Microscopic Two-Color Infrared Imaging of Ni-Al Reactive Particles and Pellets

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Abstract

Non-contact temperature measurements using infrared detection are widely used for observing combustion in reactive materials. The most common method used is multicolor ratio pyrometry, where point measurements are taken at different wavelengths and the ratios are used to estimate temperatures. It is desirable to perform spatially and temporally resolved measurements at high speeds. We report a new design that employs optical elements coupled with a high-speed infrared camera. The system has a spatial resolution of 14 micrometers/pixel and can go as high as 3900 frames per second, while simultaneously obtaining images at two different wavelengths. The system was calibrated with a black body source to permit calculation of emissivities in addition to temperatures. Reactions were observed in single particles of mechanically activated nickel-aluminum and their pellets fabricated by cold pressing. The particles were ignited using a CO₂ laser heated hot plate at 670 K, whereas the pellets were ignited using an electrical spark. The particles show multiple reaction stages corresponding to melting of aluminum and peritectic decomposition of NiAl₃ and Ni₂Al₃, with maximum temperatures reaching 1450 K, before thermal losses quench further reactions. Particles within a reacting pellet go through the same stages, but continue reacting due to the additional heating from the neighboring particles and reach

maximum temperatures of ~1900 K, close to the estimated adiabatic temperatures assuming the final phase is NiAl (1911 K). Increasing milling time had little effect on the temperatures and ignition delays but increased the overall reaction rates in particles. The same phase formation sequence occurs for all the milling times but microstructural refinement increases the reaction rates due to diffusion limited growth. The emissivity of the particles rapidly increase to about 0.9 after initial reactions, then drops to around 0.5-0.6 after phase formations and melting, but continues to gradually rise to 0.7 due to oxidation during cooling.

Keywords: infrared thermography; high speed; mechanical activation; NiAl.

1. Introduction:

Infrared (IR) thermometry is a widely used non-contact temperature measurement method for the combustion of energetic materials. Its popularity is due to the many advantages it has over intrusive measurements using thermocouples. It is non-invasive and does not have thermal lag associated with thermocouples [1]. It also does not suffer from corrosive or catalytic effects due to flames that have radical species or aging due to elevated temperatures. However, its most important drawback is the effect of emissivity on the captured signal intensity and the subsequent conversion to temperatures. Any uncertainty in the object emissivity can be a large source of error. Additionally, emissivity can change during high temperature reactions due to the formation of new species, phase transformations such as melting and oxidation that changes the surface chemistry and morphology. One method to circumvent this problem is the in-situ measurement of emissivity using reflectivity measurements [2]. However, this is difficult to accomplish if the object reflectivity is low and it is also not feasible for certain wavelength ranges due to lack of available lasers or strong light sources. Therefore, the most common method used is ratio pyrometry, where signals are collected at two or more wavelengths and their ratios are taken [1, 2]. Assuming emissivity is constant in that particular wavelength range, the ratios can be accurately converted to temperatures. These measurements are usually taken at a single spatial point using optical

fibers and beam splitters, where the sensor readings are recorded at high readout rates. It is highly desirable to perform similar measurements using a spatially extended system such as an IR camera sensor and at high magnifications while maintaining speeds.

Recent developments in IR camera technology makes it possible to perform imaging at frame rates in excess of 10000 frames/second (fps) at near and mid-IR ranges (800-5000 nm). Although such measurements can be done using two cameras for ratio pyrometry, the cameras are expensive for this purpose and alignment of images to keep the object view similar is challenging, because variations in viewing angles can produce error. It is also hard to fit the cameras and optics in the case of microscopic imaging because of space limitations. Filter wheels that can be employed with a single camera are limited to about 1000 fps, thus they are not suitable for observing rapid events.

One model system that is of interest for these measurements is nickel (Ni) - aluminum(Al), which have intermetallic compounds with large exothermic formation enthalpies such as NiAl_3 , Ni_2Al_3 and NiAl [3-7]. The microscale powder mixtures of these metals start to react at the melting point of Al, driven by liquid Al wetting, followed by the formation of solid solutions and the intermetallic phases [8-10]. All the mixing enthalpies are exothermic, so the heat liberated drives the combustion wave upon ignition. Nanoscale multilayers of this system produced using magnetron sputtering ignite at the solid state and react at much larger velocities due to reduced diffusion distances and possible formation of metastable states [11-14]. Similarly, mechanical activation (MA) using ball milling can be used to form particles consisting of Ni-Al laminates with nanoscale dimensions having similar combustion properties [15-23]. Due to the rapid nature of the reactions, it has been challenging to identify phase formation sequences in these nanostructured systems.

The objective of this paper is to describe and demonstrate a new two-color imaging system with a spatial resolution of $14\text{ }\mu\text{m/pixel}$ that can go as fast as 3900 fps, while simultaneously obtaining images at two different wavelengths within a high-speed IR camera frame for identifying reaction stages in the

MA Ni-Al particles and pellets. The system when calibrated is capable of giving an emissivity history at these wavelengths as well as temperatures.

2. Methods:

2.1 Two-color IR imaging:

The schematic for the two-color imaging system is shown in Fig. 1. The 50:50 non-polarizing near-IR beam splitter cube had an edge size of 20 mm (ThorLabs BS018). The 25.4 mm diameter band pass filters had central wavelengths at 1400 and 1500 nm with 12 nm full width half maximum (Edmund Optics). The wavelengths were selected to be sufficiently close so that the emissivity variation with wavelength would be small to justify a greybody assumption, while maintaining a good signal to noise ratio as dictated by the camera responsivity shown in Fig. 2. Although the 1400 nm is close to the H₂O absorption band, the system of interest here do not produce any gaseous H₂O products and this effect is negligible. In any case, this can be mitigated by using a different wavelength filter such as one centered at 1600 nm. The two turning mirrors were front-coated with Al (ThorLabs). The Au coated knife-edge prism mirror had an edge size of 10 mm with a 90 degree angle (Edmund Optics). The focusing lens was LM50JC from Kowa. The aperture was set at f/11 to reduce cross talk. The optics were placed such that the average path from the front focusing lens to the detector was 75 mm. The imaging was performed using a FLIR SC2500 camera with an exposure time of 250 μ s and a frame rate of 3900 fps. The frame rate was limited by the window size that was set at 160x28 pixels. The prism mirror reflects the two separate images coming through the two filters on the camera sensor, forming two mirror images side by side. The spatial resolution of the system was 14 μ m/pixel. The transmission curves for the optics, filters and the camera responsivity were multiplied with blackbody curves (Fig. 2) at different temperatures and then integrated across filter wavelengths to calculate filter intensity ratios. These ratios were tabulated for each temperature and the relation between the ratio and the temperature was fitted to a 6th

order polynomial. This allows the calculation of the temperature, when a ratio is measured from the experiments. The system was also calibrated using a blackbody source with an emissivity of 0.925 at 1200 K and a calibrated tungsten lamp operated at 2800 K with an emissivity of 0.3 using an Optronic Laboratories OL-65A power supply. By using the known temperature and the ratio of absolute intensities with the blackbody sources, the emissivity can be calculated. The sensitivity of the system allowed measurements of temperatures above 1000 K.

Figure 1: The schematic shows the two-color setup and the ignition system. The IR images are post-processed to perform ratio pyrometry.

Figure 2: The spectral response of the infrared camera, filters and a blackbody curve at 1900 K. The total response is the product of the curves. The curves are integrated to calculate intensity ratios for ratio pyrometry.

2.2 Mechanical Activation Procedure

Al (Alfa Aesar, particle size -325 mesh) and Ni (Alfa Aesar, particle size 3-7 μm) powders were ball milled at the NiAl composition. The milling system used was a Retsch PM100 planetary ball mill with a 250 mL stainless steel jar. Stainless-steel balls with diameter 10 mm were used as the milling media. The ball-to-powder ratio was 5:1 with a mixture mass of 34.5 g and the rotational speed was 650 rpm. The critical milling time, which is the time it takes for the materials to react during milling at these settings is 17.5 minutes. The material was milled using a two-step milling procedure. First, the materials were dry milled for 4.25, 8.5, 12.75 and 17 minutes (min), denoted as 25%, 50%, 75% and 97% of the critical milling time T_{cr} . Subsequent wet milling in hexane was performed for a total of 10 min with the same milling conditions. In all cases, the material was milled in a high purity (99.998%) argon (Ar) atmosphere. After wet milling, the samples were vacuum dried at 300 K for 24 h to remove any residual hexane. Once dry, the materials were sieved in the particle size range of 355-850 μm .

2.3 Combustion Experiments:

For single particle experiments, a hot plate was fabricated using an alumina DSC pan cover with a diameter of 6.35 mm and a thickness of 500 μm . A 100 μm wire diameter K-type thermocouple was attached to the center of the plate using zirconia ceramic paste to monitor the temperature. A CO_2 laser (Coherent GEM 100A) beam was focused and directed towards the bottom of the plate using two turning mirrors to heat it to a temperature of 670 K within 500 ms, which was determined to be the minimum temperature to ignite all the particles. This is also the reported ignition temperature for these particles heated on a regular hot plate [17]. The $1/e^2$ spot diameter was 4 mm. The single particles were

manually placed on top of the plate at the center of the heated spot for ignition and the optics were set for imaging them from the side. Direct laser heating of particles was avoided to minimize variations due to possible differences in particle absorptivity that might change heating rates. Approximately 15 particles were hand selected for each milling condition.

The particles were also cold pressed into cylindrical pellets using a Carver press, using a 12.7 mm diameter die from MTI Inc. The pressing force was 6 tons. The final density was approximately 80% of the theoretical maximum density (TMD). The pellet height was approximately 1 mm. The pellets were suspended sideways using metallic tweezers and ignited at one edge using a spark. The reaction was monitored using the same IR setup focused on a few particles on the pellet.

2.4 Characterization:

Differential scanning calorimetry (DSC) was performed using a TA Instruments SDT Q600. Samples with a mass of around 25 mg were placed in alumina pans and heated up to 1000 K at a heating rate of 20 K/min under an oxy-argon (20%-80%) gas flow with a flow rate of 100 ml/min to simulate the ambient environment. The particles were collected after reactions and their diameters were measured using an optical microscope. SEM imaging on these particles are reported elsewhere [17].

3. Results:

3.1 Particle microstructure

The evolution of the particle microstructure as a function of milling time was investigated previously [17]. The shorter milled particles have coarse layers of Ni and deformed Al but most of the fine mixed structure is on the surface of the particles. As the milling time is increased, more of the well mixed zones are incorporated within the particles. These finer nanolaminates have characteristic lengths that are sub-micrometer and have been shown to ignite at lower temperatures and react faster compared to coarser parts [17, 20].

3.2 Thermal Analysis

The DSC scans on Fig. 3 show at least three exothermic peaks, which are associated with the formation of NiAl_3 , Ni_2Al_3 and NiAl as observed in other studies on ball milled powders and microscale multilayers [17, 20, 22]. The absence of any endothermic peaks indicate that all the Al reacted to form intermetallic compounds before reaching its melting point. For the shorter milled particles (25% T_{cr}), the peaks were very distinct. The peaks for longer milled samples were broader and overlapping, and especially the second peak related to the growth of Ni_2Al_3 was muted. This can happen if multiple phases are forming at lower temperatures but their growth rates remain unaffected. The peak temperatures for the first two peaks were not significantly affected. Only the third peak position was lowered by about 40°C for milling times longer than 25% T_{cr} . This indicates that the formation of NiAl is slightly enhanced and the overall conversion rates are somewhat higher for longer milled samples. These observations are in contrast to smaller particles milled at the same conditions [17], which show more significant shifts in peak temperatures. The most probable reason is the relatively coarse microstructure of these larger particles. As the milling time is increased, larger proportion of the particles are fine nanolaminates. It is possible that the nanoscale mixing induces particle fragmentation, so the smaller particles are more reactive. The heat of reactions from the integrated peaks are 1278 J/g, 1258 J/g, 1284 J/g and 1283 J/g for 25%, 50%, 75% and 97% T_{cr} respectively. The ideal NiAl formation enthalpy is 1372 J/g indicating that a small amount of chemical mixing occurred during milling. Smaller particles reported elsewhere show more significant reductions due to partial reactions and diffusion during milling [17]. The adiabatic temperatures calculated are all 1911 K, corresponding to varying fractions of liquid NiAl in the final semi-solid NiAl mixture.

Figure 3: The DSC scans for particles milled for different durations. The milling time causes the distinct peaks to start to overlap due to nucleation and growth of different phases. The first peak temperature was not affected but the last peak temperature was shifted to lower temperatures with milling time. The total reaction heats were close to 93% of the theoretical formation enthalpy of NiAl for all milling conditions indicating little mixing occurs during milling.

3.3 Combustion Experiments:

A typical frame for a particle milled at 25% T_{cr} at an intermediate stage of reactions is shown in Fig. 4. As the particle is heated to the target temperature, the first sign of self-heating occurs before the end of the laser pulse. The particle heats up uniformly at this stage. The temperature at this first kink is approximately 1000 ± 50 K, and corresponds to the melting of the remaining Al in the particle that has not formed an intermetallic. At some point, a hot spot forms at an arbitrary location within the particle (at center top area in this case) and a very rapid front moves across, reaching velocities up to 1.5 m/s. This is due to the relatively inhomogeneous microstructure of the milled materials, which has areas with different characteristic thicknesses. This second reaction could be resolved for the shorter milled particles but it is faster than the interframing time of 256 μ s for the 75% and 97% T_{cr} milled materials. The temperature for the onset of the second reaction was measured to be 1200 ± 100 K. This point is close to the peritectic decomposition temperature of NiAl₃ (1183 K), which forms more Al-rich liquid

and Ni_2Al_3 . Either the nucleation of rapidly growing Ni_2Al_3 or formation of a liquid phase might be driving this rapid reaction. The particle also shoots up with speeds up to 0.3 m/s and often goes out of the imaging window for the longer milled materials due to this stage of reactions. This was also observed with purely dry milled particles, so the jump is not due to internal gas generation. It is most likely that the thermal expansion due to this rapid reaction moves the particle depending on the reaction rate. For example, using the thermal expansion coefficient of NiAl ($15 \times 10^{-6} \text{ K}^{-1}$), ΔT of 200 K, spherical particle with a diameter of 500 μm , NiAl elastic modulus of 150 GPa at this temperature [24], the maximum stress and the average force during expansion on a contact area with a radius of 25 μm is around 450 MPa and 0.45 N respectively. Using conservation of energy for the particle with a density of 5.9 g/cc (mass of about 0.39 mg), the final velocity can be roughly around 1.3 m/s, which is within the same order of magnitude as the observed velocities. This second reaction is limited at a temperature of $1500 \pm 100 \text{ K}$, corresponding to the endothermic peritectic decomposition temperature of Ni_2Al_3 (1406 K) into more Al-rich liquid and NiAl. The single particles do not heat up further. Since NiAl growth rates are approximately three orders of magnitude slower compared to Ni_2Al_3 at this temperature [7], its formation might arrest reactions. The particles eventually cool down below 1000 K within $\sim 150\text{-}200 \text{ ms}$.

Figure 4: (a) Frames from a reacting particle milled for 25% T_{cr} show initial slow uniform heating followed by a rapid reaction originating at a point at the top of the particle and propagating across the rest of the particle. The reported times are with respect to the start of the laser. (b) The maximum intensity and (c) maximum temperatures from the same particle. The insets show the initial reaction stages.

The temperatures at the kinks are plotted as a function of particle size and milling time in Fig. 5, showing no clear correlations with particle size. Most of the scatter at temperatures can be attributed to particle microstructure variations due to stochastic nature of ball milling as well as uncertainties in the

IR imaging and errors due to interframing times. For all the milled samples, these temperatures were close within error bounds pointing out to similar phase formation sequences, where the only difference was in the kinetics of the reactions. The ignition and overall reaction times for different milling times and diameters are shown in Fig. 6. The ignition times were all comparable and clustered around 500 ms, the end of the laser heating, indicating that the particles have to reach a temperature of 670 K before self-heating becomes significant. This compares well with the DSC results, which show the initial reaction related to formation of NiAl_3 happens at the same temperature for all milling times. The overall reaction durations showed considerable scatter but the general trend is a reduction with increasing milling time. This can be also compared to DSC that shows a reduction in the temperature of the last peak, so longer milled samples can be expected to finish reacting quicker. This also suggests that the nanolaminate thicknesses may be smaller to improve kinetics.

Figure 5: (a) The first kink temperatures that correspond to the initiation of the rapid reaction wave and (b) maximum particle temperatures plotted as a function of diameter for different milling times. The temperatures are relatively invariant within the error bounds and roughly correspond to the peritectic decomposition temperatures of NiAl_3 (1183 K) and Ni_2Al_3 (1406 K).

Figure 6: (a) The ignition times show no correlation to particle diameter or milling time. (b) The reaction times are generally shorter for longer milling times but there are outliers for all cases possibly due to microstructural variations among particles.

On the other hand, particles within pellets reacted further. The temperature evolution measured from one particle within a pellet pressed from 25% T_{cr} milled material is shown in Fig. 7. The particle initially reacts rapidly within 1 ms due to higher heating feedback from the neighboring reacting particles as opposed to hot plate heating at 670 K. The particle reaches the temperature 1450 ± 50 K after this wave and continues to heat up until reaching 1714 ± 50 K within 5 ms and starts cooling down. This is most probably related to endothermic melting of the remaining Ni-rich solid solution slowing the reactions. Initially, the heat losses are large due to the high conductive losses to the rest of the pellet. The particle cools down to 1410 ± 50 K and remains at that temperature for about 10 ms before it starts heating up again. The final reaction proceeds until temperature reaches 1850 ± 50 K. The 97% T_{cr} milled material pellet showed a similar initial sequence rapidly reaching 1450 ± 50 K and moderate heating up to 1715 ± 50 K within 3 ms. The heating slowed down but the particles did not cool down like the shorter milled sample and continued to slowly react and heat up for 35 ms, so the self-heating rate was sufficient to overcome the cooling due to endothermic melting of Ni. A kink could also be observed at around 1770 K ± 50 K, where the heating rate increased until reaching the final temperature of 1850 ± 50 K. The difference between the two milling times can be attributed mostly to the larger proportion of refined

nanolaminates within the particles, but it is possible that a reduction in nanolaminate size with milling time enhances the reaction kinetics due to an increase the interface area per unit volume.

The emissivity of the metallic particles is quite low as for pure Al, which can be estimated to be around 0.1-0.2. The emissivity of the particles within pellets increase rapidly to 0.9 with the initial reactions but goes down to around 0.55 after reactions are complete. Typically, molten metals have lower emissivities than solids, so the melting might be the reason for this drop. Eventually, the emissivity increases slightly to around 0.7 possibly due to some oxidation occurring on the surface. This shows that assuming a constant emissivity would be a poor assumption for IR measurements on similar reacting systems. In general, emissivity calculations were very sensitive to movements of the sample during reactions. Image stabilization methods can be used to get more accurate values.

Figure 7: (a) Maximum temperature of a particle within a pellet plotted against the arrival time of the reaction wave for 25% and 97% T_{cr} milled samples. (b) Emissivity variation for the same samples.

Conclusions:

A two-color high-speed high-magnification infrared imaging system was used to observe reactions in mechanically activated Ni-Al system. The system had a frame rate of 3900 frames per second and a

spatial resolution of 14 μm per pixel, while simultaneously imaging at wavelengths of 1400 and 1500 nm. The sensitivity of the system allowed measurements of temperatures above 1000 K. The particles were ball milled at different conditions and ignited using a CO_2 laser heated hot plate. Green compacts of the particles were ignited using a spark. The temperature evolution in particles show discontinuities in slope, corresponding to change of rate of reactions, due to endothermic transformations such as the peritectic decomposition of NiAl_3 and Ni_2Al_3 and indicates the presence of these phases during rapid reactions. The decomposition of NiAl_3 triggered very rapid rises in reaction rates possibly due to nucleation of Ni_2Al_3 , which is the fastest growing phase in the Ni-Al system. The reaction front velocities were up to 1.5 m/s within a particle. The particles were observed to eject from the hot plate at speeds up to 0.3 m/s due to rapid thermal expansion during this reaction. The heat losses were significant for single particles, whose reactions did not go beyond the peritectic decomposition temperature of Ni_2Al_3 , which was short of adiabatic temperatures calculated (1911 K) from differential scanning calorimetry. On the other hand, single particles within pellets reacted further after following the same reaction steps and reached temperatures of around 1870 K, The emissivity of the particles rapidly jumped to 0.8-0.9 within the initial part of the reaction, went down to around 0.5-0.6 and went up to 0.7 during cooling possibly due to oxidation.

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List of Figure Captions

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