The Utilization of Metal/Metal Oxide Core-Shell Powders to Enhance the Reactivity of Diluted Thermite Mixtures

Karsten Woll¹, John David Gibbins, Kyle Slusarski, Alex H. Kinsey, Timothy P. Weihs[#]

Department of Materials Science and Engineering, Johns Hopkins University, 21218 Baltimore (MD), USA

Abstract

When thermite mixtures combust considerable amounts of gas can be released which impedes their application in the field of joining. Diluting the thermite mixture with excess metal can lower the reaction temperature and thereby minimize mass ejection. However, increasing the degree of dilution reduces reaction efficiency. This paper demonstrates that the reduction of reaction efficiency is significantly less for the Al:NiO thermite system if the excess metal (Ni) is added using a fuel/core-shell mixture in which Al fuel particles are mixed with Ni/NiO core-shell particles. The use of Ni/NiO core-shell particles reduces the average distance for Al and oxygen intermixing by placing the fuel (Al) in direct contact with the oxide (NiO), separate from the diluent (Ni). Mixtures comprised of Al and Ni/NiO core-shell powders were fabricated, characterized, and compared to compacts fabricated using conventional Al, NiO, and Ni powders for dilutions up to 40 wt% Ni. The fuel/core-shell particle geometry increased combustion front velocities for all Ni dilutions. Mass ejection decreased uniformly for both particle geometries as the degree of dilution increased.

Keywords: Energetic Material; Thermite; Aluminum; NiO; Self-propagation; Core-Shell Particle;

¹now at: Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), 76344 Eggenstein-Leopoldshafen, Germany

[#]corresponding author: weihs@jhu.edu

1. Introduction

The reduction-oxidation (redox) reaction between a metal oxide and Al that forms a molten metal and alumina has been utilized in joining applications for nearly 100 years [1,2]. The classic application is the welding of railroad lines [3,4]. In this particular case iron oxide reacts with Al and the molten iron product flows out of a crucible and into a mold surrounding the joint. The less dense alumina floats to the top of the crucible and is discarded. More recent studies have demonstrated that copper-based thermite reactions can enable welding of copper conductors under reduced gravity in space [5], and self-propagating thermite reactions have been observed in thin multilayered foils [6-11]. The combination of a foil geometry and the release of large heats and molten products suggests there is potential for utilization of thermite reactions as very local heat sources for joining. When placed directly between two components, such foils may transfer the traditional railroad line welding application to a smaller scale as well as enable other types of joining such as soldering and brazing [12]. Unlike welding in which one melts the components being bonded, in soldering and brazing, a filler material melts and wets the components to enable bonding [13]. The components, themselves, do not melt. In the case of soldering, the filler material turns liquid below 450 °C and for brazing the filler material melts above > 450 °C.

Soldering with reactive foils that are based on formation reactions is an established commercial process called NanoBond™ [14,15]. These foils release heat based on the formation of intermetallic compounds, and melt pre-existing solder layers on have been place on the components. The redox reaction inherent to thermite-base reactive foils offers two significant advantages for joining compared to intermetallic formation reactions. First, the higher reaction temperatures of the redox reactions make them more capable of enabling brazing of components. Second, the molten metal produced by the redox reaction can act as a filler (brazing) material, thereby eliminating the need for pre-existing solder or braze on the components being bonded. It is anticipated that these advantages of the redox reactions have the potential to broaden the range of joining applications that can be addressed with reactive foils acting as local heat sources.

While redox reactions produce substantial heat and a molten braze, most of these reactions also produce large amounts of gas [16, 17], leading to material ejection and detrimental pore formation during bonding. Both of these factors limit joint strength. Consequently, the utilization of redox reactions in joining applications requires a significant reduction in gas release. This study explores minimization of gas production in the Al-NiO thermite system, a chemistry for which gas release is already limited [17]. The main factors thought to determine the degree of gas generation and the peak pressure for a given system are the heat of reaction, ΔH_{rx} , and the combustion front velocity, v [18]. $\Delta H_{rx} = 3,445 \text{ J/g}$ [17] for the Al-NiO system and leads to an adiabatic reaction temperature, T_{ad} , of 2914 °C [17] and gaseous Ni in the reaction products. Researchers have shown that they can affect ΔH_{rx} , T_{ad} , and v by varying the geometry or the composition of the thermite mixture and, in doing so, can reduce gas generation [18-25]. Researchers reported that three parameters can substantially reduce the amount of gas released: 1) increasing the particle size [18, 21, 22] 2) altering the fuel/oxide stoichiometry [20, 23], and 3) adding inert diluents, such as oxides and metallic elements [24,

25]. Minimization of gas production with excess metal is the focus of the current study because the excess metal has the added benefit of increasing the percentage of braze in the final bond area.

Recent studies have reported on the addition of excess metal in loose thermite mixtures with heterogeneous microstructures [26-28]. Shen et al. studied the addition of nanosized Ag powder to the Al-CuO system [26]. They diluted this thermite mixture up to 10 wt.% Ag and observed that front velocity initially increased, peaked at 2 wt.% dilution, and then decreased substantially on approaching 10 wt.% Ag. The initial rise in combustion front velocity is attributed to silver's ability to increase the mixture's thermal conductivity. At higher dilutions, though, the drop in the total heat of reaction dominates over the improved heat transfer and reaction front velocity drops significantly. In a related study, Bohlouli-Zanjani et al. investigated the effects of Cu dilution on two redox systems: Al nanopowder and NiO nanowires and conventional Al-CuO powder mixtures [28]. The dilutions range from 50 wt.% to 80 wt.% Cu, and the mixtures were all very fuel-rich. They examined phase transformations up to 800 °C under slow heating conditions and the associated heat releases. However, the propagation behavior was not studied. Alumina, AlNi, and Cu were the main reaction products after heating the Al-rich Al-NiO mixtures to 800 °C. The measured ΔH_{rx} dropped by a factor of 5 when the amount of excess Cu was increased from 50 to 80 wt.%. They found an even stronger effect of excess Cu in the Al:CuO thermite system. Bohlouli-Zanjani et al. noted that the excess Cu decreased reaction efficiency by creating relatively nonreactive Al/excess metal interfaces [28]. At the same time, the addition of excess Cu reduces the density of highly reactive Al/NiO interfaces. Such geometric effects are expected whenever diluent powders are added to compacts of fuel and oxide powders and they can lead to lower reaction front velocities and the risk of reaction quenching, particularly for heavily diluted systems.

This paper explores a core-shell powder geometry in the Al:NiO thermite system that demonstrates a significant boost in reaction efficiency and hence a lower chance of quenching as excess Ni is added as a diluent. The basic concept is demonstrated schematically in Figure 1. When diluting a thermite mixture the excess metal can act as a barrier to oxygen transfer. If Ni is added as an elemental powder to the Al:NiO mixture, Al/Ni interfaces form in addition to the desired Al/NiO interfaces that are most reactive (see Figure 1 (a)). Hence, the density of the reactive Al/NiO interfaces is reduced by dilution and reaction efficiency drops; further still, the average spacing between the fuel (Al) and the oxide (NiO) increases. In order to prevent the formation of Al/Ni interfaces and to minimize the decrease in reaction efficiency when diluting, compacts using Ni:NiO core-shell particles were fabricated. These particles comprise NiO as the outer shell and elemental Ni diluent as the inner core (see Figure 1 (b)). In this case, it is expected that Al particles exclusively form interfaces with the oxide and not the diluent (Ni). Consequently, the density of the reactive Al/NiO interfaces is substantially increased causing a boost in reaction efficiency. As a side effect, a substantial reduction in the average spacing of reactants is anticipated, which in turn will speed the rate of atomic mixing and combustion front velocities. Both the boost in reaction efficiency and the reduction in average reactant spacing should decrease the risk of quenching for a redox reaction that is

heavily diluted to minimize gas production and therefore should open the possibility of bonding with thermite reactions.

2. Experimental

2.1. Sample Preparation

An ideal geometry for utilizing a redox reaction for joining is a fully dense foil, measuring 100 to 500 μm thick, with a fine continuous or discontinuous layering of reactants. There are two common approaches for fabricating thermite foils with fine reactant spacings: bottom-up deposition techniques [29-31] and top-down mechanical processes [32-36]. Deposition techniques are known to produce reactive foils with well-defined layering and total thicknesses. Mechanical processes offer less control of reactant spacing and foil thickness but do have the potential to produce thermite foils at lower costs and in higher volumes. Hence, the reactive foils for this study were fabricated using low cost powders and a combination of inexpensive mechanical processes that include compaction, swaging and rolling.

Rotary swaging is a mechanical processing method in which a rod or tube is rapidly compressed through a series of radial reductions. The swager itself contains a large flywheel that rotates a roll cage with roller bearings over different interchangeable dies with varying diameters. In contrast to cold-rolling, there is close to 100% materials utilization, and the amount of microstructural refinement can be controlled by the total reduction of the rod's diameter. A successful utilization of swaging to fabricate Ni/Al reactive powders was recently demonstrated in [36].

After mixing the powders thoroughly, they were poured into carbon steel tubes in small increments to avoid segregation and compressed under normal stresses equal to 40 MPa. The compacted tubes were then swaged from an outer diameter of 15 mm down to an outer diameter of 3.2 mm (referred to as powder-in-tube technique). After swaging nearly full density is achieved. The particles elongated during the radial deformation, resulting in a discontinuous layered microstructure. Then the swaged tubes were rolled down to thin stripes using multiple passes with 10% thickness reductions per pass, similar to foils prepared in [36]. After removing the steel jacket, cold-formed, 500 μm thick thermite foils were obtained.

This process was used to fabricate two types of reactive foils. Both are based on the Al:NiO system and contain different degrees of Ni dilution. The individual compositions were denoted as Al:NiO-nNi, where n is the weight fraction of Ni that is added as a diluent. The first set of samples is referred to as conventional and starts with a mixture of Al, NiO, and Ni powders (supplied by AlfaAesar). All powders had sizes $\leq 45 \mu\text{m}$. In the conventional mixtures, the ratio of Al and NiO was kept constant according to the stoichiometry of the $2\text{Al} + 3\text{NiO} \rightarrow \text{Al}_2\text{O}_3 + 3\text{Ni}$ redox reaction. To achieve different degrees of dilution up to 50 wt.% of Ni was added to the powder mixtures prior to compaction.

The second set of samples is denoted as “core-shell” type and comprises Al powder and NiO-coated Ni powder. In order to fabricate the NiO-Ni core-shell powder, Ni powder was

oxidized in still air at 550 °C for different durations between 8.5 min and 30 min. The choice of temperature was based on a literature survey of Ni oxidation [37-39] and a preliminary study in which Ni powders were oxidized at different temperatures. 550 °C was identified as an optimal temperature for growing the desired NiO thicknesses reproducibly, in a reasonable amount of time, while also avoiding particle sintering. In order to further minimize particle sintering, the Ni powder was placed inside a quartz tube that was heated in air and continuously rotated inside a tube furnace. Particle movement substantially reduced the amount of sintering. After oxidation, the core-shell particles were sieved and only particle sizes < 45 µm were used. The oxidized Ni-powders were analyzed in terms of morphology and the nature of the oxide. Powders were mounted in epoxy, cross-sectioned, metallographically prepared, and then imaged in a SEM. Lastly, the nature and volume fraction of the nickel oxide were determined via X-ray diffraction. An XRD θ -2 θ diffractometer (MPD, Panalytical) was used to record symmetric diffraction patterns with $\text{CuK}\alpha$ -radiation (anode settings: voltage 40kV and current 40 mA).

Quantitative phase analysis was performed using the method of internal standard [40] In this method a diffraction line from the phase of interest is compared with that measured from a sample with known compositions and a standard substance. First, a calibration curve was prepared. The integrated intensities of $I_{\text{Ni}}(\text{s})$ and $I_{\text{NiO}}(\text{s})$ were measured for a set of synthetic specimens with a known composition of Ni and NiO and a fixed concentration of 15 wt.% W standard. $I_{\text{Ni}}(\text{s})$ and $I_{\text{NiO}}(\text{s})$ was measured relative to the integrated intensity of W. Second, the concentration of the phase of Ni and NiO in an unknown sample is obtained by measuring the individual ratios $I_{\text{Ni}}/I_{\text{W}}$ and $I_{\text{NiO}}/I_{\text{W}}$ for a composite sample containing the unknown and the same proportion of W standard (15 wt.%) as was used for the calibration. A comparison of the ratios with those obtained during calibration enables one to determine the weight fraction of Ni and NiO.

2.2. Combustion Front Velocity

Self-propagating reactions were ignited in the as-fabricated foils using electrical leads and a 1 s current pulse that rose as high as 200A [41]. As the reactions propagated down the length of the foils, emitted light was collected by an array of fibers in order to measure front velocity and temperature. Most of the fibers were bundled at one end and directed onto a single Si PIN photodiode. The signal output was recorded by an oscilloscope, and the resulting plots of intensity versus time had a stepped appearance, indicating travel time between the fibers. Velocity was calculated by dividing average fiber spacing by the average time of travel between fibers [42].

2.3. Quantifying Mass Ejection

Vapor and hot particles are typically expelled as reactions are ignited and self-propagate across the samples. In an effort to quantify mass ejection as a function of dilution, ejected material was collected on 2.5 x 2.5 cm² steel coupons mounted 2.5 cm above the top surface of the sample foil. The foil was bounded on two sides by a clamp to prevent significant sample translation and ignited using a current pulse. The mass and thickness of each sample was measured prior to ignition. Conventional and core-shell samples had average thicknesses

of $489 \pm 51 \mu\text{m}$ and $477 \pm 17 \mu\text{m}$, respectively. In addition, the mass of each steel coupon was measured before and after the reaction. The difference in initial and final coupon mass was normalized by the original foil mass to determine the mass ejection fraction α . It is noted that these are relative measurements and do not account for all ejected material

2.4. Calorimetry

Differential scanning calorimetry was performed in a Perkin-Elmer Pyris 1 DSC in an atmosphere of 99.999% pure argon flowing at 20 ml/min. The calorimeter was calibrated by a two-point calibration utilizing the melting temperatures T_m and heat of melting H_m of Indium ($T_m = 156,6 \text{ }^\circ\text{C}$ [43], $H_m = 3.26 \text{ kJ/mol}$ [43]) and Zinc ($T_m = 419,47 \text{ }^\circ\text{C}$ [43], $H_m = 7.35 \text{ kJ/mol}$ [43]). Samples (approximately 5–8 mg) were placed in Al_2O_3 pans and heated at a constant rate of 40 K/min from 50 to 725°C. Perkin-Elmer Pyris software was used to analyze the DSC data. The heat of reaction of a given sample was measured by performing two heating scans: The first one with the as-fabricated material and a second one with the same material after a brief cool-down. The second scan serves as a baseline scan that is subtracted from the first scan to quantify most accurately the net power of the exothermic phase transformations. The heat of reaction ΔH_{rx} was calculated by integrating the difference of the two scans.

3. Results and Discussion

3.1. Characterization of the microstructure

3.1.1. Ni/NiO powders with core-shell particle geometry

For this study knowledge of the Ni and NiO fractions within the Ni/NiO core-shell particles is essential when mixing the powders so as to maintain the stoichiometry of the thermite reaction. Hence, our characterization of the core-shell particles starts with a quantitative XRD phase analysis using the method of internal standard [40]. Figure (2) shows diffraction patterns for different oxidation times. The clear separation of NiO, Ni, and W peaks, enables a precise quantification of the phase content. Note the increase of the NiO peak with annealing time while the Ni peak decreases, and the W peak remains constant. The inset of Figure (2) shows a schematic of Ni/NiO core-shell particles that comprise an inner Ni core and an outer NiO shell. Increasing the duration of oxidation for a given Ni particle decreases the fraction of the Ni core, resulting in decreased metal dilution. Systematic variation of the oxidation time hence allows us to obtain core-shell particles containing specific Ni dilutions.

To quantify the amount of pure Ni in the Ni/NiO core-shell particles, the integrated peak areas were calculated as a function of time. The ratio of the integrated peak area of Ni with respect to that of the W peak yields the weight fraction of the Ni phase. Table 1 summarizes the results for the different oxidation times. The core-shell particles were considered as a 2-phase-mixture comprised of Ni and NiO. Hence, the weight fractions of Ni and NiO sum to one which allows the calculation of the NiO fraction. It is important to note, though, that the

samples contain core/shell particles with a range of sizes less than 45 μm but the oxide thickness is relative constant for a given sample and degree of oxidation. Thus, the Ni fraction varies for the individual particles within a sample, depending on the size of each particle. In general, the smaller the particles have lower Ni content for the same degree of oxidation. Hence the Ni fractions reported in Table 1 as a function of oxidation time are average values.

Next, scanning electron microscopy (SEM) was used to inspect the morphology of NiO that grows on the surface of the Ni particles at 550 $^{\circ}\text{C}$ as shown in Figure 3. The core-shell geometry is evident. The morphology of the NiO scale on the surface of the particle is porous, presumably due to oxidation conditions. It is known for bulk nickel that porous oxide scales develop when the growing oxide exhibits cracking or microchannel formation due to either stress development during growth or mechanical movement of the particles during the oxidation process [44, 45]. However, the NiO does form a closed shell around the Ni core which provides effective separation of the Ni diluent and the Al fuel in Al:NiO-nNi thermite compacts.

3.1.2. As-fabricated Al:NiO-nNi reactive foils

Figure 4 compares as-fabricated microstructures of (a) a conventional powder mixture with 30 wt.% Ni and (b) a core-shell powder mixture containing 33.7 wt.% Ni. The images were taken parallel to the rolling direction that is identified with a black arrow. In both samples elongated Ni particles (bright contrast) were observed that are surrounded by an Al matrix (dark contrast) where NiO is imbedded (grey contrast). Some porosity is also evident. An important parameter for layered reactive systems is the reactive spacing. It is denoted as the average distance that the atoms have to diffuse to intermix. In the case of a multilayer sample with ideally flat interfaces, this distance is defined by the bilayer thickness. For more irregular microstructures, such as those considered in the present study, this distance is less well defined. By comparing the average distance between the bright individual Ni segments in Figure 4 (a) with the average distance between the bright Ni segments in Figure 4 (b), it is qualitatively evident that the reactant spacing is smaller for the core-shell mixtures, even though its dilution is slightly higher. This qualitative comparison suggests that the core-shell particles enable one to fabricate diluted thermite mixtures with a smaller average reactive spacing than conventional powders.

3.2. Low Temperature Reaction Behavior

In order to assess sample reactivity, heat production, and the onset of ignition the low temperature phase transformations under slow heating were explored using DSC experiments. Figure 5 (a) presents typical DSC scans as a function of excess Ni for both types of powder mixtures. In undiluted samples two overlapping exotherms appear between 400 and 600 $^{\circ}\text{C}$, as well as a sharp exotherm with a peak temperature of 636 $^{\circ}\text{C}$. As the amount of dilution increases the conventional samples retain two overlapping exotherms in the 400 to 600 $^{\circ}\text{C}$ temperature range but the core-shell samples appear to have only one distinct exotherm in this range. The third exotherm, which is very large for low dilutions, is attributed to the eutectic

melting of a Al(Ni) solid solution at 636 °C (639.9 °C is the equilibrium melting temperature according to the equilibrium diagram [46]). While melting itself is an endothermic process, the melting of the Al(Ni) solution facilitates very rapid mixing of the components and leads to a net release of heat. This net exothermic effect of Al melting has also been suggested for mechanically fabricated Ni/Al powders in [32] and [33]. Beyond 10 wt.% Ni the sharp exotherm at 636 °C decreases significantly in magnitude for both types of samples.

To understand the underlying phase transformations leading to the exotherms that appear within the DSC scans, samples were quenched after the second exotherm at 575 °C and XRD phase analysis was performed. Figure 5 (b) shows representative diffractograms for the conventional mixtures with 0, 20, and 40 wt.% Ni. For comparison, the signal of an as-fabricated sample is also shown. For the quenched undiluted sample we can clearly detect the presence of the intermetallic NiAl_3 . A small shoulder at about 25.3° also indicates small amounts of the Ni_2Al_3 phase. The formation of the latter phase becomes more obvious for the diluted samples (see the signals for the specimen with 20 and 40 wt% excess Ni). The relative intensities of the respective XRD peaks suggest a larger amount of Ni_2Al_3 in the quenched diluted samples. In the extreme case of 40 wt.% Ni, Ni_2Al_3 is now the major phase in the sample whereas only small shoulders at 25.6° and 36.4° still show the presence of NiAl_3 . This indicates that the Ni diluent facilitates the Ni_2Al_3 formation. In contrast, no peaks for NiAl_3 or Ni_2Al_3 are seen in the XRD data for the as-fabricated sample. In addition, we see XRD evidence of pure Ni in the quenched undiluted sample indicating that NiO is reduced on heating to 575 °C. This suggests that alumina is forming in addition to the intermetallics but presumably as an amorphous or nanocrystalline phase and hence is not observable via XRD. Note, XRD peaks for Ni only appear above 44.508° and therefore are not seen in the plotted 2θ range for Figure 5 (b) but are observable at higher ranges of 2θ .

In a next step, the results for a quenched conventional mixture diluted with 40 wt.% Ni are compared with those for a quenched mixture of core-shell particles with a similar dilution (37 wt.% Ni). Figure 5 (c) shows the diffractograms. The XRD results demonstrate that the Ni_2Al_3 peaks are small relative to the NiAl_3 peak for the core-shell sample and, hence, Ni_2Al_3 is not the dominating phase. This suggests a difference in the degree of transformation of NiAl_3 to Ni_2Al_3 . This difference is attributed to the core-shell geometry. As noted above for the conventional mixtures, the excess Ni facilitates the Ni_2Al_3 formation. In case of the core-shell particles, however, Ni is covered by a NiO shell and this geometrical constraint reduces the reaction of Ni and Al, thereby limiting the formation of Ni_2Al_3 . Only very small XRD peaks for Ni_2Al_3 can be seen in the diffractogram for the core-shell sample. The limited formation of Ni_2Al_3 is likely due to small, local breaks in the NiO shell. The presence of the elemental Al reflex at $\sim 38^\circ$ (contrasting the diffractogram of the conventional mixture), also supports the assumption that the formation of Ni_2Al_3 is very limited.

Exploring the DSC and XRD results in combination, the first exotherm that begins around 400 °C is attributed to both Ni and NiO reacting with Al to form crystalline NiAl_3 and amorphous alumina products. The second, smaller exotherm starting at above 500 °C relates to the formation of Ni_2Al_3 and more amorphous alumina products. The formation of Al-rich Ni-Al intermetallics due to elemental mixing of Ni and Al at low temperatures was reported for Ni/Al composites of various morphologies such as mechanically fabricated foils

[32,47,48] and Ni-coated Al-particles [49]. The formation of amorphous alumina was also suggested for other thermite systems such as the Al-CuO system, where researchers have reported on the reaction of CuO with Al [50]. Thus, both types of reactions are likely happening but it appears that the formation of NiAl_3 and Ni_2Al_3 dominates the heat release in the first two overlapping exotherms, in large part based on a comparison of the results for the conventional and core-shell samples. As detailed above, the first of the two overlapping exotherms correlates with the formation of NiAl_3 and the second with Ni_2Al_3 . Furthermore, the second exotherm and the formation of Ni_2Al_3 are almost absent in the core-shell samples. The near absence of the second exotherm and Ni_2Al_3 in quenched core-shell samples is attributed to the NiO shell isolating the Ni core from the Al and thereby limiting the formation of Ni_2Al_3 . In contrast, if a reduction-oxidation reaction was responsible for the second exotherm, this exotherm would be larger for the core-shell samples, compared to the conventional samples, and not smaller. Thus, the reduced second exotherm and the reduced formation of Ni_2Al_3 indirectly demonstrate that the core-shell geometry can physically separate the diluent from the fuel and thereby minimize their reaction. This becomes increasingly important for heavier dilutions.

Turning to the third exotherm it is noted above that increasing the degree of dilution reduces the intensity of this exotherm. The very large, third exotherm at 636 °C becomes very small or no longer observable for dilutions > 30 wt.% Ni. With increasing Ni dilution presumably more Al is consumed by the low temperature formation of NiAl_3 and Ni_2Al_3 (and a small amount of alumina), and less Al is available to melt at 636 °C. The XRD experiments support this hypothesis (see discussion above). In contrast, if a reduction of NiO and the formation of alumina dominated the first two overlapping exotherms, then most of the Al would still be present as an elemental reactant given the small heats for these exotherms. In this case the third, very large exotherm would not decrease substantially with dilution. Hence, the substantial decrease of the third exotherm with dilution corroborates the abovementioned conclusion that the first two exotherms are produced mainly by the formation of NiAl_3 and Ni_2Al_3 .

Comparing the DSC results of the conventional mixtures with those of the core-shell ones enables us to identify an additional effect of the core-shell geometry on the transformation behavior. One draws on the observation that the first exotherm in Figure 5 (a) begins at lower temperatures in the core-shell samples. This indicates smaller reactant spacings for the samples using the core-shell powders. Our qualitative microstructural analysis of Figure 4 supports this argument of reduced reactant spacing in the core-shell mixtures.

Using the DSC traces in Figure 5 (a) the heat of reaction (ΔH_{rx}) for both sets of samples was calculated as a function of dilution and is plotted in Figure 5 (d). For the conventional and the core-shell mixtures, ΔH_{rx} decreases with the amount of excess Ni. Generally, the measured heats of reaction range from 0.2 to 0.36 times the full heat of reaction for the stoichiometric Al:NiO thermite reaction (3445 J/g [17]). The low measured values can be attributed in part to the Ni dilution but mainly to the fact that the reaction does not run to completion during the DSC scans. Additional transformations are expected at elevated temperatures. The DSC traces and the range of ΔH_{rx} compare well with those measured by Stover et al. for the Ni-Al transformations in Ni:Al cold-rolled foils [47]. This suggests that the formation of Ni:Al

intermetallics may dominate the low temperature reaction behavior in the Al:NiO-Ni thermite foils. In Figure 5 (d) the measured heats decrease with Ni dilution and plateau temporarily between 20 and 30 wt.% Ni dilution. Stover et al. found a similar decrease in ΔH_{rx} with changing stoichiometry of their Ni:Al particles Ni-rich chemistries. Hence, the observed variation in ΔH_{rx} is attributed to the formation of more Ni-Al intermetallics at low temperatures with higher concentrations of Ni. In addition, the conventional samples consistently show higher heats of reaction than the core-shell samples for dilutions between 20 and 40 wt% Ni. These higher heats are attributed to the closer proximity of the diluent Ni to the Al and the ease of forming Ni-Al intermetallics as noted above.

3.3. Self-Propagating Combustion Reactions

After characterizing the slow phase transformations that appear at low temperatures in DSC scans, the rapid self-propagation of the redox combustion reactions is considered at much higher temperatures. In a first set of experiments high-speed videos were captured for the reaction of the samples, and selected videos are presented in the supplementary material. All samples show unstable combustion propagation in which reaction bands travel perpendicular to the net propagation direction. The reaction bands are narrow regions and travel ahead of the combustion front, along the warm boundary of previously reacted material. When these bands impinge upon each other, a new set of bands nucleate and grow, again normal to the net propagation direction. The sites for band nucleation are more broadly spaced in the diluted foils compared to the undiluted foils, making the reaction propagation appear more irregular and unstable with dilution. Figure (6) presents net propagation velocities for combustion reactions of the conventional as well as the core-shell mixtures. The measured values decrease steadily for both sample types as dilution increases. The combustion front velocity drops from approximately 0.7 m/s for no dilution to approximately 0.02 m/s for a 50 wt% dilution of Ni. The mixtures containing 50 wt.% excess Ni were difficult to ignite, indicating that 50 wt% Ni is near the quenching limit for samples with this degree of mechanical processing and average reactant spacing. Most importantly, it is noted that the core-shell samples consistently show higher velocities than conventional samples with similar dilutions.

Besides slowing the self-propagating reactions, the addition of Ni also changes the nature of the combustion behind the moving front. The high-speed videos clearly reveal droplet formation and spraying of molten products from the undiluted samples (see videos of the Supplementary Material). However, for Ni dilutions greater than 20 wt.% droplet formation disappears and the reaction products coarsen to form large slugs in which the Al_2O_3 and elemental Ni products phase separate. More importantly, the ejection of mass from the samples decreases significantly with dilution. As a quantitative metric, the normalized mass ejection fraction, α , (as defined in the Experimental Section) is considered. Figure 7 plots α as a function of excess Ni for both mixtures. For the conventional samples α drops by 2.5 orders of magnitude with increasing Ni dilution and α plateaus near 0.6% for 10 to 30 wt.% Ni. Very similar behavior is seen for the core-shell foils across their full range of dilutions, from 17 wt.% to 37 wt.% Ni. Hence, the same reduction of mass ejection can be achieved by

the utilization of core-shell powders. The plateau in α may be associated with the plateau observed for ΔH_{rx} in Figure 5 (d). Additional studies will be needed to confirm this relation.

In order to explain the drop in α , the adiabatic combustion temperature T_{ad} was calculated as a function of degree of Ni dilution. To calculate T_{ad} as a function dilution the sum of the temperature dependent specific heats of the products is integrated from room temperature to the adiabatic temperature. Under adiabatic condition, the value of the integral equals the theoretical heat of reaction of the redox reaction, $\Delta H_{rx} = 3,445 \text{ J/g}$ [16, 17]. The calculations are implemented in a MatLab code taking the heats of transformation (melting, boiling) for the product species into account. An iterative scheme is performed to obtain the adiabatic temperature as a function of dilution. The thermo-physical properties of the individual products needed for the calculations are taken from [43]. The result of the calculation is also plotted in Figure 7. T_{ad} is constant at Ni's boiling temperature up until 10 wt.% Ni. For higher degrees of dilution T_{ad} decreases until 44 wt.% Ni where T_{ad} plateaus again at the melting temperature of Al_2O_3 . The maximal combustion temperature, T_{max} , is expected to show a similar trend with dilution for the samples studied here. Hence, for dilutions greater than 10 wt.% Ni, T_{max} should decrease below the boiling points for the reaction products, Al_2O_3 (2977 °C [43]) and Ni (2913 °C [43]). Figure 7 also shows that α starts to decrease for a dilution between zero and 10 wt.% Ni. Hence, it is hypothesized that gas release is related to the evaporation of combustion products, Ni in particular. Once T_{max} falls below Ni's boiling point, gas release and mass ejection should decrease with dilution. The lack of a consistent decrease in the normalized mass ejection between 10 and 40 wt% Ni suggests that some other factor is playing a role.

While the conventional and core-shell samples show similar trends in front velocity and mass ejection with dilution in Figures 6 and 7, the core-shell samples clearly have higher combustion front velocities. The higher speeds are attributed to the geometry of the core-shell particles. Our DSC results indicate the ability of these particles to insure diluent separation from the Al fuel. Further still, and probably more importantly, the separation of the Ni diluent and the Al fuel shown in Figure 1 insures a finer spacing of Al and NiO reactants. Both factors are thought to enhance combustion front velocity compared to conventional powder compacts. The boost in front velocity is as large as 100 % for a dilution of 30 wt.% Ni. Such increases can be beneficial in helping to avoid quenching within a bonding application. However, it is noted that the benefit of the core-shell geometry appears to vanish beyond dilutions of 40 wt.% Ni. Additional studies will be needed to confirm whether or not this trend continues at higher dilutions and to identify its cause.

4. Conclusion

In this study, diluted Al:NiO thermite mixtures were fabricated and characterized using conventional Al, NiO, and Ni particles in one set of samples and Al, Ni/NiO core-shell particles in another set of samples. For both sets of samples DSC heats of reaction, combustion front velocities, and mass ejection decreased substantially with Ni dilution. Theoretical calculations indicate that maximum combustion temperatures decrease with

dilution and potentially cause the drop in reaction front velocity and mass ejection. For a given dilution the core-shell samples demonstrated lower DSC peak onset temperatures, higher heats of reaction, and higher combustion front velocities. DSC peak onsets decreased by approximately 15 °C, heats of reaction rose from 0 to 10%, and combustion front velocities increased by as much as 100% for dilutions near 30 wt.% Ni. All three changes are attributed to a finer spacing of Al and NiO in the core-shell samples, and the shielding of Al from the Ni diluent. The shielding is also thought to reduce the formation of Al-Ni intermetallics at low temperatures.

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Table Captions

Table 1: Summary of the weight fractions of Ni as a function of oxidation time for the core shell particles used in this study. The calculations are based on the XRD results presented in Figure 2. Since the XRD measurements average over a range of particle sizes, the Ni content determined for the core-shell powders is an averaged value.

Figure Captions

Figure 1: Schematics showing the use of (a) elemental Ni powders or (b) core-shell, Ni/NiO powders in the formation of Al/NiO-Ni thermite foils with excess Ni. The Al/NiO reactive interfaces are indicated by black arrows.

Figure 2: X-ray diffraction patterns of oxidized Ni powder as a function of oxidation time. The data indicate that NiO is the oxide. A fixed amount of W powders was added to each XRD test specimen to accurately quantify the relative amounts of Ni and NiO. The individual diffraction patterns are shifted in 2θ to show the increasing intensity of the NiO peaks with increasing oxidation time. The inset shows schematically how the ratio of Ni and NiO changes within the core shell particles as a function of oxidation time.

Figure 3: Cross-sectional view of an oxidized Ni powder after 10 min of oxidation. A Ni core and a porous NiO scale covering the particle were identified.

Figure 4: As-fabricated microstructures of a) a conventional mixture containing 30 wt.% Ni and b) a core-shell mixture containing 33.7 wt.% Ni. Regions of Al, Ni, and NiO are indicated by arrows, respectively. The rolling direction is identified by a black arrow.

Figure 5: a) DSC scans of conventional and core-shell mixtures as a function of excess Ni taken at a heating rate of 40 K/min (the individual DSC scans are shifted along the y-axis for illustration). b) XRD phase analysis of the quenched samples at 575 °C. c) compares the phases for conventional and core-shell samples with nearly equal dilutions. d) Heats of reaction that were calculated by integrating the traces in (a).

Figure 6: Combustion front velocities of conventional and core-shell foils as a function of excess Ni

Figure 7: Comparison of the normalized mass ejection fraction as a function of Ni dilution for conventional and core-shell foils and calculated adiabatic combustion temperatures as a function of excess Ni. The boiling points of the products Al_2O_3 and Ni are also indicated.

Table 1

Time of Oxidation (min)	Averaged fraction of the Ni-core (wt.%)
8.5	37
10	33
15	23
17	19
30	17

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7