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Exothermic reaction characteristics of continuously ball-milled Al/Ni powder compacts

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ABSTRACT

Self-propagating reactions in compacted pellets of continuously low-energy ball-milled aluminium (Al) and nickel (Ni) powders at a composition corresponding to $AlNi_3$ were investigated. The formation of a bi-modal structure with nanoscale lamellae of Al and Ni surrounding thicker Ni layers was observed. The milled powder sizes decreased for milling durations longer than 4 h, but the pellet green densities remained mostly constant for longer than 2 h of milling. The ignited pellets observed using high-speed optical and infrared imaging revealed that the thermal wave velocity, maximum reaction temperature, ignition initiation duration and ignition temperature decreased with increasing milling times due to solid-state diffusion. X-Ray Diffraction (XRD) analysis after ignition tests showed that the $AlNi_3$ amount increased with milling time. Thermal analysis using interrupted Differential Scanning Calorimetry (DSC) in combination with XRD revealed that the ball-milled pellets have similarities to nanoscale magnetron sputtered multilayer foils in terms of phase formation sequence and exothermic peak shifts.

1. Introduction

Materials with nanoscale features offer unique and enhanced properties compared to their conventional bulk forms [1–3]. One type of improvement is in the enhanced kinetics of exothermic reactions in bi-metallic foils consisting of many nanoscale multi-layers of aluminium (Al) and nickel (Ni). The reactions, started by local heating using an electrical spark or laser, self propagate at room temperature at layer thicknesses less than ~200 nm. Such materials have potential uses for micro/nanoscale device manufacturing through thermal material removal, deposition, joining, or shaping or as miniaturized thermal energy sources for such devices. The investigations of the reactions, microstructures and thermal characteristics of these foils showed that they have a low ignition threshold energy and the reaction velocity correlated well with the bilayer thickness [4–9]. One drawback is the manufacturing of these foils, which is based on vacuum deposition methods that are expensive and time consuming.

One possible economic processing route is the use of ball milling (BM), which can produce equivalent nanoscale lamellae within the powders of Al and Ni through mechanical deformations [2,3,10–18], AlNi and $AlNi_3$ intermetallics from elemental powders [10–23] or their nanocrystalline forms from alloyed powders [24,25]. Ball-milled elemental powders have been shown to be highly reactive when uniformly heated to react explosively, if the milling is interrupted before any intermetallic phases form [2,3,12,14,16,18–21,23].

The focus on the Al/Ni binary metallic system is due to the high stability of its microscale powders used in BM, which are relatively inexpensive, and the intermetallic compounds that have superior physical properties and highly exothermic formation enthalpies. The BM parameters can be carefully controlled to permit substantial milling of these powders before any reactions start in the vial.

An overall composition corresponding to $AlNi_3$ was selected to permit longer milling times to produce finer nanoscale lamellae, while ensuring that no intermetallics form, since the AlNi composition has been reported to be highly reactive, producing the intermetallic compounds during BM within 3 h (h) [10,11,14]. However, it is possible that low enough milling energies can permit longer milling times for the AlNi composition [15–17,21,22].

Our previous work focused on stopping BM before the reactions start and use the highly reactive powders to produce locally ignitable cold-pressed compacts that produce a visible self-propagating thermal front [2,3]. However, due to the removal of some powders from the mixture in interrupted BM runs, the total mass was reduced with each sampling point. Such changes increase the ball to powder mass ratio, affecting the reproducibility of the results and complicate comparisons of equivalent milling energy

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with other work. Additionally, previous studies reported that the ball-milled powders can react after the interruption when the vials are opened or shortly after the milling is resumed [10,15,16,19].

Therefore, we investigated the continuous BM of Al/Ni powders for different durations up to 8 h, where the ball to powder mass was held constant. The milled powders were cold-compacted into pellets and ignited along their edges using a propane flame source. The reactions were investigated using high-speed optical and infrared cameras to measure the thermal front velocity, local ignition and maximum pellet temperatures, overall sample temperatures during ignition and the time required for ignition. The pellets were characterized using Differential Scanning Calorimetry (DSC) to measure the overall reaction enthalpies. DSC scans were interrupted between the exothermic peaks. X-Ray Diffraction (XRD) was used to determine the phases that form before and after ignition, and for the interrupted DSC scans to compare the pellet thermal response and the phase evolution to those of vacuum deposited multilayer foils (MFs).

2. Material and methods

Al and Ni powders of 325 mesh with purities of 99.5% and 99.8% at a molar ratio of 1:3 were milled using a low energy Planetary Mono Mill "Pulverisette 6". 7.5 g of powder was placed inside the 80 ml vial with 5 stainless steel balls of 20 mm in diameter, corresponding to a ball to powder mass ratio of 21.8:1. In order to minimize Al oxidation before processing, the vial was sealed in a nitrogen glove box. Each sample was continuously milled for 1–8 h in independent BM runs at a milling speed of 300 rpm. BM was stopped at 8 h which showed AlNi phase formation during milling. Approximately 0.5 g of powder of each sample was compacted under a pressure of 500 MPa to form cylindrical pellets with a diameter of 10 mm and an average thickness of $\sim 1.3 \pm 0.1$ mm for ignition analysis. The density of the pellets was calculated using their mass and volume. The suspended pellets were ignited in air using a small propane flame directed on a small part of the pellet's edge, which was removed after ignition was initiated. Thermal wave was monitored using an infrared (IR - FLIR System A40 Thermovision) camera at 50 Hz with temperature ranges of 573 K (300 °C) to 1973 K (1700 °C) and 273 K (0 °C) to 773 K (500 °C), and a high-speed (HS-MegaSpeed) optical camera at 25 Hz. The pellet IR emissivity values were measured before and after reactions using a hot plate.

The pellets were characterized by scanning electron microscopy (SEM) in secondary electron (SE) and back scattered electron (BSE) mode (Tescan Vega LSU), XRD (Shimadzu 6000 Series) and DSC (Linseis TG-DTA/DSC). Continuous DSC measurements were carried out by placing the pellets in alumina crucibles and heating up to 1773 K (1500 °C) at a heating rate of 10 K/min under argon flow and additional interrupted DSC measurements were performed to determine the intermediate phases using XRD.

3. Results and discussion

3.1. Morphology and microstructure

Fig. 1 shows the SE, BSE and profilometry images of the polished surface of the unreacted pellets as a function of milling time. Increasing milling time resulted in particle size reduction, accompanied by the refinement of the microstructures with decreasing amount of pure Ni layers, which appear as light grey regions in the SEM images, similar to other work [2,3,18]. The transformation of the microstructures initially proceeded with the plastic flow of softer Al particles (darker grey regions) that mixed with the hard Ni particles up to 4 h of milling. The microstructure remained bi-modal with relatively large Ni layers surrounded by increasingly finer lamellae, comprising of sub-micron and nanoscale Al and Ni layers. Starting at 5 h of milling time, the particle sizes started to decrease and the microstructures showed more mechanical mixing and uniformly distributed lamella, possibly due to formation of Ni-rich solid solutions with Al as the solute, which are work hardened by the impact events during BM, as no other phases were observed in XRD data (Section 3.3).

3.2. Thermal analysis

Fig. 2 illustrates the continuous DSC scans of the samples up to 1773 K (1500 °C) and the phases identified at various interruption temperatures (reproduced from [26]).

All samples exhibited numerous exothermic peaks, followed by endothermic peaks starting at around 1653 K (1380 °C), corresponding to the melting of the remaining phases. Only the 1 h sample 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 other 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 [2,3,12].

Interrupted DSC analysis was performed on the samples to identify the phases that form after each peak using XRD except for the 1 and 8 h samples. Up to until 473 K (200 °C), no additional phases were detected. Therefore, the first peak at around 423 K (150 °C), which was very muted for milling times longer than 2 h, can be attributed to solid-state diffusion that yields larger amounts of solid solutions with increasing milling time, which have slightly exothermic heats of mixing. For example, the 7 h sample, which initially exhibits Al and Ni peaks, shows only Ni peaks at 473 K (200 °C). Fig. 3 demonstrates the results for the 4 h sample as an example, where the reactions continue until the endothermic melting peaks. The broad peaks starting around 1000 K (727 °C) in Fig. 2 are attributed to the slow growth of $AlNi_3$ from the remaining Ni-rich solid solution. For example, the 4 h sample had this broad peak starting around 850 K (577 °C) (Fig. 2), and the XRD analysis in Fig. 3 shows Ni peaks decreasing beyond this temperature.

The 2 and 3 h samples were similar in their phase evolution with three exothermic peaks. The phases present were (a) Al, Ni and Al_3Ni after the second peak, (b) Ni, AlNi and Al_3Ni after the third peak and (c) Ni, AlNi and $AlNi_3$ after the fourth peak. The endothermic peaks for the 2 h sample indicate melting of Ni-rich solid solution, $AlNi_3$ and pure Ni, whereas for the 3 h sample the melting of pure Ni was absent.

The 4 h and 5 h samples had five exothermic peaks with superimposed second and third peaks. It has been previously shown that these two peaks correspond to the formation of Al_3Ni when the growth mode switches from 1D to 2D [8,27]. The phases present were (a) Al, Ni and Al_3Ni after the second and third peaks, confirming these previous results, (b) Ni and AlNi for 4 h and additionally $AlNi_3$ for 5 h after the fourth peak and (c) Ni, AlNi and $AlNi_3$ after the fifth peak. The phase amounts shifted to an increasing percentage of $AlNi_3$ compared to AlNi with increasing temperature, until all of AlNi was transformed by 1073 K (800 °C). The endothermic peaks were similar, indicating the melting of Ni-rich solid solution and $AlNi_3$.

The 6 h and 7 h samples had four exothermic peaks, most of which were less energetic compared to previous samples. The phases that formed were (a) Ni, AlNi and $AlNi_3$ for the 6 h and Ni and AlNi for 7 h samples, (b) Ni, AlNi and $AlNi_3$ after the third peak