CHARACTERIZATION AND MODELING OF THE EARLY-STAGE REACTIONS IN ALUMINUM-NICKEL COMPOSITES PRODUCED BY ULTRASONIC POWDER CONSOLIDATION

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ABSTRACT

Recent advances in the micro/nanomanufacturing industry have called for the development of novel heaters that can be used for localized heating applications. Reactive metal matrix composites may apply to such heaters where the heat output of the exothermic reaction can be passed on to the exact spot of interest in calculated amounts. This research focuses on the fabrication and characterization of Al-Ni reactive composites by an ultrasonic powder consolidation (UPC) technique. Since as-compact ed Al-Ni structures are thermodynamically metastable, they may self-ignite prior to use. Therefore, early-stage reaction kinetics is also addressed for safety concerns.

UPC provides a viable route for the consolidation of reactive metal powders since the consolidation can be achieved at room to warm temperatures by high strain-rate deformation in a short time of about 1 s. In this study, systematic experiments were conducted to determine the processing window for full-density consolidation. These consolidates were characterized by optical and electron microscopy. Results showed that full-density consolidates can be obtained under 90 MPa uniaxial pressure at 573 K.

It is extremely crucial to understand the ignition characteristics of these structures since they are to be utilized as heaters. Therefore, continuous-heating ignition tests, differential scanning calorimetry (DSC), and spark ignition tests were employed for thermal characterization of select specimens. X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS)
results indicated that ignition was preceded by the solid-state reaction $Al + Ni \rightarrow Al_3Ni$ which then catalyzed ignition through the formation of eutectic liquid between $Al_3Ni$ and $Al$.

Experimental findings revealed that Al-Ni nanostructures may ignite while being held at temperatures as low as 500 K. This situation raises the need for a model which would predict the kinetics of early-stage reactions that lead to ignition. To this end, a non-isothermal Avrami-type equation was developed for determining the solid-state exothermic reaction kinetics of Al-Ni composites with different geometries. This equation was employed under site saturation conditions, the results of which showed that an Al-Ni multilayer foil may reach the eutectic temperature (913 K) in less than 1 s while being held at 550 K which is well-matched with experimental findings.
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XRD  X-ray diffraction
1. INTRODUCTION

1.1 Problem Statement

Heat is widely used in macro-scale manufacturing industry for microstructural modifications which directly affect the material performance. This is because temperature is a major variable that changes the thermodynamic state of the material as apparent in $dG = -SdT + VdP$. There are several heating systems available for this purpose. However, recent advances in the micro/nanomanufacturing industry have made these systems inapplicable due to the incompatibility between macro and nano-scale characteristic lengths and times of heat transfer. Therefore, there is a need for the development of novel heaters that can be used for small scale heating applications. Al-Ni micro/nanostructures may apply to such heaters where the heat output of the exothermic reaction can be passed on to the exact spot of interest. Although there are various geometries in which this idea can be applied, this research focuses on the fabrication of Al-Ni composites by the consolidation of micro/nano sized particles.

Conventional techniques for the consolidation of particles generally require a two-step process, cold compaction and sintering. The first step forms a green compact which has a high amount of porosity and the second step facilitates compact densification and metallurgical bonding which requires heating the compact to a high enough temperature, generally well above half of the melting point of the material on homologous scale. Such a method would cause exothermic reactions between Al and Ni particles and make the consolidated material impotent.
for heating applications. Therefore, a new technique is necessary for the consolidation of reactive powders.

Ultrasonic welding (USW) is a solid-state joining process that facilitates rapid-joining of similar or dissimilar materials at room temperature. USW is widely used in the electronic, semiconductor, and automotive industries for rapid joining of metal wires, cables, and sheets. Ultrasonic powder consolidation (UPC) [1] is a USW technique that applies to the consolidation of metallic powders. Previous research on vibratory compaction resulted in the production of green compacts that required further sintering at elevated temperatures for full metallurgical consolidation [2-4]. However, it has recently been shown that UPC can create fully dense Al consolidates without subsequent sintering within a fraction of a second [5]. A preliminary application of UPC on Al-Ni particle mixtures was conducted by Gulsoy [6] and promising results were obtained. Further work is required to establish a processing window for the full consolidation of Al-Ni particles and also to test the quality of consolidated structures.

In order to exploit the heat output of Al-Ni composites for localized heating applications while maintaining safety during storage and manufacturing, one needs to understand the ignition behavior of such structures. Ignition temperatures must be determined for composites of different particles, and reaction characteristics at different heating rates should be evaluated for effective use of such materials.

It is known that heterostructures with a high value of Al-Ni interfacial area, such as sputtered multilayer foils, can ignite while being held at temperatures as low as 500 K [7] suggesting that these materials are highly metastable and may self-ignite prior to use. Therefore,
a kinetic model is necessary to predict solid-state exothermic reaction kinetics of various Al-Ni structures.

1.2 Objectives

Objectives of this study are listed below:

- Production of Al-Ni reactive composite materials by UPC under various conditions.

- Determination of the processing window for full metallurgical consolidation.

- Analysis of produced specimens in terms of residual porosity and ductility.

- Thermal characterization of Al-Ni consolidates by differential scanning calorimetry (DSC), spark ignition, and continuous-heating ignition tests.

- Analysis of the resultant microstructure after ignition by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD).

- Modeling the early-stage reaction kinetics of various Al-Ni heterostructures.

1.3 Significance

Fabrication, characterization, and kinetic modeling of reactive composite materials require research in the areas of powder metallurgy, solid-state joining, self-propagating high-temperature synthesis (SHS), thermal explosion (TE) and exothermic reaction kinetics. This
study utilizes a novel technique for the consolidation of metallic powders which is capable of producing full density materials in a fraction of a second. Use of relatively low temperatures during consolidation avoids grain growth and deterioration of material properties. Therefore, UPC can be used for the consolidation of nano-structured powders for different applications.

There is a vast amount of research on SHS and TE of the Al-Ni system, but there is still a need for modeling the early-stage solid-state reaction kinetics. This study developed an Avrami-type equation to address these reactions and evaluates the material behavior for different geometries. Fabrication of novel heaters can create new processing techniques, such as micro-joining of micro-devices. Modeling results will determine the critical conditions to assure safe production, storage and service of such heaters.
2. BACKGROUND

This research aims at the production of reactive metal matrix composites through the consolidation of Al-Ni particles, thermal characterization of as-consolidated specimens, and modeling of early-stage solid-state exothermic reaction kinetics of Al-Ni binary system. Therefore, background information on reactive composites, powder metallurgy, Al-Ni system, and solid-state kinetic modeling is necessary. This study utilizes a novel powder consolidation technique [1, 5] which is a special application of USW. Thus, the fundamentals of ultrasonic welding are also needed to be addressed in this section.

Previous work related with this research are summarized under four subsections on: (1) the types, production methods, and applications of reactive metal matrix composites, (2) powder consolidation techniques that can be applied to reactive systems, (3) the fundamentals of solid-state joining processes with a particular emphasis on the ultrasonic welding technique, (4) the properties of Al-Ni binary system in terms of reaction kinetics and phase evolution.

2.1 Reactive Metal Matrix Composites

Reactive metal matrix composite (RMMC) materials (also known as metal-based energetic composites) consist of two or more reactive elements or compounds and are utilized for the heat output or the products of their reactions. The biggest concern in utilizing RMMC materials is the safety in terms of production, storage, and service, due to their high reactivity
and the possibility of self-ignition and the occurrence of undesired reactions prior to use. These materials are primarily used as propellants, explosives, and pyrotechnics, although new applications are being developed, such as micro-joining of metals [8-11]. This section summarizes types, fabrication methods, and applications of RMMC materials.

Current material processing technologies allow us to produce various types of reactive composite materials. Among these, the most popular compositions consist of Al combined with another metal (e.g., Ni, Ti, Nb, Pt), a metal oxide (e.g., CuO, Fe₂O₃, NiO, MoO₃) or a polymer (e.g., Teflon) [12]. All these materials can be produced with different geometries, i.e., powder compacts, multilayer foils, and composite powders [13-17]. Recently, a review was published by E.L. Dreizin [15] about the preparation and properties of metal-based reactive nanocomposite materials. He discussed different types of energetic nanocomposites, processing methods, and material properties.

The majority of Al-Ni and Al-Ti research is focused on the reactive synthesis of aluminide phases which are widely used in the aerospace industry due to their resilience at high temperatures [18-22]. Moussa and El-Shall [18] fabricated Ni and Ti aluminides starting from elemental nanopowders by placing the cold pressed specimen in a pre-heated air-furnace. In-situ temperature measurements showed that Al-Ni specimens started reacting at 743 K and reached a maximum temperature of 1423 K. There are also a small number of studies that utilized Al-Ni composites for heating applications [6, 8-11, 23].

Gulsoy [6] produced Al-Ni composites by ultrasonic consolidation of elemental powders and roll bonding of elemental foils. Differential thermal analysis (DTA) of Al-Ni powder
composites revealed the formation of an exothermic peak at 923 K which is slightly below the melting point of aluminum.

Jun et al. [11] used a rolling mill to produce multilayered Al-Ni foils and utilized them for mounting microelectronic components. They conducted experiments to join a Cu sheet and a Cu coated printed circuit board (PCB) with a reactive soldering technique in which an Al-Ni multilayer foil was sandwiched with two layers of Sn-Pb solder materials, as schematically shown in Figure 2.1. Reaction characteristics of the Al-Ni binary system are further discussed in Section 2.4.

Figure 2.1 Schematic representation of reactive soldering process [11].
Blobaum et al. [13] reported on the production and characterization of sputtered multilayer Al/CuO\textsubscript{x} structures. The DTA results revealed that reactions started at \( \sim 400 \) K and two major exothermic peaks formed; the first peak at 900 K and the second one at \( \sim 1120 \) K. This reaction released a total heat of \(-3.9 \pm 0.9\) kJ/g. Due to the high reactivity of the materials, special precautionary measures were taken, such as cooling the substrate with water and shielding the sputter guns to contain the plasma in a small volume. Al/CuO nano composite powders were also produced by applying arrested reactive milling (ARM) which is a high energy mechanical ball milling process, but mechanical triggering of the reaction was avoided by stopping the milling. The authors reported formation of undesired products due to partial reactions between starting materials [13, 17].

Stamatis et al. [16] studied production of Al/CuO nanocomposite powders by ARM and their reaction kinetics. The results showed that the ignition temperature was \( 870 \pm 30 \) K regardless of the heating rate.

Tillotson et al. [24] used a sol-gel method to prepare both aerogel and xerogel monoliths of Al/Fe\textsubscript{2}O\textsubscript{3} nanocomposites that consisted of 30 nm Al particles and even smaller Fe\textsubscript{2}O\textsubscript{3} clusters. They have concluded that aerogel composites were more prone to ignition than xerogel composites since an aerogel has a lower thermal conductivity, hence needs a longer time to dissipate the heat.

Hossain et al. [25] spin coated amorphous Si thin films with Al/CuO nanoparticle mixture and used the heat output \( (604\) kJ/mol) of the reaction for crystallization of Si. Microstructural studies showed that the coating contained microvoids which would cause nonuniform heating.
Therefore, the authors introduced a multilayer Al/Pt foil in between Si films and Al/CuO coating. The thermite reaction ignited the Al/Pt foil and the heat output (280 kJ/mol) of the latter reaction was used for the crystallization of Si films.

2.2 Powder Consolidation Techniques

Powder metallurgy (PM) is a widely used technique to produce metal matrix composites (MMC). Conventionally, it consists of four major steps: (1) production of powders, (2) blending or mixing, (3) pressing powders into green compacts which still contain porosity, (4) formation of a bulk material by a consolidation process. In a conventional method, green compaction is normally achieved by cold pressing, while consolidation is obtained by sintering at an elevated temperature. Another widely used method is hot isostatic pressing (HIP) in which powders vacuum-encapsulated in a metal container is held under isostatic pressure at an elevated temperature for a sufficient amount of time depending on the material and selected temperature. Generally, this method takes 12-24 h for full consolidation at 80% of the absolute melting temperature [26].

Nath, Tiwari and Babu [27] applied cold isostatic compaction to Al-Ni powders at 125-500 MPa pressure and subsequent sintering at temperatures up to 913 K to Al-Ni powders. Results revealed formation of Al$_3$Ni intermetallic phase after 1 h of sintering. In another study, Matsuura et al. [28] sintered Al-Ni powders at a lower temperature of 723 K, but they were not able to avoid formation of intermetallic phases, as seen in Figures 2.2 and 2.3. HIPping is a well-established technique suited for densification and pore removal purposes. In this technique, an
isostatic pressure is applied to the material at a temperature that is lower than that used in sintering [26], but reduced temperatures employed in this technique are still too high to be applied for reactive powders. Since the purpose of the present research was to produce Al-Ni composites without causing any reactions, neither of the techniques mentioned above is applicable.

Figure 2.2 An Al-Ni compact sintered at 723 K for 44.4 h [28].
Since the compaction and subsequent sintering processes are time consuming, there is a vast amount of research in the field of high strain-rate processes [29-41] that may minimize the processing time. However, these methods still require the powders to be compacted prior to deformation processing. Among the most commonly employed high strain-rate powder consolidation techniques are powder forging, rolling and extrusion, equal channel angular pressing (ECAP), and shock wave consolidation. Although, materials produced by these techniques generally possess more than 99% density, they may still need to be further processed in order to improve mechanical properties.
Many studies have been performed on the extrusion of Al and Al alloy powders at temperatures starting from room temperature up to 773 K [37-39]. Application of the extrusion technique is generally a two-step process where the powders are first cold pressed into a can, and after evacuation and sealing, extruded at room temperature or an elevated temperature. Lee et al. [37] applied the extrusion technique into SiC reinforced Al-Li alloy composites. They conducted cold isostatic pressing (CIP) at 350 MPa followed by hot extrusion at 773 K and obtained full density composites. Kawamura et al. [38] extruded amorphous Al alloy powders at 383 – 443 K and obtained full density consolidation.

In 1991, a review on fabrication of powder compacts by the dynamic consolidation process was published by Rosato, Vreeland, Jr, and Prinz [34]. They summarized various studies covering the production of materials via shock wave consolidation techniques. The shock wave consolidation process facilitates the formation of a bulk material by passing a shock wave through the powders. The necessary shock wave is generated by detonating an explosive. Jin-Yuan et al. [41] used this technique to consolidate rapid solidification processed (RSP) Al-Li alloy powders. They concluded that the shock wave broke up the surface oxide layer and resulted in compacts with relative densities above 98% while preserving the initial microstructure of the powders. However, they also stated an abnormal softening in comparison with the original powders. Flinn et al. [35] also applied this technique to Al powders and they reported that the die was still warm to cause microstructural recovery which resulted in the loss of mechanical properties to a certain extent. They also observed some porosities that formed due to entrapped gas which is one of the major drawbacks of this technique.
In the current research, a vibratory technique [1] is applied for the consolidation of Al-Ni particles. The majority of previous studies on vibratory consolidation techniques produced only green compacts that required further sintering at elevated temperatures [2, 34, 42-46]. In 1972, Gray [43] published a review on the vibratory compaction technique and summarized the effects of various parameters on the compaction behavior. Brackpool and Phelps [44] conducted experiments with Cu powders and reported that a vibratory compaction technique improved the uniformity and the green density of specimens. Kromp et al [45] applied ultrasonic vibrations to RSP Al alloy powders and stated that lower pressures were sufficient to achieve desired green densities. Emeruwa et al. [2] stated that there was an optimum pressure at which the compaction is the most effective.

2.3 Ultrasonic Welding and Ultrasonic Consolidation

USW is a solid-state joining process that facilitates rapid joining of similar or dissimilar materials at room temperature. USW is widely used in the electronic, semiconductor, and automotive industries for rapid joining of metal wires, cables, and sheets. The advantages of the USW include low energy consumption, low cost infrastructure, no atmosphere control required, no preprocessing required, and the ability to weld dissimilar materials [47].

Kodama [48] summarized the bonding process, parameters, and applications of USW. During welding, two materials are held under clamping loads and ultrasonic oscillations are applied parallel to the bonding surface. The relative motion of the specimens breaks the oxide
films and facilitates full contact. Bonding takes place in the solid-state by the help of high-strain rate plastic deformation. A schematic overview of the mechanism is shown in Figure 2.4.

![Figure 2.4 Schematic overview of ultrasonic welding process](image)

Figure 2.4 Schematic overview of ultrasonic welding process, (a) Contact surface under clamping load, (b) Bonding surface with slip, (c) Bonding surface with plastic deformation [48].

In 1971, Joshi [49] suggested three possible mechanisms of USW: (1) mechanical interlocking, (2) interfacial melting, and (3) diffusion. All these three mechanisms may help the formation of a weld at the interface or there may be only one mechanism dominating the process. Joshi also mentioned a softening effect which involves plastic deformation followed by the formation of excess vacancies. Langenecker [50] also observed a softening effect in his experiments and claimed that acoustic energy increases the amplitude of dislocations and releases them from pinned positions.
In 2003, Dawn R. White of Solidica, Inc. reported a new rapid tooling process called Ultrasonic Consolidation (UC) which is basically an automated combination of ultrasonic welding and milling processes [51]. In UC, parts with desired geometry are produced by joining 0.1 mm thick layers of metal sheet by ultrasonic welding, where unwanted parts of each layer are trimmed by a milling head. Successive additive and subtractive operations result in the production of a near-net shape geometry.

In 2005, Gunduz et al. [52] used USW at elevated temperatures (513 K) for joining an Al foil and a Zn sheet. They observed a thin featureless region at the interface, as seen in Figure 2.5, indicating local melting. Thermodynamic calculations showed that melting point depression might have occurred due to the increase in excess vacancy concentration which is caused by high strain-rate deformation during USW. Therefore, local melting may be possible for the Al/Zn couple under these conditions.

Figure 2.5 SEM micrograph showing the morphology of the Al-Zn weld [52].
In 2009, Yang, Janaki Ram, and Stucker [53] applied UC to similar (Al 3003/Al 3003 and Ni 201/Ni 201) and dissimilar (Al 3003/Ni201 and Al 3003/Cu) metallic materials at room temperature. They did not observe any evidence of mechanical interlocking or interfacial melting, thus concluded that the weld occurred due to diffusion at room temperature.

2.4 Aluminum-Nickel System

The Al-Ni binary system has been a hot research topic for a long time, since the intermetallic compounds (i.e., Al3Ni, Al3Ni2, AlNi, Al3Ni5, and AlNi3), seen in the binary phase diagram in Figure 2.6, are candidate materials for high temperature applications. Much of the attention has been focused on the synthesis of compounds by SHS [21, 54-67] and volume combustion synthesis (VCS), also known as thermal explosion (TE) [55-59, 68-77]. In the SHS mode, the material is generally ignited at one point to start a reaction locally which then propagates through the whole material. In the TE mode, the whole specimen is heated in a furnace to the reaction temperature and the product phase forms via simultaneous reactions. The heat of formation and adiabatic temperatures for the Al-Ni compounds are given in Table 2.1. Many researchers have investigated various Al-Ni composites to understand the ignition characteristics and the phase evolution sequence for efficient production of high temperature structural and coating materials [27, 54, 78-86].
Table 2.1 Adiabatic temperatures for nickel aluminide compounds [57]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heat of formation at 298 K (kJ mol$^{-1}$)</th>
<th>Adiabatic temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlNi$_3$</td>
<td>-153.1</td>
<td>1586.5</td>
</tr>
<tr>
<td>AlNi</td>
<td>-118.4</td>
<td>1911</td>
</tr>
<tr>
<td>Al$_3$Ni$_2$</td>
<td>-56.5</td>
<td>1406</td>
</tr>
<tr>
<td>Al$_3$Ni</td>
<td>-150.7</td>
<td>1127</td>
</tr>
</tbody>
</table>
Use of Al and Ni elemental powders as starting materials for reactive synthesis of nickel aluminides have been studied by a number of scientists [19, 74, 88-96]. Thiers et al. [74] conducted ignition tests on various cold-pressed Al-Ni powder compacts and reported that specimens consisted of small-sized particles ignited more readily.

Hunt, Plantier, and Pantoya [83] also discussed the effect of nano-scale reactants in Al-Ni composites which were cold-pressed and laser-ignited. They concluded that ignition time and temperature were significantly decreased when compared with those of to micron-scale reactants.

Cardellini et al. [90, 91] discussed the solid-state reactions induced by plastic deformation during high-energy ball milling. They observed different reaction paths with respect to thermal annealing.

Liu and Dupont [96] used the laser-engineered net shaping (LENS) process to obtain nickel aluminide intermetallics starting from elemental powders. Intermetallics with various compositions were fabricated, although they all had high amounts of porosity.

There is a vast amount of research on the fabrication and reactions of Al/Ni multilayer foils [7, 73, 81, 97-104]. Michaelsen, Lucadamo, and Barmak [101] investigated the early-stage reaction kinetics of Al/Ni multilayer films with pair thicknesses of 10 and 20 nm. They reported that the B2 AlNi phase with a metastable composition was the first phase to form and that Al3Ni was the second phase forming in the system. Takahashi and Greer [7] reported on the phase formation sequence of Al/Ni multilayer foils and they observed Al3Ni phase to form first, followed by AlNi. During a DSC test, the first exothermic peak appeared at 500 K. Al3Ni2 phase
formed at a later stage. Sieber et al. [102] also worked on Al/Ni multilayer foils and they agreed with Takahashi and Greer [7] on the formation of Al₃Ni as the first phase to form.
3. EXPERIMENTAL PROCEDURE

3.1 Materials

The materials used in this study are (1) Al (99.5% pure) and Ni (99.8% pure) powders, 7-15 µm and 45-150 µm in size, respectively, shown in Figure 3.1, and purchased from Alfa Aesar, (2) Al and Ni nanoflakes with sub-micron thicknesses (100-300 nm), shown in Figure 3.2, produced by a proprietary hammer milling technique and supplied by Fukuda Metal Foil and Powder Co. Ltd., Japan.

The Al and Ni powders were initially mixed in 1:1 molar ratio in a cylindrical container rotating at 750 rpm for 1 h without using any additives. In order to improve the particle distribution, ethanol was added to the container for additional mixing for 1 more hour. Subsequently, the mixture was left in open air to dry. Since the nanoflakes, due to their small size, have a high surface energy, they agglomerate and form clusters. Therefore, nanoflake mixtures were sonicated in ethanol for up to 5 h to break up these clusters and further improve the particle distribution. Subsequent to the sonication step, the mixture was once again left in open air to dry.
Figure 3.1 SEM pictures of as-received (a) Ni powder and (b) Al powder.
Figure 3.2 SEM pictures of as-received (a) Ni flakes and (b) Al flakes.
### 3.2 Ultrasonic Powder Consolidation

A STAPLA Condor ultrasonic welding unit, shown in Figure 3.3, was used for systematic consolidation experiments. This unit operates at a maximum power of 3 kW and a fixed frequency of 20 kHz. The amplitude can be adjusted by changing the power level and measured with the micro-gauge shown in Figure 3.3(a). The micro-gauge is connected to the machine by using a fixture. The drawing of the fixture was provided by STAPLA Ultrasonics Corporation, Wilmington, MA and given in APPENDIX-A. The controller unit (Figure 3.3 (c)) transmits high frequency signals to the converter that creates ultrasonic vibrations. A reducer is used to amplify the vibration amplitude to a value between 4-9 μm, as listed in Table 3.1. A uniaxial force is applied by using the Z-axis positioning knob and measured through a calibrated Rubbermaid Pelouze 4040 digital scale. A foot pedal was used to initiate the ultrasonic vibrations.
Figure 3.3 STAPLA Condor ultrasonic welding unit, (a) Front view, (b) Side view, (c) Control unit.

Table 3.1 Amplitude value with respect to the power level.

<table>
<thead>
<tr>
<th>Power level</th>
<th>Amplitude (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>9</td>
</tr>
</tbody>
</table>
The sonotrode is made of high speed tool steel, thus the maximum UPC temperature is limited to 773 K in order to avoid exceeding the tempering temperature of the high speed tool steel. The sonotrode tip is in the size of 3.68 mm x 3.68 mm and has a 14 x 14 grid of knurls with the dimensions as shown in Figure 3.4.

![Figure 3.4 Schematic diagrams showing the sonotrode tip.](image)

In order to conduct experiments at elevated temperatures, a heater plate (Figure 3.3(b)) was designed and built to be used with the ultrasonic welding unit. Two cartridge heaters (TUTCO, 9.5 mm diameter, 51mm length, 400 W) and a K-type thermocouple (OMEGA Model SP-GP-K-6) probe are inserted in a stainless steel plate, as seen in Figure 3.5. The heater plate is attached to a base plate and insulated with 50 mm thick alumina-silica fiber sheets. Insulated setup was inserted into a 20.3 cm x 20.3 cm x 10.2 cm NEMA 1 steel electrical enclosure. Drawings are given in APPENDIX-A.
The heaters and the thermocouple are connected to a control box (Figure 3.6) which is controlled by a computer equipped with a National Instruments (NI) PCI-6035E multifunction data acquisition (DAQ) card through a NI BNC-2110 connector block. The control box consists of a solid state relay (SSR), a fuse block with a 250 V, 5 A fuse, and an Omega FHS-7 finned heat sink. A wiring diagram is given in Figure 3.7. A computer program, coded on LabView 8.6 [105], acquire the temperature data from the thermocouple and sends signals to the heaters to heat the plate to the set temperature. This program is set to record the temperature data with a sampling rate of 1000 data points per second. Additional K-type thermocouples are used to monitor the specimen temperature during experiments.
Two different methods were used for UPC of Al-Ni particles. In the first method, uniaxial pressure and ultrasonic vibrations were applied to the specimen through a punch-die arrangement, as shown in Figure 3.8(a). The die and the punch were both made of 0.78 mm thick Ni sheet and had a diameter of 4.1 mm. The particles were placed in the die, preheated to a temperature between room temperature and 573 K, held under a uniaxial pressure, normal to the
die, ranging between 30 and 135 MPa for 30 s. They were subjected to ultrasonic vibrations in open air for 1 s followed by an after-burst time of 0.02 s, at a fixed frequency of 20 kHz with amplitude of 9 µm. Control specimens were produced under the same temperature and pressure without the application of ultrasonic vibrations in order to distinguish the effects of vibrations on the consolidation of powders. The control specimens were held under specified conditions for 2 minutes, four times longer than the specimens consolidated with vibration.

In the second method, a small amount of the particle mixture was charged into a packet made of 50 µm thick Ni foil. The packet was heated to the processing temperature ranging from room temperature to 573 K and subjected to a uniaxial pressure between 30 and 80 MPa through the sonotrode. A schematic view of the packet technique was shown in Figure 3.8(b). Systematic experiments were conducted at a fixed ultrasonic frequency of 20 kHz and amplitude of 9 µm. Welding duration was also fixed at 1 s followed by an after-burst time of 0.02 s.
Figure 3.8 Schematic view of an ultrasonic welder specially modified for UPC method using, (a) A punch-die arrangement, (b) A powder packet.
3.3 Metallography and Microscopy

The consolidates were removed from the die or the packet and mounted with epoxy that was cured in 5-10 minutes at room temperature. The specimens were ground with SiC abrasive papers. Several coarse to fine grit sizes (240, 320, 400, 600, 800, 1200, 1500, 2000) were used. Subsequent to grinding, the specimens were polished on rotating wheels with fine alumina powder of size 1, 0.3, 0.05 μm. A Buehler ECOMET 5 2-speed grinding-polishing unit was used for the preparation of metallographic specimens.

Microstructural characterization was performed with an Olympus VANOX-T optical microscope with magnifications up to 1000x. For higher magnifications, a JEOL JSM-6360 scanning electron microscope (SEM) (3 nm resolution at 30 kV accelerating voltage) and a Carl Zeiss SUPRA 25 field-emission scanning electron microscope (FESEM) (1.7 nm resolution at 15 kV accelerating voltage) were used in the secondary electron (SE) mode.

3.4 Porosity Measurements

As a measure of the specimen quality, porosity measurements were conducted. Since the specimen size was too small to apply the Archimedes’ principle, an image analysis software ImageJ [106] was used to calculate the area fraction of the porosities. ImageJ simply counts the number of pixels that is associated with the porosities and divides it by the total number of pixels in the image. This calculation was carried out for specimens fabricated under different processing conditions, as summarized in Table 3.2, with or without the application of ultrasonic vibrations. In some cases, Ni particles came off during metallographic specimen preparation.
Since this type of cavities did not form during processing, they should not be counted as porosity. Therefore, those spaces were filled with the image processing software, as marked with arrows in Figure 3.9. Then, a threshold process was conducted at which the software detects the contrast differences in the image and paints the darker pixels as they represent the porosities, as seen in Figure 3.10. The software removes everything but the porosities from the image (Figure 3.11) and calculates the total area fraction.

Figure 3.9 Cavities created during metallographic specimen preparation were filled with the image processing software.
Figure 3.10 Threshold process paints the porosities to red.

Figure 3.11 Software only keeps the red painted regions in the image and calculates the area fraction.
Table 3.2 Processing parameters of the specimens used for porosity measurements.

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (K)</th>
<th>Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-Ni Powders</td>
<td>298-373-423-473-523-573</td>
<td>30-90-135</td>
</tr>
</tbody>
</table>

3.5 Bending Tests

As another measure of specimen quality, manual bending tests were performed [107]. Results were used to discuss the material ductility and the level of metallurgical bonding. Specimens with a diameter of 4 mm were held with tweezers from both ends and manually bent until they failed, as shown in Figure 3.12. Subsequently, the fracture surfaces were examined by SEM to investigate the mode of fracture. This procedure was carried out for specimens that were produced from both powders and nanoflakes.
Figure 3.12 Bending tests were applied to Al-Ni composites as shown in (a) Holding the specimen in one end, (b) Holding the specimen in the other end, (c) Specimen was bent until it failed, (d) Brittle fracture occurred at the early stages of the test.

3.6 Differential Scanning Calorimetry

A power compensated Perkin Elmer Pyris 1 DSC capable of heating up to 973 K was used for testing particle composites. Table 3.3 shows the processing conditions of the specimens tested. Before starting each test, a warm-up program was run to detect any irregularities with the machine. After setting up the parameters for the real test, a baseline curve was plotted with empty pans in order to eliminate equipment based errors. Both pans were made of alumina.
Specimens were weighed with a precision scale which has a resolution of 0.0001 g. The specimen was placed in one of the pans and the other one was left empty as the reference pan. Nitrogen gas was used to create an inert atmosphere. All tests were started from a temperature of 323 K and a heating rate of 20 K/minute was used. The heat flow from the specimen pan to the reference pan was plotted with respect to the furnace temperature by subtracting the baseline curve from the actual curve.

Table 3.3 Processing conditions of the specimens tested in DSC.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mixing Condition</th>
<th>Consolidation Temperature (K)</th>
<th>Consolidation Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powders</td>
<td>Dry mixing (1 h)</td>
<td>523</td>
<td>80</td>
</tr>
<tr>
<td>Powders</td>
<td>Dry mixing (1 h) + Mixing in Ethanol (1 h)</td>
<td>523</td>
<td>80</td>
</tr>
<tr>
<td>Nanoflakes</td>
<td>Dry mixing (1 h)</td>
<td>523</td>
<td>80</td>
</tr>
<tr>
<td>Nanoflakes</td>
<td>Dry mixing (1 h) + Mixing in Ethanol (1 h)</td>
<td>523</td>
<td>80</td>
</tr>
<tr>
<td>Nanoflakes</td>
<td>Dry mixing (1 h) + Mixing in Ethanol (2 h) + Sonicated in ethanol (5 h)</td>
<td>523</td>
<td>80</td>
</tr>
</tbody>
</table>

3.7 Spark Ignition Tests

An OMEGA TL-WELD fine wire welder with an energy output of up to 60 J was employed for spark ignition tests. Figure 3.13 shows the spark ignition procedure. Application of a spark melts down a small portion of the Al-Ni composite specimen and initiates a reaction which may self-propagate throughout the whole volume if the microstructure is suitable for SHS. This test was applied to select specimens of both Al-Ni powder and nanoflake composite to evaluate their applicability to SHS. In order to avoid exposing the specimen-holding pliers to the
heat output of potential exothermic reactions, the specimens were placed on Ni foils and brought close to the carbon electrode to initiate a spark between the specimen and the electrode.

![A fine wire welder used for spark ignition tests.](image)

Figure 3.13 A fine wire welder used for spark ignition tests.

### 3.8 Continuous Heating Ignition Tests

A setup, schematically shown in Figure 3.14, was designed and built in the Advanced Materials Processing Laboratory (AMPL) at Northeastern University to determine the ignition temperature, the maximum temperature reached after ignition, and the total time required to reach the maximum temperature. The system consists of a heater plate connected to a PC through a DAQ system, as explained in detail in Section 3.2. Heating is conducted under enclosed Ar bath. The DAQ system acquires temperature data with a K-type thermocouple probe inserted to the heater and another K-type thermocouple wire attached to the specimen at a rate of 1000 data points per second. The heater plate is set to heat up to 933 K, which is the melting temperature of
the aluminum, at heating rate of 125 K/minute. The changes in the heater temperature and the specimen temperature were recorded by the PC and T-t diagrams were created.

Figure 3.14 Schematic representation of the continuous heating ignition test setup.

3.9 X-Ray Diffraction

The phases formed during DSC were determined by XRD on a Rigaku RH3 Cu-source Diffractometer (185 mm) using Cu K$_\alpha$ radiation at an operating power of 10 kW. Since the main purpose of the XRD studies was to determine the intermetallic phase formation in an Al-Ni composite, a $1^\circ$ divergence slit was used to increase the diffracted area on the specimen. The scatter slit was selected to have the same size as the divergence slit to reduce the background noise. A 0.3 mm receiving slit was used, since the machine was optimized for this size [108]. The specimens were scanned between the diffracting angles ($2\theta$) of $20^\circ$-$110^\circ$ with a step size of 0.02°. A scanning rate of 2° per minute was employed in the continuous scanning mode. The collected data were later analyzed with MDI Jade XRD analysis software which searches and
matches the data within a database maintained by the International Center for Diffraction Data [109].

3.10 Energy Dispersive X-Ray Spectroscopy

A JEOL 2010 FEG analytical electron microscope equipped with an energy dispersive x-ray detector was used at an accelerated voltage of 15 kV for compositional analysis of select specimens. EDS was used only for a powder composite produced at 523 K and 80 MPa to determine the phase evolution during the solid state reaction stage. Five measurements were carried out for each region and the average values are reported. The EDS results were interpreted together with XRD patterns to determine the phase formation sequence.
4. ULTRASONIC POWDER CONSOLIDATION OF ALUMINUM-NICKEL PARTICLES

This chapter addresses the production of Al-Ni reactive composites by UPC. Two types of raw materials, Al-Ni powder mixtures and Al-Ni nanoflake mixtures, were used to investigate the effects of particulate size on the fabricability of Al-Ni composites by UPC and also on the reaction kinetics during fabrication, storage and use. Processing conditions have to be determined in order to obtain full-density consolidates without causing any reactions. Ultrasonic powder consolidation and testing of Al-Ni powder mixtures are discussed in Section 4.1. The results obtained from the experiments with the powder mixtures were applied to Al-Ni nanoflakes to produce composites with higher interfacial areas. The findings were given in Section 4.2.

4.1 Ultrasonic Powder Consolidation of Al-Ni Powder Mixtures

UPC is a novel technique for the consolidation of metal particles by the application of high strain rate deformation which allows full-density consolidation at low to moderately elevated temperatures. Intense vibrations break and displace oxide layers and surface contaminants, thus facilitate full metal contact between particles and form a metallurgical bond. The softening effect observed during ultrasonic welding of sheets and wires [49, 50] should be applicable for the deformation of metallic particles, hence enhance the consolidation process.
4.1.1 Microstructural analysis

Figure 4.1 shows a specimen that was produced at 523 K under 80 MPa uniaxial pressure in 1 s. The micrograph exhibits well distributed Ni particles (light gray) surrounded with a highly dense Al (dark gray) matrix. The Al particles softened under the elevated-temperature UPC conditions, which caused Al particles to deform and consolidate while Ni particles remained nearly undeformed. High magnification micrographs revealed intimate contact between Al and Ni, as seen in Figure 4.2, which indicates that Al powders were deformed and filled the interstices.

![SEM image of an Al-Ni powder composite consolidated at 523 K under 80 MPa uniaxial pressure.](image)
Figure 4.2 Image reveals intimate contact between the Al matrix and the Ni particles. No evidence of reactions was noted at the interface.

Figure 4.3 shows optical micrographs taken from specimens which were produced under four different conditions. At room temperature, only green compacts were obtained with a high amount of porosity remaining in the material. At 135 MPa pressure, partial metallurgical bonding was observed, as seen in Figure 4.3(a). Spherical voids seen in these micrographs, such as the ones marked by arrows, were created when Ni powders came off during metallographic specimen preparation, indicating that the metallurgical bonding between Al and Ni was insufficient.

At temperatures below 473 K, compacts were obtained, but the Al particle boundaries were still visible which indicated that full metallurgical bonding was not achieved. At 373 K and 90 MPa a higher level of bonding was achieved (Figure 4.3(b)).
The specimen shown in Figure 4.3(c) was produced at 473 K under 90 MPa pressure which possesses a high level of densification. Figure 4.4 shows the microstructure of a control specimen produced under the same conditions without the application of ultrasonic vibrations. It was observed that there was no metallurgical bonding between particles. It is very clear that ultrasonic vibrations have a big impact on the elimination of porosities and formation of metallurgical bonding between particles.

Figure 4.3(d) shows a specimen produced at 523 K under 90 MPa pressure which demonstrates a high level of pore elimination and consolidation. Increase in temperature reduces the materials yield point with the help of thermal activation to overcome the energy barrier for dislocation motion [110]. This situation makes the material easier to deform. Therefore, materials processed at higher temperatures possess less porosity and a higher level of metallurgical bonding. However, due to the reactive nature of the Al-Ni system, temperature has to be kept as low as possible. In this work, the maximum temperature employed was 573 K at which no evidence of reactions was observed.

Pressure is also an important factor which affects the level of compaction. Emeruwa et al. [2] conducted research on the production of green compacts with the assistance of ultrasonic vibrations. They reported that there was an optimum pressure level for efficient compaction with vibration assistance. In the present work, a maximum pressure of 135 MPa was used which provided full consolidation at temperatures above 523 K.
Figure 4.3 Optical micrographs showing Al-Ni powder composites produced by using the punch technique at (a) 298 K/135 MPa, (b) 373 K/90 MPa, (c) 473 K/90 MPa, (d) 523 K/90 MPa.
4.1.2 Porosity measurements

The residual porosity in the composite specimens decreased with increasing consolidation temperature and pressure (Figure 4.5). Under 30 MPa pressure, densification was slow and porosity remained high (>15%), even at 573 K. The composites consolidated under 90 and 135 MPa densified much faster and almost identically with increasing temperature up to 473 K. At higher temperatures, some porosity still remained in the composites consolidated at 90 MPa, while nearly full densification was achieved in the composites consolidated at 135 MPa. The latter specimens contained only a very small amount of pores (0.2%) that remained at 573 K.
under 135 MPa pressure. However, for the same level of densification, higher consolidation temperature and pressure are required for Al-Ni particles than for monolithic Al particles [111].

![Graph showing change of porosity with respect to processing temperature and pressure. Specimens were produced from spherical powders by using the punch method.](image)

Figure 4.5 Change of porosity with respect to processing temperature and pressure. Specimens were produced from spherical powders by using the punch method.

Microstructural characterization of specimens prepared without ultrasonic vibration (Figure 4.4) also revealed that the application of ultrasonic vibration is essential for full densification of Al-Ni powder composites (Figure 4.3). Figures 4.6 and 4.7 compare the porosity of the materials produced at 90 and 135 MPa, respectively, with and without ultrasonic vibration. Clearly, the application of ultrasonic vibration increases the rate of densification. It is
particularly important to note that consolidation at 573 K and 135 MPa for 1 h without ultrasonic vibration still leaves a significant amount (~8%) of porosity in the compact, whereas full densification is achieved by ultrasonic consolidation in just a second under the same temperature and pressure. Therefore, it is concluded that UPC is an effective way to rapidly produce full-dense composite aluminum and nickel structures from elemental powders. The processing window for high-density consolidation was given in Table 4.1.

Figure 4.6 Plot showing the effect of ultrasonic vibrations on residual porosity. Specimen was produced from spherical powders by using the punch method under constant pressure of 90 MPa.
Figure 4.7 Plot showing the effect of ultrasonic vibrations on residual porosity. Specimen was produced from spherical powders by using the punch method under constant pressure of 135 MPa.

Table 4.1 Processing window in terms of residual porosity for Al-Ni powders.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>298</th>
<th>373</th>
<th>423</th>
<th>473</th>
<th>523</th>
<th>573</th>
</tr>
</thead>
<tbody>
<tr>
<td>P (MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>35.2</td>
<td>25.4</td>
<td>21.8</td>
<td>19.3</td>
<td>17.4</td>
<td>15.8</td>
</tr>
<tr>
<td>90</td>
<td>33.2</td>
<td>19</td>
<td>11</td>
<td>5.9</td>
<td>4.3</td>
<td>3.4</td>
</tr>
<tr>
<td>135</td>
<td>33</td>
<td>17.9</td>
<td>10.3</td>
<td>5.1</td>
<td>2.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>
4.1.3 Bending tests

The consolidated specimens were subjected to manual bending tests to evaluate the material ductility and examine the fracture surfaces. The fracture surface, shown in Figure 4.8, reveals a ductile fracture of the Al matrix. However, all specimens were brittle and failed without appreciable deformation, due to insufficient metallurgical bonding between Al and Ni. Another study with consolidated Al powders showed that UPC can create ductile specimens that withstand 180° bending tests [111, 112].

Specimens produced at temperatures below 473 K and 90 MPa did not keep their integrity and partially shredded into powders. Control specimens produced without applying vibrations turned back to loose powders upon bending regardless of the temperature or the pressure applied. Combining these findings with porosity measurements, it can be concluded that specimens fabricated below 473 K do not have full metallurgical bonding and possess high amounts of porosity, therefore cannot keep their integrity upon bending. Specimens produced above 473 K showed sufficient metallurgical bonding of Al particles and low porosity values, as a result they stayed intact upon bending, but there was insufficient bonding between Al and Ni, thus none of the specimens withstood 180° bending tests.
4.1.4 X-ray diffraction

A powder composite produced at 573 K under 80 MPa uniaxial pressure was tested by XRD to see if there was any intermetallic phase formed during consolidation. This specimen was selected due to the fact that 573 K was the highest temperature employed and if there were any reactions occurred during fabrication this specimen should show all the evidence. The resultant XRD pattern, given in Figure 4.9, shows only Al and Ni peaks and no evidence of intermetallic phase formation.
4.2 Ultrasonic Powder Consolidation of Nanoflake Mixtures

To produce Al-Ni composites with high interfacial areas, mixtures of Al and Ni nanoflakes were also consolidated by UPC. The processing window for full density consolidation obtained with the powders (Table 4.1) was applied to the UPC of nanoflakes. Much of the attention was given to produce composites with a homogeneous distribution of nanoflakes which tend to form clusters that decrease the Al-Ni interfacial area.
4.2.1 **Microstructural analysis**

Initial studies were conducted with flakes that were blended for 1 h without using any additives. Micrographs taken from dry mixed specimens showed large agglomerates of Ni nanoflakes, as seen in Figure 4.10, due to the high surface tension of these particles. Presence of such clusters decreases the Al-Ni interfacial area drastically which affects the reaction kinetics. Since these materials are to be used as heaters, the Al-Ni interfacial area must be maximized by breaking up these clusters in the pre-consolidation stage.

![Figure 4.10 Al-Ni nanoflake composite, consolidated at 523 K under 80 MPa uniaxial pressure. Flakes were dry-mixed for 1 h.](image-url)
For this purpose, ethanol was added to the mixture for an additional of mixing. Subsequently, the mixture was left in open air for drying and specimens were produced under various conditions by UPC. The micrograph given in Figure 4.11 shows a much better particle distribution, emphasizing the importance of mixing media. Although the particle distribution is significantly improved, there are still some Ni and Al clusters visible in this specimen which would produce optimum ignition properties. Therefore, further improvements on the mixing operation were required.

Figure 4.11 Al-Ni nanoflake composite, consolidated at 573 K under 90 MPa uniaxial pressure. Flakes were mixed in ethanol for 1 h subsequent to 1 h dry mixing.
Since mixing in ethanol did not break up all clusters, a sonication step was added to the mixing process. Subsequent to the mixing and drying, the batch was filled with ethanol once again and placed in an ultrasonic cleaner and sonicated for 5 h. After the sonication was completed, the samples were left in open air to dry. Figure 4.12 shows a specimen consolidated at 523 K under 80 MPa pressure which exhibits a much better particle distribution. These mixing conditions were applied to specimens that were tested for their ignition characteristics.

Figure 4.12 An SEM image of an Al-Ni nanoflake specimen that was consolidated at 523 K under 80 MPa uniaxial pressure in 1 s. Particles were dry-mixed for 1 h, further mixed in ethanol for 2 h, and sonicated in ethanol for 5 h.
4.2.2 X-ray diffraction

A specimen was examined by XRD to see if any reactions occurred during consolidation. Results showed no evidence of intermetallic phase formation, as seen in Figure 4.13. Although the nanoflake specimens had a much higher interfacial area available for reactions, the consolidation temperature and time were low enough to avoid any kind of reactions. We can conclude that UPC provides a viable route for the consolidation of Al-Ni particles without causing any unwanted reactions.

Figure 4.13 XRD pattern of an as-consolidated Al-Ni nanoflake composite processed at 573 K under 80 MPa uniaxial pressure.
5. IGNITION PROPERTIES OF VARIOUS ALUMINUM – NICKEL COMPOSITES

The ignition characteristics of ultrasonically consolidated Al-Ni particle composites are reported in this section with a main focus on processing conditions. The composites were ignited through the application of a spark or continuously heating in a DSC furnace or an atmosphere controlled ignition chamber. Results were evaluated to determine the reaction temperatures, the maximum temperature reached, and the time required to reach the maximum temperature. XRD analyses were performed to determine the phase evolution in the reacting composites. Considering that these materials are candidates for micro/nano heating applications, a full understanding of ignition characteristics is crucially important. Overall, the thermal characterization results ensure safe production, storage, and use of these materials. DSC results are discussed in Section 5.1. Spark ignition test results are given in Section 5.2. Last section deals with continuous heating ignition tests.

5.1 Differential Scanning Calorimetry

5.1.1 Powder composites

DSC tests were conducted for powder composites prepared under two different mixing conditions, as summarized in Table 3.3, to determine the critical reaction temperatures. A representative micrograph of the as-consolidated specimen was given in Figure 5.1. Figure 5.2 shows a DSC plot of an Al-Ni powder composite consolidated at 523 K (250°C) and 80 MPa.
Exothermic heat flow became noticeable at 829 K (556°C) and increased upon further heating. A small endothermic peak occurred at 913 K (640°C) which corresponds to the eutectic point of Al and Al_3Ni. The Al-rich phases, Al_3Ni and Al_3Ni_2, are known to form as a result of the early-stage solid-state reactions [28, 57]. Thus, the initial exothermic flow was probably caused by the formation of Al_3Ni via the reaction Al(s) + Ni(s) = Al_3Ni and followed by the exothermic flow due to the possible formation of Al_3Ni_2 via the reaction Al_3Ni(s) + Ni(s) = Al_3Ni_2. Finally, formation of the eutectic liquid at the Al-Al_3Ni interface, reflected by the endothermic peak at ~913 K, boosted the reaction kinetics producing the exothermic peak at 922 K (649°C) that reflected the additional formation of intermetallic phases through the exothermic reactions. XRD of this specimen revealed the presence of AlNi, Al_3Ni, and Al_3Ni_2 intermetallic phases along with unreacted Al and Ni.

Figure 5.1 SEM image of an Al-Ni powder composite consolidated at 523 K under 80 MPa uniaxial pressure.
Figure 5.2 DSC plot of an Al-Ni powder composite consolidated at 523 K under 80 MPa uniaxial pressure. Powders were mixed in ethanol prior to consolidation.

Figure 5.3 shows optical and SEM micrographs of the Al-Ni powder composite tested with DSC. These micrographs depict four different regions, as they are numbered on the figure. Clearly, regions #1 and #4 are unreacted Ni and Al, respectively. According to the reaction sequence explained above, region #2 should be Al$_3$Ni$_2$ and region #3 should be Al$_3$Ni. The XRD pattern also showed presence of AlNi phase, however AlNi could not be located in the microstructure. AlNi may form between the unreacted Ni and the Al$_3$Ni$_2$ layer. However, the reaction would be sluggish in the absence of a liquid phase. The latter was probably the case in this specimen where the eutectic liquid between Al and Al$_3$Ni was largely confined outside the Al$_3$Ni$_2$ and Al$_3$Ni layers. This is seen in Figure 5.3(b) where the eutectic structure is formed.
primarily outside the Al$_3$Ni$_2$ and Al$_3$Ni layers although a large part of the outer Al$_3$Ni layer has been lost to form the eutectic liquid. If the eutectic liquid penetrated the Al$_3$Ni$_2$ layer, direct contact of Ni and Al through the liquid would have allowed more AlNi to form at higher rates, bringing the maximum temperature even higher. This, however, did not happen because of the relatively low Al-Ni interfacial area of this specimen.
Figure 5.3 (a) Optical and (b) SEM micrographs showing an Al-Ni powder composite heated in DSC up to 973 K.
Another specimen was prepared under the same conditions of the specimen tested with DSC. The new specimen was held at 893 K (620°C), which is below the eutectic temperature, for 5 minutes to form the intermetallic phases in the solid state. The XRD pattern, given in Figure 5.4, reveals Al$_3$Ni and Al$_3$Ni$_2$ phases, as expected. An SEM image, given in Figure 5.5, shows two layers between Ni and Al, similar to what was seen in Figure 5.3. In order to confirm the sequence of the reactions, EDS was conducted to analyze the numbered regions in Figure 5.5. The results, as summarized in Table 5.1, show that region #1 is unreacted Ni, region #2 is Al$_3$Ni$_2$, region #3 is Al$_3$Ni, and the rest is unreacted Al. No evidence of eutectic melting is observed at the Al-Al$_3$Ni interface. Also, the interface between the unreacted Ni and the Al$_3$Ni$_2$ is clean, i.e., no AlNi is formed at 893 K (620°C).

Figure 5.4 XRD pattern of an Al-Ni powder composite was held at 893 K (620°C) for 5 minutes. Results revealed the formation of Al-rich phases.
Figure 5.5 SEM image of an Al-Ni powder composite was held at 893 K (620°C) for 5 minutes. Numbered regions were analyzed by EDS.

Table 5.1 EDS results showing the atomic percentages of the numbered regions in Figure 5.5.

<table>
<thead>
<tr>
<th>Region #</th>
<th>at.% Al</th>
<th>at.% Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>60.2</td>
<td>39.8</td>
</tr>
<tr>
<td>3</td>
<td>75</td>
<td>25</td>
</tr>
</tbody>
</table>

We can conclude that the Al-rich compounds Al$_3$Ni and Al$_3$Ni$_2$ form at the early stages of reactions. At 913 K (640°C) eutectic melting occurs at the Al-Al$_3$Ni interface and triggers ignition which results in the formation of AlNi phase. Due to the large particle size (or low interfacial area) used, the reaction cannot be completed; some Al and Ni phases remain unreacted.
5.1.2 Nanoflake composites

High interfacial-area Al-Ni nanoheaters were produced with nanoflakes of Al and Ni. DSC tests were conducted to analyze the effect of the initial interfacial area on reaction characteristics. Section 4.2.1 discusses the importance of mixing conditions on the particle distribution which affects the reaction kinetics. Figure 5.6 shows a DSC plot of an Al-Ni nanoflake composite consolidated at 523 K (250°C) under 80 MPa uniaxial pressure. Nanoflakes were dry-mixed for 1 h. A representative micrograph is given in Figure 5.7. The first exothermic peak occurred at 796 K (523°C) and the second peak at 918 K (645°C). This result suggests the solid-state formation of Al rich phases above about 773 K (500°C) and eutectic liquid formation at Al3Ni-Al interface around 913 K (640°C) which triggered the ignition. Dry-mixing and consolidation left Ni clusters in the Al matrix, which limited the initial interfacial area between Al and Ni much below the ideal value of homogeneous mixing. Thus, the initial solid state reactions to form Al3Ni and Al3Ni2 were limited causing the first peak to be small. Also, a small endothermic peak was observed at 586 K (313°C). The as-received nanoflakes were covered with stearic acid to prevent pyrophoric reactions. Therefore, the nanoflake mixture, after the mixing procedure, still contained trace amounts of stearic acid which evaporated around 586 K (313°C).
Figure 5.6 DSC plot of an Al-Ni nanoflake composite consolidated at 523 K under 80 MPa pressure. Nanoflakes were dry mixed for 1 h.
A second specimen was produced from the nanoflakes dry mixed for 1 h and mixed in ethanol for 1 more hour, in order to improve the particle distribution and dissolve stearic acid. A micrograph given in Figure 5.8 shows a better particle distribution, hence increased Al-Ni interfacial area. In this specimen, a two-peak feature in DSC was also observed with mid-points at 778 K (505°C) and 904 K (631°C), both in the vicinity of the exothermic peaks that appear in Figure 5.6. However, this time both peaks had almost the same size as opposed to a small first peak and a large second peak. Similarly, a low temperature endothermic peak was observed at 586 K (313°C), indicating that stearic acid was not removed completely during the mixing procedure.
Figure 5.8 Al-Ni nanoflake composite, consolidated at 573 K under 90 MPa uniaxial pressure. Flakes were mixed in ethanol for 1 h subsequent to 1 h dry mixing.
Figure 5.9 DSC plot of an Al-Ni nanoflake composite consolidated at 523 K under 80 MPa pressure. Nanoflakes were mixed in ethanol for 1 h subsequent to 1 h dry mixing.

In another experiment, Al and Ni nanoflakes were, after initial dry mixing, further mixed in ethanol for 2 h, and then sonicated in ethanol for 5 h. The consolidated structure exhibited a much more homogeneous distribution of nanoflakes, as can be seen in Figure 5.10. The DSC trace, shown in Figure 5.11, has a two-peak feature, at similar temperatures to those of the prior specimens, but with much larger intensity for the first peak and lower intensity for the second peak, owing to a higher initial interfacial area in the nanoflake composite. The large intensity of the first peak also suggests the formation of localized high temperature zones as a result of high
rate solid state reactions. These hot zones may reach the eutectic temperature and cause local formation of the eutectic liquid, hence further increase the reaction kinetics.

No low temperature endothermic peaks were seen in this case, indicating that the stearic acid was removed completely during the sonication process. An SEM image of the reacted specimen was given in Figure 5.12. XRD analysis on this specimen, as seen in Figure 5.13, revealed formation of high temperature intermetallic phases, AlNi and AlNi₃, along with the Al-rich phases, Al₃Ni and Al₃Ni₂. The Al rich phases can form in the early stages of reaction (solid-state) and also during re-solidification of the liquid through the peritectic reactions.

Figure 5.10 An SEM image of an Al-Ni nano flake specimen that was consolidated at 523 K under 80 MPa uniaxial pressure in 1 s. Particles were dry-mixed for 1 h, further mixed in ethanol for 2 h, and sonicated in ethanol for 5 h.
Figure 5.11 DSC plot of an Al-Ni nanoflake composite consolidated at 523 K under 80 MPa pressure. Nanoflakes were sonicated in ethanol for 5 h after 1 h dry mixing and 2 h mixing in ethanol.
Figure 5.12 An SEM image showing the microstructure of an Al-Ni nanoflakes composite tested with DSC.
To further confirm the phases formed at the early stages, another specimen, prepared in the same way, was heated to the first exothermic peak, as seen in Figure 5.14, and analyzed by XRD. The results showed formation of $\text{Al}_3\text{Ni}$ and $\text{Al}_3\text{Ni}_2$, as expected from the results with powder composites. The micrograph of this specimen is given in Figure 5.15. The rugged interface between Al and $\text{Al}_3\text{Ni}$ layer suggests possible formation of local eutectic liquid though not confirmed in the present research.
Figure 5.14 DSC plot of an Al-Ni nanoflake composite heated up to the first exothermic peak to analyze the solid state reactions.
5.2 Spark Ignition Tests

5.2.1 Powder composites

Al-Ni powder composites with 1:1 molar ratio were subjected to spark ignition tests to initiate self-propagating reactions. It was observed that the application of a spark only created local reactions that did not propagate throughout the whole volume due to their low Al-Ni interfacial area ($\sim 2 \times 10^4 \text{ m}^{-1}$). In a previous study at Northeastern University, Gulsoy [6] used a propane torch to ignite specimens produced from the same powder materials via UPC. He reported ignition of full density composites in which reactions occurred in the thermal explosion (TE) mode due to the heating of the whole specimen. We can conclude that Al-Ni powder
composites can be ignited in the TE mode but not by self-propagating reactions, since the local reactions do not create sufficient heat output to sustain the reactions. Therefore, in the event of using these materials for heating applications, the ignition method has to be selected accordingly.

5.2.2 Nanoflake composites

The Al-Ni nanoflake composites produced from both 1Al:1Ni and 3Al:1Ni molar mixtures were also subjected to spark ignition tests, as seen in Figure 5.16. Subjecting the Al-Ni powder composites (~2x10⁴ m⁻¹) to a spark never initiated a self-propagating reaction as mentioned in the previous section. On the other hand, having much higher interfacial area (~4x10⁶ m⁻¹), composites produced from a 1:1 molar mixture of Al-Ni nanoflakes transformed completely to AlNi, as shown in Figure 5.17. Thiers et al. [74] conducted ignition tests on Al-Ni powder compacts produced by cold pressing and reported that compacts consisted of small particles ignited more readily due to their larger Al-Ni interfacial area per unit volume which enhanced the overall rate of the exothermic compound forming reactions. Thus, the ultrasonically consolidated specimens also exhibited ignition behaviors consistent with the previous observations. Moreover, the fact that the nanoflake specimen transformed completely to the high-temperature phase AlNi upon spark ignition indicates a high potential for UPC nanoflake composites may be used as energetic materials that generate heat in calculated amounts.
Figure 5.16 Spark ignition test conducted on an Al-Ni nanoflake composite that was produced at 573 K under 90 MPa pressure (a) Application of spark, (b) Ignited specimen.

Figure 5.17 XRD pattern of an Al-Ni nanoflake composite produced from 1:1 molar mixture ignited during the spark test.
Another spark ignition test was conducted with 3Al:1Ni molar ratio mixture of nanoflakes. The spark created self-propagating reactions and the specimen was completely ignited. The XRD pattern given in Figure 5.18 shows the presence of Al-rich phases, Al$_3$Ni and Al$_3$Ni$_2$. Although no unreacted Al or Ni phases were detected, there must be a small amount of Al left in the specimen since the molar ratio of Al and Ni must be the same before and after the ignition. No high temperature phase was formed due to lower heat output of the 3:1 molar composition.

Figure 5.18 XRD pattern of an Al-Ni nanoflake composite produced form 3:1 molar mixture ignited during the spark test.
5.3 Continuous Heating Ignition Tests

The Al-Ni nanoflake composites produced from 1:1 molar ratio mixture were subjected to continuous-heating ignition tests. Two sets of specimens were prepared from (1) nanoflakes mixed in ethanol for 1 h, subsequent to dry mixing for 1h, (2) nanoflakes sonicated for 5 h, subsequent to 1 h dry mixing and 1h mixing in ethanol. A preliminary test was conducted in open air with a specimen produced at 573 K and 135 MPa by the consolidation of nanoflakes mixed by condition #1. The results showed that ignition occurred around 913 K (640°C), as seen in Figure 5.19, before reaching the melting point of aluminum, which is indicative of a prior solid state reaction. It is generally believed that bulk temperature of the material should reach the melting point of Al (933 K) in order to initiate ignition. However, the DSC plot of an Al-Ni powder composite, given in Figure 5.2, clearly shows that ignition can take place at lower temperature, such as the eutectic temperature of Al-Al$_3$Ni (913 K). Moreover, high rate solid state reactions can create local hot zones where the temperature can reach the eutectic temperature and initiate ignition while the bulk temperature reading can be well below the eutectic temperature.

The thermograph in Figure 5.19 reveals that the maximum temperature reached after the ignition was around 1573 K (1300°C). During the cooling, two temperature arrests were detected; the first one is around 1410 K (1133°C) which is the peritectic temperature of Al$_3$Ni$_2$, and the second one is around 1127 K (854°C) which is the peritectic temperature for Al$_3$Ni intermediate phase. This provides evidence for the formation of AlNi which partially reacted with the liquid to form Al$_3$Ni$_2$ at 1410 K (1133°C). Upon further cooling below 1127 K (854°C), some of the Al$_3$Ni$_2$ then transformed to Al$_3$Ni by reacting with the liquid.
Having a full density consolidation is very important if the ignition test is conducted in open air, since oxygen can travel through the pores and form oxide phases that hinder the reactions. A specimen that was produced at 473 K under 90 MPa, with 6% porosity, was heated up to 973 K in open air. No ignition was observed. The XRD pattern of this specimen, as seen in Figure 5.20, only revealed NiO along with unreacted Al and Ni.
Figure 5.20 XRD pattern of an Al-Ni nanoflake composite that was heated up to 973 K in open air.

Additional tests were conducted under Ar bath to prevent oxidation. A specimen produced from the nanoflakes sonicated for 5 h was tested. The screen shots given in Figure 5.21 shows four different stages of an ignition test. The specimen sitting on the heater plate creates bright light, Figure 5.21(c), during ignition. It took only a few milliseconds to reach the maximum temperature and about 5 s to cool back to the heater temperature.
Figure 5.21. Screen shots showing four different stages of the continuous-heating ignition test applied to a nanoflake composite, (a) before ignition, (b) initiation of the ignition, (c) bright light observed during ignition, (d) after the ignition.
As seen in Figure 5.22, the specimen heating rate started to deviate from the heating rate of the heater at a temperature around 820 K (547°C) and a temperature spike formed at 850 K (577°C). As mentioned above, solid state reaction may cause the formation of local hot zones. Whether such a prior solid state reaction can actually create these hot zones will depend on the interfacial area between the reactive materials. As the interfacial area increases, the hot zones can form at a lower bulk temperature. In this case, the bulk temperature reading was at 850 K (577°C) when the ignition occurred. This strongly suggests that the temperature locally reached the eutectic point. A maximum temperature of 1280 K (1007°C) was recorded. The screen shots given in Figure 5.21 are marked in Figure 5.22.

Figure 5.22 Thermograph of a specimen produced from sonicated Al-Ni nanoflakes continuously heated under Ar bath.
6. MODELING OF EARLY-STAGE REACTION KINETICS

6.1 Introduction

Reactive composites possessing high interfacial areas, such as nanoflake composites, may ignite at a monitored temperature lower than the ignition temperature of their counterparts with low interfacial areas. Thermal analyses of Al-Ni composites, as discussed in Chapter 5, show the importance of such solid state reactions. At a high rate of an exothermic solid state reaction, local hot zones can form due to such a reaction and create a small amount of liquid phase which would trigger ignition. Recent developments in nanotechnology enable the fabrication of Al-Ni composite structures with very high values of interfacial areas, such as multilayer thin films produced by physical vapor deposition (PVD) [7, 69, 98, 113, 114]. These type of materials can self-ignite in an unwanted manner at temperatures as low as 500 K [7]. Therefore, there is a need for the development of a model that predicts the material thermal behavior in the solid state. In the present research, a kinetic model was developed to predict the early-stage solid-state reaction kinetics of Al and Ni [115]. This model employs the Avrami equation [116], but with a modification in a form appropriate for the prediction of the overall reaction kinetics under non-isothermal conditions encountered in the reactive composite ignition. This model calculates the increase in volume fraction ($\Delta x_v$) of the product phase that forms via exothermic reactions at a specific temperature ($T$) in a small time step ($\Delta t$). The calculated value of product volume fraction is then used in a thermal balance equation to obtain the temperature increase ($\Delta T$) due to the formation of the product phase. In the next step, the volume fraction increase is calculated for the same time increment $\Delta t$, but this time for a temperature of $T + \Delta T$. Successive iteration of
this step yields a T-t plot of an Al-Ni composite for a given starting temperature. If the starting temperature is sufficiently low, the heat generated by the reaction during the time increment $\Delta t$ is smaller than the heat dissipated out of the composite, and there is no rise in temperature, i.e., $\Delta T = 0$. Under such conditions, the composite will remain at the starting temperature and is safe for storage. If, however, the starting temperature is high enough to make the rate of reaction exceed the rate of heat dissipation, $\Delta T \geq 0$, and the composite temperature rises. Thus, the critical starting temperature for safe fabrication, storage, and service can be predicted.

6.2 Theory

6.2.1 Total volume of product phase

The reaction $A(s) + B(s) \rightarrow \alpha$ (compound) occurs at the A/B interface, as shown in Figure 6.1. Assume that $\alpha$ disks nucleate at a rate of $I$ and grow laterally on the A/B interface at a growth rate of $G$, each having a thickness of $W$. The thickness $W$, in a general sense, may depend on both temperature and time. However, the thickening of $\alpha$ disks requires through-thickness diffusion and thus is sluggish. Therefore, in the present model, it is assumed that $W$ is determined by the rate of reaction at the triple junction of the $\alpha$ disk and in A-B interface. Under such condition, $W$ is related to the rate of lateral growth $G$ and the effective diffusivity $D$ via $W = D/G$, and as such may be regarded as dependent only on temperature.
Figure 6.1 A schematic showing compound particles forming at the A-B interface.

The total volume of $\alpha$ particles in the A-B composite increases at higher rates as time elapses, as schematically shown in Figure 6.2, since the heat generated by the formation of $\alpha$ increases the temperature of the composite, increasing the reaction rate further.

Figure 6.2 Graphical illustration of the change of $\alpha$ volume with respect to time.
Let $V^\alpha(t_i,t)$ be the volume of $\alpha$ particles (disks) that nucleate between $t_i$ and $t_i + dt$ at time $t$, which is expressed by

$$dV^\alpha(t_i,t) = V_0 I_i dt S_{A/B}^i W \pi \left[ \int_{t_i}^t G d\tau \right]^2$$

(6.1)

where $I_i$ is the nucleation rate at $t_i$, $S_{A/B}^i$ is the area of A/B interface available for $\alpha$ nucleation per unit volume at $t_i$, $V_0$ is the total volume of the A-B composite. Assume that $\alpha$ disks impinge on each other only in lateral growth, as shown in Figure 6.3, i.e., no impingement in normal growth (thickening). Then, the total $\alpha$ volume at $t$ is given by

$$V^\alpha(t) = \int_{t_0}^t V_0 I_i S_{A/B}^i W(T) \pi \left[ \int_{t}^{t_i} G d\tau \right]^2 dt_i$$

(6.2)

Figure 6.3 Compound disks impinging on each other only in lateral growth.

Thus, the calculation of $V^\alpha(t)$, along a non-isothermal path, requires an expression for $S_{A/B}^i$. How this may be achieved is shown in the next section.
6.2.2 Extended area of disks

Suppose that $S(t_j, t_i)$ is the area of the broad surface of an $\alpha$ disk that nucleates at $t_j$ and grows over the period from $t_j$ to $t_i$ without impinging on each other. Then, the total broad surface area ($dS^\alpha$) of the $\alpha$ disks at $t_j - t_j + dt_j$ is given by

$$dS^\alpha = S^j_{A/B} I_j dt_j \pi \left[ \int_{t_j}^{t_i} G d\tau \right]^2$$  \hspace{1cm} (6.3)

In the imaginary case where the interfacial area between the two metals is continually extended such that $S^j_{A/B} = S^0_{A/B}$ at all times,

$$dS^\alpha_{ext} = S^0_{A/B} I_j dt_j \pi \left[ \int_{t_j}^{t_i} G d\tau \right]^2$$  \hspace{1cm} (6.4)

Integrating Eq. (4) over the period $t_0$ to $t_i$ yields

$$f^{\alpha,i}_{ext} = \frac{S^{\alpha}_{ext}}{S^0_{A/B}} = \pi \int_{t_0}^{t_i} I_j \left[ \int_{t_j}^{t_i} G d\tau \right]^2 dt_j$$  \hspace{1cm} (6.5)

where $f^{\alpha,i}_{ext}$ is the extended area fraction of $\alpha$ disks at time $t_i$.

6.2.3 Avrami Correction

The impingement of $\alpha$ disks, which actually occurs, is addressed by applying the Avrami correction [116] to Equations (6.4) and (6.5), i.e.,

$$\frac{S^{\alpha,i}_{ext}}{S^0_{A/B}} = \frac{f^{\alpha,i}_{ext}}{f^{\alpha,i}_{ext}} = \frac{S^0_{A/B} - S^{\alpha,i}_{ext}}{S^0_{A/B}} = 1 - f^{\alpha,i}_{ext} = \exp(-f^{\alpha,i}_{ext})$$  \hspace{1cm} (6.6)

which gives
\[ f^{\alpha,i} = 1 - \exp \left( - f^{\alpha,i}_{\text{ext}} \right) = 1 - \exp \left\{ - \pi \int_{t_0}^{t_i} \left( \int_{t_j}^{t_i} G \, d\tau \right)^2 \, dt_j \right\} \quad (6.7) \]

Substituting Equation (6.7) in \( S'_{A/B} = S_{A/B}^{0} \left( 1 - f^{\alpha,i} \right) \) gives

\[ S'_{A/B} = S_{A/B}^{0} \exp \left\{ - \pi \int_{t_0}^{t_i} \left( \int_{t_j}^{t_i} G \, d\tau \right)^2 \, dt_j \right\} \quad (6.8) \]

which is the expression for \( S'_{A/B} \) required in Equation (6.2). Substituting Equation (6.8) in Equation (6.2) yields

\[ V^\alpha(t) = \int_{t_0}^{t_i} V_{0} I_{i} S_{A/B}^{0} \exp \left\{ - \pi \int_{t_0}^{t_i} \left( \int_{t_j}^{t_i} G \, d\tau \right)^2 \, dt_j \right\} W(T) \left( \int_{t_0}^{t_i} G \, d\tau \right) \, dt_i \quad (6.9) \]

or for the change in volume fraction \( x_\alpha \)

\[ x_\alpha(t) = \frac{V^\alpha(t)}{V_0} = \pi S_{A/B}^{0} \int_{t_0}^{t_i} I_{i} \exp \left\{ - \pi \int_{t_0}^{t_i} \left( \int_{t_j}^{t_i} G \, d\tau \right)^2 \, dt_j \right\} W(T) \left( \int_{t_0}^{t_i} G \, d\tau \right) \, dt_i \quad (6.10) \]

**6.2.4 Heat Generation**

The heat generated at temperature \( T \), \( \Delta H(T) \), by the solid-state exothermic reaction, \( xA(s) + yB(s) \rightarrow \alpha \) (compound), is given by

\[ \Delta H(T) = \int_{T}^{298\text{K}} (x C_p^A + y C_p^B) \, dT + H_{\alpha,298\text{K}}^0 + \int_{298\text{K}}^{T} C_p^\alpha \, dT \quad (6.11) \]

where \( C_p^i \)'s are the heat capacities of the reactant elements A and B and the product phase \( \alpha \).

\( \Delta H_{\alpha,298\text{K}}^0 \) is the heat of formation for \( \alpha \) compound. The heat of reaction per unit volume is calculated from
\[ \Delta H_V(T) = \frac{\Delta H(T)}{V^\alpha} \]  

where \( V^\alpha \) is the molar volume of \( \alpha \) compound.

### 6.2.5 Thermal Balance

The amount of heat generated along a non-isothermal path during the progression of the reaction can be calculated with Equations (6.11) and (6.12). Suppose that the volume fraction of the compound \( \alpha \) increases by \( dx^\alpha \) during a time increment, \( dt \), spent at \( T \). The corresponding volume increase of the compound is \( V^0 dx^\alpha \). Thus, the heat generated, \( dh \), over \( dt \) is given by

\[
dh = -\Delta H_V(T) V^0 dx^\alpha
\]  

This increases the temperature of the specimen by \( dT \) for a sufficiently small composite in which the temperature may have a uniform distribution. For adiabatic conditions, the temperature increase, \( dT \), is given by

\[
-\Delta H_V(T) V^0 dx^\alpha = C_p V^0 dT
\]  

where \( C_p \) is the heat capacity of the specimen, consisting of the reactant elements A and B and the product phase \( \alpha \), which is expressed by

\[
C_p = x_A C_p^A + x_B C_p^B + x_\alpha C_p^\alpha
\]  

The next iteration step is done at \( T + dT \), with the same time increment \( dt \). This procedure continues until a critical temperature is reached.

Depending on the starting temperature, at the very early stages, the reaction rate would not be very high; therefore adiabatic conditions may not apply to such cases. To apply non-adiabatic conditions, heat dissipation can be calculated by a simple convection heat transfer
Assuming that the sample is sitting on a ceramic pan and heat transfer is caused by natural convection from the top surface. Thus, the heat loss can be calculated by the following equation

\[ dH_L = h A_S \, dt \, (T - T_0) \]  \hspace{1cm} (6.16)

where \( A_S \) is the surface area, \( T_0 \) is the starting temperature (or surrounding temperature), and \( h \) is the convection heat transfer coefficient which can be obtained from

\[ h = \frac{k}{L_C} \, \mathrm{Nu} \]  \hspace{1cm} (6.17)

where \( k \) is the thermal conductivity of the surrounding atmosphere, \( L_C \) is the characteristic length or simply the thickness of the sample, and \( \mathrm{Nu} \) is the natural convection Nusselt number expressed by

\[ \mathrm{Nu} = 0.54 \, \mathrm{Ra}^{1/4}_L \]  \hspace{1cm} (6.18)

and \( \mathrm{Ra} \) is the Rayleigh number which can be calculated by

\[ \mathrm{Ra}_L = \frac{g \beta (T - T_0) L_C^3}{\nu^2 \, \Pr} \]  \hspace{1cm} (6.19)

where \( g \) is the gravitational acceleration, \( \beta \) is the coefficient of thermal expansion and defined by \( \beta = 2/(T + T_0) \), \( \nu \) is the kinematic viscosity of the surrounding gas, and \( \Pr \) is the Prandtl number.

Thus, the thermal balance equation (Equation (6.14)) can be modified for non-adiabatic conditions:

\[ \Delta H_V(T)V_0 \, dx^a - dH_L = C_P \, V_0 \, dT \]  \hspace{1cm} (6.20)
6.3 Numerical Solution

Since the calculations are carried out step-by-step with a constant time increment, we can change the equations from integral form to summation form, such as the $\alpha$ volume given by Equation (6.2) is replaced by

$$V_i^\alpha = V_0 \Delta t^3 \pi \sum_{k=0}^{i-1} I_k S_{A/B}^k W_k \left[ \left( \sum_{j=k}^{i-1} G_k \right)^2 - \left( \sum_{j=k}^{i-2} G_k \right)^2 \right]$$  \hspace{1cm} (6.21)

and $S_{A/B}^i$ given by Equations (6.5) and (6.6) is replaced by

$$S_{A/B}^i = S_{A/B}^0 \exp \left[ -\pi \Delta t^3 \sum_{k=0}^{i-1} I_k \left( \sum_{j=k}^{i-1} G_j \right)^2 \right]$$  \hspace{1cm} (6.22)

Then, Equation (6.10) takes the following form

$$x_i^\alpha = S_{A/B}^0 \Delta t^3 \pi \sum_{k=0}^{i-1} I_k W_k \exp \left[ -\pi \Delta t^3 \sum_{k=0}^{i-1} I_k \left( \sum_{j=k}^{i-1} G_j \right)^2 \right] \left[ \left( \sum_{j=k}^{i-1} G_k \right)^2 - \left( \sum_{j=k}^{i-2} G_k \right)^2 \right]$$  \hspace{1cm} (6.23)

The modeling scheme is coded in MATLAB® and given in APPENDIX-B. The solution was obtained for a 10 mm x 10 mm Al-Ni multilayer foil with a total thickness of 10 µm and a bilayer thickness of 100 nm, shown in Figure 6.4. Due to the small layer thickness, the initial Al-Ni interfacial area per unit volume is very high. Therefore, the heat output per unit volume would be very high and the temperature increase would make the reaction go faster. There are various models that predicts the kinetics of solid-state reactions of multilayer foils [69, 73, 113], but none of the existing models includes the temperature increase due to the reactions.
First, all the parameters required to solve Equation (6.10) should be determined. These are $S_{Al/Ni}^0$, $W$, $G$, and $I$. $S_{Al/Ni}^0$ can be calculated for the select geometry. The interfacial area was obtained in the dimension of area per unit volume ($m^{-1}$).

![Figure 6.4 Schematic view of a multilayer foil with alternating layers of Al and Ni.](image)

For a unit volume of a multilayer specimen, every interface has an area of 1 $m^2$, so that the number of interfaces $n_{int}$ is given by

$$n_{int} = n_{layer} - 1$$

(6.24)

where $n_{layer}$ is the number of layers. For a 1 m thick specimen, the number of layers is obtained from

$$n_{layer} = \frac{\text{sample thickness}}{\text{layer thickness}} = \frac{1}{(100 \times 10^{-9}/2)} = 2 \times 10^7$$

(6.25)

Since $n_{layer} >> 1$, $n_{int} = n_{layer}$. Consequently,

$$S_{multi}^{int} = 2 \times 10^7 m^{-1}$$

(6.26)

The lateral growth rate $G$ may be given by an Arrhenius type equation [113]:

$$G = K \exp \left( -\frac{Q}{kT} \right)$$

(6.27)
where $k$ is the Boltzmann constant and $K$ and $Q$ are the lateral growth factor and activation energy, respectively.

The thickness of the compound phase is assumed to be constant as explained in Section 6.2.1. During these calculations, for the sake of simplicity, $W$ is taken as the half of the bilayer thickness. For specimens with lower Al-Ni interfacial area, $W$ needs to be treated as a function of $T$, and is most probably given by $W = D/G$ where $D$ is the inter-diffusivity that applies to the reaction occurring at the triple junction of Al, Ni, and the compound.

The final and most important parameter is the nucleation rate. However, there is no certain way of obtaining this parameter. Therefore, site saturation conditions were applied to this model. It is known that in Al-Ni multilayer foils a continuous film of the compound phase is forming almost immediately during solid state reactions [69, 101, 113]. This can be simply explained by the formation of a very high number of nuclei at the interface and their rapid lateral growth to form a continuous film. These nuclei are most likely forming through heterogeneous nucleation at the grain boundaries in the Al-Ni interface, more specifically on the triple junctions, as shown in Figure 6.5. If we assume that all of these triple junctions are site saturated at $t = 0$, then the number of nuclei ($N$) can be the same as the number of triple junctions. Then, the nuclei grow laterally at a rate of $G$ and have thickness of $W$. Then, we can calculate $x^a$ for a time step of $\Delta t$. For this purpose, Equation (6.10) should be modified and become:

$$
\frac{x_i^a}{W} = W S_{A/B}^0 \left[ 1 - \exp \left( -N \pi \Delta t^2 \left( \sum_{k=1}^{i} G_k \right)^2 \right) \right]
$$

(6.28)
The parameters used for the calculations are given in Table 6.1. The compound related values belong to the Al$_3$Ni phase, which is most likely to form at the early stages of reactions, as it was discussed in Section 5.1.1. Figure 6.6 shows the change in lateral growth rate with respect to temperature which was calculated by using Equation (6.27).
Table 6.1 Parameters used for calculations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial interfacial area per unit volume (m⁻¹)</td>
<td>$S_{A/B}^0$</td>
<td>2 x 10⁷</td>
<td></td>
</tr>
<tr>
<td>Compound thickness (m)</td>
<td>$W$</td>
<td>5 x 10⁻⁸</td>
<td></td>
</tr>
<tr>
<td>Number of nuclei per unit area (m⁻²)</td>
<td>$N$</td>
<td>10¹⁴ - 10¹⁶</td>
<td></td>
</tr>
<tr>
<td>Time step (s)</td>
<td>$\Delta t$</td>
<td>10⁻³ – 10⁻⁴</td>
<td></td>
</tr>
<tr>
<td>Boltzmann constant (eV K⁻¹)</td>
<td>$k$</td>
<td>8.617 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>Lateral growth factor (m s⁻¹)</td>
<td>$K$</td>
<td>10⁴</td>
<td>[113]</td>
</tr>
<tr>
<td>Lateral growth activation energy (eV)</td>
<td>$Q$</td>
<td>1.44</td>
<td>[113]</td>
</tr>
<tr>
<td>Molar volume of the compound (m³ mol⁻¹)</td>
<td>$V_c$</td>
<td>2.4 x 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>Enthalpy of formation at 298 K (J mol⁻¹)</td>
<td>$\Delta H^o_{\alpha,298K}$</td>
<td>150624</td>
<td>[57]</td>
</tr>
<tr>
<td>Characteristic length (m)</td>
<td>$L_C$</td>
<td>10⁵</td>
<td></td>
</tr>
<tr>
<td>Surface area of the thin film (m²)</td>
<td>$A_s$</td>
<td>10⁴</td>
<td></td>
</tr>
</tbody>
</table>
6.4 Results and Discussion

By using the parameters given in Table 6.1 and the calculated values of lateral growth rate in Figure 6.6, the temperature of the multilayer foil was calculated at different starting temperatures, for both adiabatic and non-adiabatic conditions. It was assumed that no prior reactions took place in the multilayer foil at the starting temperature immediately. Figure 6.7 shows the calculation results for adiabatic conditions. A material held at 550 K can reach up to the eutectic point (913 K), where the liquid phase forms and triggers ignition, in 0.83 s. Another material held at 600 K reaches the same point in less than 0.1 s. On the other hand, holding
initially at 500 K did not result in a rapid temperature increase in 1 s. Another run for a longer duration showed that multilayer foil reaches the eutectic temperature in 16 s.

Figure 6.7 Temperature change in Al-Ni multilayer foils while being held at 500, 550, and 600 K, for adiabatic conditions.

Similar results were obtained under non-adiabatic conditions. Figure 6.8 shows the results for three runs starting at 500, 550, and 600 K. Due to the heat dissipation, 550 K and 600 K runs took slightly longer than the adiabatic counterparts. The run started at 500 K reached the eutectic temperature in 60 s, three times longer than 16 s obtained under adiabatic conditions.
The above calculations were carried out for \( N = 10^{16} \), the maximum value corresponding to the number of triple junction per unit area of Al-Ni interface. Additional T-t plots were calculated for \( N = 10^{14} \) and \( N = 10^{15} \) at a starting temperature of 600 K. The results, given in Figure 6.9, show that a multilayer foil with a two-orders-smaller \( N \) can still reach the eutectic temperature in less than 1 s, when initially held at 600 K.
Figure 6.9 T-t plots generated for $N = 10^{14}$, $N = 10^{15}$, $N = 10^{16}$. Starting temperature is 600 K.

Figure 6.10 shows the effect of heat removal rate on the temperature rise during reactions at a starting temperature of 550 K. If the material is held in an environment where the heat transfer coefficient was 10 times higher than the coefficient for natural convection in air, then it takes 1.8 s to reach the eutectic temperature. If the coefficient is 20 times higher, the material never reaches the eutectic temperature. Although 550 K is high enough to cause solid state reactions, the increased heat removal rate prevents the reactions from proceeding at a high rate, thus inhibiting the temperature rise. Figure 6.11 shows the heat removal rate from the specimen.
with respect to time. Figure 6.12 shows the change in volume fraction of the compound phase with respect to time.

Figure 6.10 T-t plots generated for different heat removal conditions, \( h = h_{\text{air}}, h = 10 \times h_{\text{air}}, \) and \( h = 20 \times h_{\text{air}} \). Starting temperature is 550 K.
Figure 6.11 Heat removal rate with respect to time for different heat removal conditions, $h = h_{\text{air}}$, $h = 10 \times h_{\text{air}}$, and $h = 20 \times h_{\text{air}}$. Starting temperature is 550 K.
Overall, the results showed that Al-Ni multilayer foils can self-ignite while being held at a temperature as low as 500 K, which agrees with the experimental results [7]. All plots shown above have the same type of behavior. The slope starts to deviate after a certain amount of time and a temperature spike forms shortly after the deviation becomes significant. This behavior is a result of the increasing rate of solid-state reaction due to the heat output of the reactions. We have seen a similar behavior in Figures 5.19 and 5.22. The nanoflake composites also have a high interfacial area (~4x10^6 m\(^{-1}\)), therefore the early-stage solid-state reactions have a significant effect on the ignition behavior.
7. CONCLUSIONS

UPC provides a viable route for the consolidation of metastable compositions at low temperatures in a short duration. Al-Ni reactive metal-matrix composites were successfully fabricated with spherical powders and nanoflakes by UPC. Full-density Al-Ni composites with a metallurgically consolidated Al matrix were obtained at 573 K under 135 MPa uniaxial pressure without any noticeable reaction between Al and Ni. Softer Al particles took most of the deformation and metallurgically bonded. Harder Ni particles remained essentially undeformed. Porosity measurements showed that ultrasonic vibration plays an essential role in achieving full-density consolidation.

DSC experiments showed that solid-state exothermic reactions proceeded above 829 K forming the Al$_3$Ni and Al$_3$Ni$_2$ phases. At 913 K, eutectic liquid formed between Al and Al$_3$Ni, which triggered ignition. However, due to the low interfacial area between Al and Ni, the reaction was incomplete and left unreacted Ni in the final microstructure. Therefore, smaller sized nanoflakes were used to increase the rate of reaction. Spark ignition transformed composites produced with the nanoflakes completely to AlNi, while the reaction did not self-propagate in specimens produced with coarser powders. DSC tests with nanoflake composites revealed a lower ignition temperature than the powder composites. These specimens exhibited a two-peak feature in which the first peak formed around 800 K and the second peak around 900 K. The first peak was initiated by solid-state reactions and the second peak reflected the exothermic reactions occurred subsequent to the formation of the eutectic liquid. If the initial Al-
Ni interfacial area is high, the first peak has a higher intensity due to high-rate solid-state reactions which can cause local melting. Continuous-heating ignition tests showed that the nanoflake composites can ignite at temperatures as low as 850 K and reach a peak temperature as high as 1580 K.

A non-isothermal Avrami-type equation was developed to predict the temperature increase as a result of early-stage solid-state exothermic reactions. Results showed that when initially held at 550 K, a multilayer specimen with a bilayer thickness of 100 nm can reach the Al-Al$_3$Ni eutectic temperature (913 K) in less than 1 s. This model is potentially applicable to different Al-Ni composites, such as the nanoflake composites; and as such provides a tool to safely process, store, and use Al-Ni composites as energetic materials in advanced manufacturing.
8. RECOMMENDATIONS

Mixing conditions can be further improved to obtain a more homogenous distribution of Al and Ni nanoflakes. To increase the effectiveness of the sonication step, an ultrasonic probe can be inserted into the solution. This may help to break all clusters and obtain the highest interfacial area possible with the nanoflakes. In addition, use of surfactants needs to be explored.

The UPC setup can be modified to enable the production of larger specimens. This can be achieved via layer-by-layer fabrication of the consolidates.

Preliminary UPC experiments were conducted with Al-Ni nano core-shell particles and promising results were obtained. These materials have a particles size of 50-100 nm. Therefore, consolidation of such materials would provide composites with very high interfacial areas, comparable to multilayer foils. Continuous heating ignition tests were also conducted in open air. Although a temperature spike was observed the maximum temperature reached was not as high as expected, most probably due to oxidation. Further work is required to analyze ignition characteristics of consolidated core-shell particles.

UPC can be applied to other metastable compositions, such as thermite systems. Therefore, reactive composites with higher heat output can be created. This technique can also be applied to RSP powders to produce bulk materials while preserving initial microstructure of the particles. Conventional techniques cause grain growth which reduces the mechanical properties.
Trial experiments with RSP Mg droplets were conducted and compacts were obtained with 90-95% relative density. Further work is necessary to achieve full metallurgical bonding.
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APPENDIX-A: DRAWINGS
APPENDIX-B: MATLAB® CODES

Kinetic model:

```matlab
clc, clear

%inputs
T_0 = 600; %initial temperature (K)
S_i = 2*10^7; %initial interfacial area (m^2/m^3)
W = 50*10^-9; %compound thickness (m)
H_C = 150624; %enthalpy of formation at 298 K (J/mol)
K = 10000; %lateral growth factor (m/s)
k = 8.617343*10^-5; %Boltzmann constant (eV/K)
Q = 1.44; %lateral growth activation energy (eV)
N = 10^16; %number of nuclei per unit area (1/m^2)
V_C = 2.4*10^-5; %molar volume of the compound phase (m^3/mol)
dt = 0.001; %time step (s)
steps=1000; %number of iterations
g = 9.81;
L_c = 10^-5;
A_s = 10^-4;

for i = 1:steps
    if i==1
        T = T_0;
    else
        T = T1(i-1);
    end
    G(i) = K*exp(-Q/(k*T)); %lateral growth rate
    G1(i) = sum(G);
    x_a(i) = 1-exp(-N*pi*(dt^2)*(G1(i)^2));
    x_v(i) = S_i * W * x_a(i); %volume fraction
    if i==1
        dx_v(i)=x_v(i);
    else
        dx_v(i)=x_v(i)-x_v(i-1);
    end

    %heat loss
    T_f(i) = (T+T_0)/2;
    beta(i)=1/T_f(i);
    Ra(i) = (g*beta(i)*(T-T_0)*(L_c^3)*Pr(T))/(Nu(T)^2);
    Nus(i) = 0.54 * (Ra(i)^0.25);
    h(i) = k_air(T) * Nus(i) / L_c;
    delH_L(i) = h(i) * A_s * dt * (T-T_0);

    %thermal balance
    h1=quad(@Cp_Al_mol,T,298);
    h2=quad(@Cp_Ni_mol,T,298);
    delH_L(i)=3*h1 + h2;
```
\[ \text{delH}_2 = \text{H}_C; \]
\[ \text{delH}_3 = \text{quad}(\text{Cp}_\text{Al}_3\text{Ni}_\text{mol}, 298, \text{T}); \]
\[ \text{delH} = -\text{delH}_1 + \text{delH}_2 - \text{delH}_3; \]
\[ \text{delH}_V = \text{delH}/V_C; \]
\[ \text{x}_A(i) = 0.5 - (0.86\times \text{x}_v(i)); \]
\[ \text{x}_B(i) = 0.5 - (0.19\times \text{x}_v(i)); \]
\[ \text{B} = (\text{delH}_V \times \text{dx}_v(i)\times \text{A}_s\times \text{L}_c) - \text{delH}_L(i); \]
\[ \text{sm} = 0; \]
\[ \text{dT} = 0.0001; \]

\text{if} \ \text{B} < 0
\text{while} \ \text{sm} < \text{abs}(\text{B})
\text{Cp} = (\text{x}_A\times \text{Cp}_\text{Al}(\text{T})\times \text{A}_s\times \text{L}_c) + (\text{x}_B\times \text{Cp}_\text{Ni}(\text{T})\times \text{A}_s\times \text{L}_c) + (\text{x}_v(i)\times \text{Cp}_\text{Al}_3\text{Ni}(\text{T})\times \text{A}_s\times \text{L}_c) ;
\text{sm} = \text{sm} + \text{Cp}\times \text{dT};
\text{T} = \text{T} - \text{dT};
\text{end}
\text{end}
\text{if} \ \text{B} > 0
\text{while} \ \text{sm} < \text{B}
\text{Cp} = (\text{x}_A\times \text{Cp}_\text{Al}(\text{T})\times \text{A}_s\times \text{L}_c) + (\text{x}_B\times \text{Cp}_\text{Ni}(\text{T})\times \text{A}_s\times \text{L}_c) + (\text{x}_v(i)\times \text{Cp}_\text{Al}_3\text{Ni}(\text{T})\times \text{A}_s\times \text{L}_c) ;
\text{sm} = \text{sm} + \text{Cp}\times \text{dT};
\text{T} = \text{T} + \text{dT};
\text{end}
\text{end}
\text{if} \ \text{B} = 0
\text{T} = \text{T};
\text{end}

\text{t}(i) = i\times \text{dt};
\text{T1}(i) = \text{T};
\text{if} \ \text{x}_a(i) > 1
\text{break}
\text{end}
\text{if} \ \text{x}_v(i) > 1
\text{break}
\text{end}
\text{if} \ \text{T1}(i) > 913
\text{break}
\text{end}
\text{end}

\text{figure1}=\text{figure};
\text{plot}(\text{t}, \text{T1}, '\text{LineWidth}', 2)
\text{ylabel('Temperature (K)', 'FontSize', 12)}
\text{xlabel('Time (s)', 'FontSize', 12)
\[ C_p \text{ of Al:} \]
\[
\text{function } \text{al}_m = \text{Cp}_\text{Al}_\text{mol}(T) \\
\text{al}_m = 7.5 \times 10^{-6} \cdot T^2 + 0.003 \cdot T + 23.4;
\]

\[ C_p \text{ of Ni:} \]
\[
\text{function } \text{ni}_m = \text{Cp}_\text{Ni}_\text{mol}(T) \\
\text{ni}_m = -1.875 \times 10^{-6} \cdot T^2 + 0.008675 \cdot T + 25.37;
\]

\[ C_p \text{ of Al}_3\text{Ni:} \]
\[
\text{function } \text{al3ni}_m = \text{Cp}_\text{Al3Ni}_\text{mol}(T) \\
\text{al3ni}_m = 43.144 + 138.406 \times 10^{-3} \cdot T + 14.611 \times 10^5 \cdot T^{-2} - 67.314 \times 10^{-6} \cdot T^2;
\]

\[ \text{Thermal conductivity:} \]
\[
\text{function } k = k_\text{air}(T) \\
k = -1.174 \times 10^{-8} \cdot T^2 + 7.265 \times 10^{-5} \cdot T + 0.005754;
\]

\[ \text{Nusselt number:} \]
\[
\text{function } \text{nun} = \text{Nu}(T) \\
\text{nun} = 4.701 \times 10^{-11} \cdot T^2 + 8.947 \times 10^{-8} \cdot T - 1.734 \times 10^{-5};
\]

\[ \text{Prandtl number:} \]
\[
\text{function } \text{Prnd} = \text{Pr}(T) \\
\text{Prnd} = -6.05 \times 10^{-11} \cdot T^3 + 2.469 \times 10^{-7} \cdot T^2 - 0.0002611 \cdot T + 0.7798;
\]