaction). For later samples, Al must have been completely consumed by intermetallic growth by the time the temperature reached 900 K, as no peak was observed. The other exothermic peak locations shifted to lower temperatures with milling time up to 4 h and remained stationary afterwards with diminishing heat outputs, similar to other reports [6, 7].

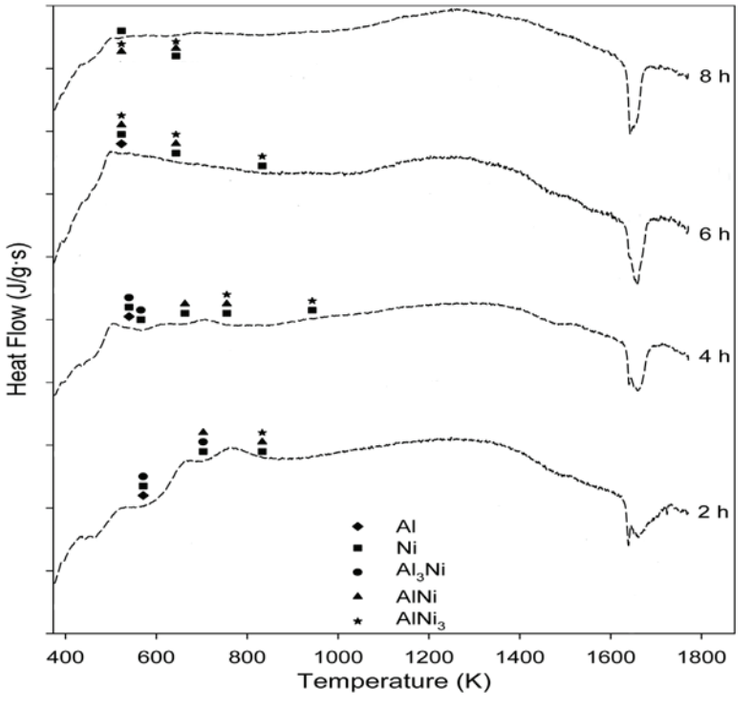


Figure 6. DSC scans for samples ball milled for 2, 4, 6 and 8 h with the intermediate phases observed with XRD on interrupted DSC scans. Each tick mark on y-axis corresponds to 1 J/gs.

Figure 7 shows IR camera images of samples of 2, 4 and 6 h of BMA time. The 8 h sample was not included because it did not react at all. The thermal front propagation of the samples milled for 2 and 4 h was very fast, such that it was not possible to withdraw the flame source before the thermal front had already travelled across the pellet. The images of the sample milled for 6 h indicate that the cooling due to the sample support was significant enough to affect the thermal wave front, which lost its uniformity when it passed beyond the halfway point on the pellets. The reaction velocities were two orders of magnitude lower than those of magnetron sputtered MFs that has an overall composition of AlNi [4, 5], which are much more reactive but were comparable to other ball-milled powders [5, 6].

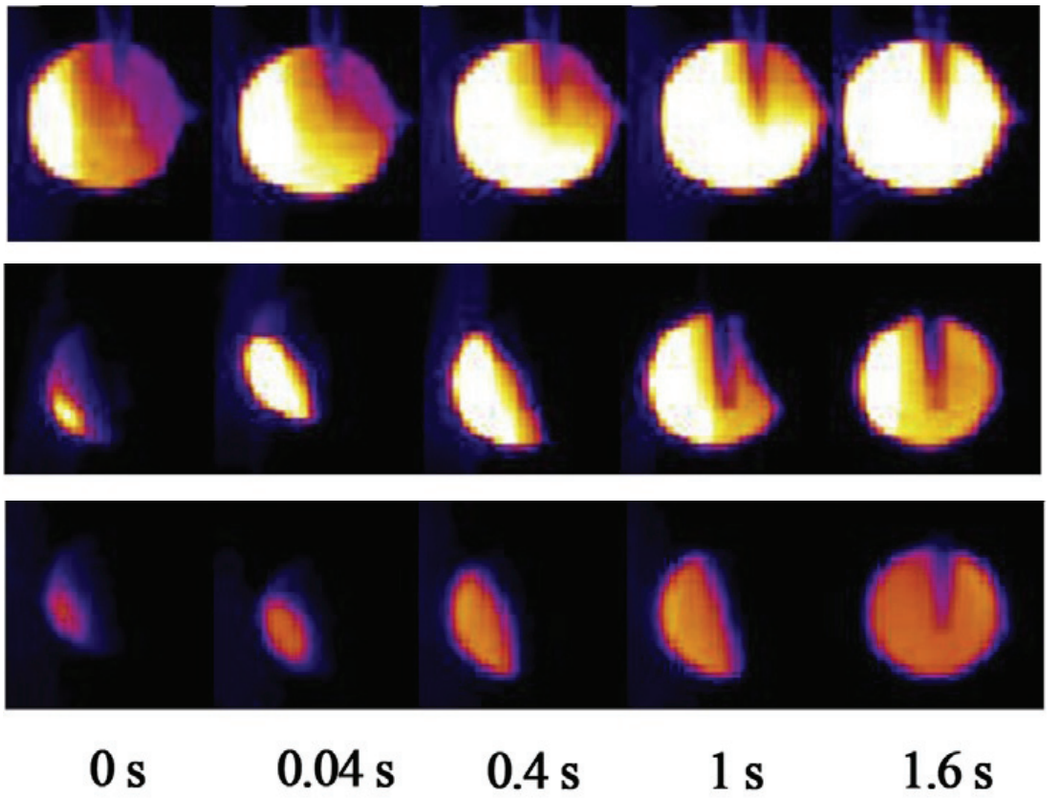


Figure 7. Infrared pyrometry images for samples milled continuously for 2, 4 and 6 h (respective rows), at various times after ignition.

4. Discussion and conclusions

Reactive composites 2Al-Fe_2O_3-x(Al-Ni) and 2Al-3CuO-x(Al-Ni) (x = 1 - 4), ultrasonically consolidated from nano-thick flakes of Al and Ni mixed with Fe_2O_3 or CuO nanoparticles at 573 K under 100 MPa pressure, exhibited a composite structure in which Ni flakes and oxide particles were distributed evenly in a fully densified, metallurgically bonded Al matrix. The 2Al-Fe_2O_3-1(Al-Ni) and 2Al-3CuO-1(Al-Ni) composites ignited at the melting point of aluminum, but all the other composites ignited well below the melting point, indicating that the reaction(s) between the Al and Ni flakes produced hot spots where liquid formed and triggered the ignition. Upon continuous heating at 125 K/min, the composites began self-heating just before they ignited. The hybrid bimetallic-thermite compositions, 2Al-Fe_2O_3-x(Al-Ni) and 2Al-3CuO-x(Al-Ni), combine the large heat output of the Al-metal oxide thermite reaction and the low ignition temperature of Al-Ni exothermic reactions in single reactive composites.

Similar bimetallic Al-Ni (1:3) lamellar micro/nano-structures were obtained with low-energy ball milling. Near optimum SPER behavior was obtained after 4 h of continuous milling with nanoscale lamellae and some remaining relatively thick Ni layers. BMA beyond the optimum point increases the solid-state diffusion of Al into Ni-rich solid solutions that negatively impacts the heat output and the thermal wave velocity. Upon proper activation, reactivity of such multilayer structures critically depends on the size distribution of the bilayer dimension, i.e. the thickness of its elementary components: Thinner bilayers between smaller particles, because of their higher surface/volume ratio, seem to require less specific activation energy and upon ignition tend to react at lower temperatures and faster rates, as the thermal conduction / material diffusion – limited reaction process needs to penetrate smaller depths; While larger components tend to react at higher stimuli with slower kinetics. Therefore, in a hybrid self-similar structure spanning a range of bilayer dimensions, uniform ignition activates smaller particles first, which upon reaction produce the necessary thermal activation (i.e. temperature raise) for larger particles to react and so on. The high thermal conductivity and low eutectic temperature of aluminium appears to play an enabling role towards such a cascaded SPER with a moving front.

5. References

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