Gas Atomization Processing of Tin and Silicon Modified LaNi\textsuperscript{5} for Nickel-metal Hydride Battery Applications

by

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DEDICATION

To my wife Murielle who have supported me throughout my studies.
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Numerous researchers have studied the relevant material properties of so-called AB₅ alloys for battery applications. These studies involved LaNi₅ substituted alloys which were prepared using conventional cast and crush alloying techniques. While valuable to the understanding of metal hydride effects, the previous work nearly ignored the potential for alternative direct powder production methods, like high pressure gas atomization (HPGA). Thus, there is a need to understand the relationship between gas atomization processes, powder particle solidification phases, and hydrogen absorption properties of ultra fine (<25 μm) atomized powders with high surface area for enhanced battery performance. Concurrently, development of a gas atomization nozzle that is more efficient than all current designs is needed to increase the yield of ultrafine AB₅ alloy powder for further processing advantage.

Miniature convergent-divergent jets (CDJs) based on design principles developed for large rocket motors were used in designing two new atomization nozzles, HPGA-II and HPGA-III. The HPGA-II had a jet apex angle of 45 degrees, similar to the existing Ames HPGA nozzle that used straight-bored jets, but HPGA-II operated with a mismatched 22° melt tip apex angle. The HPGA-II nozzle was demonstrated to be more efficient in producing fine powders at half the operating pressures of the existing Ames HPGA nozzle that operated at 7.57 MPa. However, measurements of the gas velocity indicated a severe limitation on the possible kinetic energy from the HPGA-II nozzle caused by the extreme tip mismatch required for stable operation. A design concept advanced in this thesis aided in the design of the HPGA-III. The HPGA-III nozzle had CDJs that have an apex angle of 22.5 degrees and was able to form stable subambient melt aspiration with a matching angle melt tip 1.27 mm (0.050 inches) long. Therefore, the HPGA-III nozzle could make more efficient use of the atomization gas kinetic energy than the HPGA-II nozzle. The HPGA-III was determined to be more efficient than HPGA-II, and produced a 40 wt.% yield of <25 μm powders of 316L stainless steel operated at 3.13 MPa. This was a 10% increase in yield over HPGA-II.

We have showed that the design concept set forth in this dissertation enabled design of the highly efficient HPGA-III gas atomization nozzle that has matching CD jets and melt tip apex angles. The nozzle is able to utilize the maximum available gas kinetic energy of the CD discrete jets by avoiding the formation of oblique shocks that can result from the use of a mismatched melt tip. The HPGA-III was able to produce a stable subambient plateau-like aspiration pressure that should make the nozzle easy to tune to control particle size by directly varying operation pressure. The nozzle was demonstrated to produce a high yield of ultrafine
powders that are essential for development of a direct production process for AB\textsubscript{5} alloys for powders for battery applications.

Rapid solidification by gas atomization of LaNi\textsubscript{4.6}Si\textsubscript{0.4} and LaNi\textsubscript{4.85}Sn\textsubscript{0.15}, LaNi\textsubscript{4.75}Sn\textsubscript{0.25} and LaNi\textsubscript{5.5}Sn\textsubscript{0.3} alloys was studied. We observed that small atomized particles (< 25 \textmu m) were resilient to hydrogen induced fracture in gas-phase hydrogen cycling. Quenched-in non-equilibrium phases with different Si and Sn content were observed in the La-Ni-Si and La-Ni-Sn alloys, respectively, and annealing was necessary to achieve the desired hydrogen absorption properties. Rapid annealing of the gas-atomized AB\textsubscript{5} alloys at 900\textdegree C for 5 minutes was sufficient to fully remove the Sn and Si segregations. During annealing, preferential diffusion paths for Sn were observed on \{002\} and \{202\} planes from the XRD patterns. The approximate interdiffusion parameters could be estimated using a simple isotropic diffusion model. The activation enthalpy, Q', and interdiffusion coefficient, D'\textsubscript{o}, for tin diffusing in La(Ni,Sn)\textsubscript{5} intermetallic were determined to be 152.24 KJ.mole\textsuperscript{-1} and 1.975 (10\textsuperscript{-4}) cm\textsuperscript{2}.sec\textsuperscript{-1}, respectively.

Gas atomization processing of the AB\textsubscript{5} alloys was demonstrated to be effective in producing ultrafine spherical powders that were resilient to hydrogen cycling for the benefit of improving corrosion resistance in battery application. These ultrafine powders benefited from the rapid solidification process by having refined solute segregation in the microstructure of the gas atomized powders which enabled a rapid anneal treatment of the powders. We have demonstrated the ability to produce high yields of ultrafine powder efficiently and cost effectively, using the new HPGA-III technology. Thus, the potential benefits of processing AB\textsubscript{5} alloys using the new HPGA technology could reduce manufacturing cost of nickel-metal hydride powder. In the near future, the manufacture of AB\textsubscript{5} alloy powders could become a continuous and rapid production process. The economic benefit of an improved AB\textsubscript{5} production process may thereby encourage the use of nickel-metal hydride rechargeable batteries in electrical vehicle applications in the foreseeable future.
CHAPTER 1. INTRODUCTION

1.1 General Problem Statements

Ultrafine (dia. <20 μm) spherical metal alloy powders produced by the gas atomization process have very attractive material properties because of the high (10^4-10^6 °C/sec) cooling rates and high undercooling promoted by this rapid solidification process. Gas atomization can produce many rapid solidification benefits, including impressive particle microstructure refinement, that are unattainable by conventional ingot casting metallurgy (see Figure 1.1). The material property improvements can include improved strength, toughness, hardness, and corrosion resistance. These benefits are particularly obvious for materials with high alloying additions, i.e., such as tool steels and superalloys.

Powders produced by rapid solidification have very different structures from materials solidified under equilibrium conditions. New phases (including amorphous structures), with much smaller scale microstructures, nonequilibrium compositions, and reduced segregation can be found in rapidly solidified materials. In addition, the uniform spherical shape and enhanced purity of powders produced by inert gas atomization have encouraged wide spread applications in areas such as powder injection molding and thermal spray applications that require dense packing and good flow characteristics [36,52]. More recently, it was determined that ultrafine, spherical gas atomized powders of a nickel-based metal hydride forming alloy, LaNi5 (also known as the AB5 prototype phase), are well suited for resisting hydrogen induced fracture [9,112]. This is important because accelerated oxidation-corrosion on fresh alloy surfaces, resulting from hydrogen induced fracture, is a principle factor causing nickel-metal hydride battery degradation after repeated recharging cycles [12,62,66,69,128]. The observed improvements in hydride particle stability of gas atomized AB5 particulate placed a high value on experiment to develop increase yields of ultra fine powders with gas atomization technology.

During the past three decades, between 1960 when Duwez [33] first recognized rapid solidification processing (RSP) as a mean of controlling microstructure, to the present day, the benefits resulting from rapid solidification processes have been widely demonstrated in a large number of metals and alloy systems [2,25,36,38,54,84]. The performance driven need for highly alloyed, high cost materials encouraged the development and invention of new atomization techniques. Major emphasis was placed on quench rate to produce powders with sharply decreased segregation, extensive refinement of excess phases, elimination of certain segregation phases, and large increases in solubility.
Figure 1.1. Electron backscatter images showing refinement in microstructure in (a) gas atomized powder particle compared to (b) as-cast alloy of composition LaNi$_{4.75}$Sn$_{0.25}$. The Sn segregation is shown in light contrast in both micrographs. Arrows in as cast material show La$_2$O$_3$ impurities.
Generally, the scale of the microstructure (grain size or secondary dendrite arm spacing) varies inversely with the cooling rate. In turn, the cooling rate varies with the inverse of the particle size. Therefore, the particle size associated with rapid solidification during a gas atomization process is the single most important powder characteristic affecting the microstructure, and, thus the properties of the product. For a spherical droplet in gas atomization, the cooling rate is restricted primarily by heat flow at the surface. Typically, convective cooling dominates and radiation has a minor contribution. The general heat extraction rate is given as

\[
\frac{dT_m}{dt} = 6h \left( \frac{T_m - T_s}{\rho c_p d_m} \right)
\]

where convective gas heat transfer coefficient, \( h \), for a sphere \([87]\) is:

\[
h = \frac{k_g}{d_m} \left[ 2.0 + 0.6 \left( \frac{d_m V_g \rho_g}{\eta_g} \right)^{1/2} \left( \frac{C_p \eta}{k} \right)^{1/3} \right]
\]

Here \( d_m \) is the mean particle diameter, \( \rho \) is the particle density, \( c_p \) and \( C_p \) are the heat capacities of the metal and the gas, respectively, \( T_m \) and \( T_s \) are the powder particle and gas temperatures, respectively; \( V_g, \rho_g \) and \( \eta_g \) are the velocity, density and viscosity of the gas, respectively, and \( k_g \) is the thermal conductivity of the gas. Rapid solidification requires the achievement of a maximum heat transfer coefficient, \( h \). Although this can be done by using higher conductivity gases, \( k_g \), and higher heat capacity of the gases, the influence of gas type on cooling rate is determined to be minor as predicted by Couper and Singer \([25]\) with rates for helium approximately 6 times and 4 times greater than for argon and nitrogen, respectively, for aluminum powders. Since material properties from rapid solidification are related to the cooling rate during solidification, small objects with larger surface-to-volume ratio cool more rapidly than massive objects, so in fine powder fabrication it is possible to rapidly extract heat and refine microstructure. A rapid solidification rate can be obtained during the initial stage of particle solidification if a high undercooling can be achieved prior to nucleation. Today there is essentially agreement that to maximize the heat transfer coefficient, the most important variable in rapid solidification is the powder size: the finer the particle size, the higher the solidification rate. Efforts to decrease particle diameter offer the greatest payoff in attained solidification rate \([36,38,51]\), improving both the degree of undercooling and the cooling rate.

Although numerous rapid solidification technologies have been successfully developed, the production of ultra fine spherical metal and alloy powders via a gas atomization technique is
often preferred because of its broad applicability, high production capability, relatively low cost, and opportunity for microstructure control. The gas atomization process also permits production of metal or alloy powders directly from the liquid state in an easier and more economical way than the traditional cast and crush metallurgical technique.

The current standard route for manufacturing the brittle AB₅ battery materials follows the traditional metallurgical technique involving several steps: 1) melting and chill casting of large ingots; 2) extensive heat treatment of the ingots for at least several days, to eliminate macroscopic compositional inhomogeneities; 3) hydriding and dehydriding of bulk alloy to break the small pieces into powders, and 4) mechanical grinding of the annealed ingots into small pieces. These steps are, however, laborious and cost ineffective, and present a processing cost barrier to wide spread commercialization of the Ni/MH batteries, especially as large prismatic cells for electric vehicle applications. Rapid solidification processing of tin modified LaNi₅ powders by high pressure gas atomization (HPGA) has been suggested [9,112] as a mean to suppress the Sn segregation effect observed in conventional chill casting of LaNi₄.₇₅Sn₀.₂₅. The successful implementation of RSP using the HPGA process could combine the conventional 4 steps of AB₅ powder fabrication into one by the HPGA approach and produce useful powder directly, eliminating lengthy and expensive steps 1 through 4 from the above mentioned list.

In a typical gas atomization process, a molten metal stream flows from a heated crucible through a melt feed tube and encounters a high velocity gas stream as it exits the orifice (see Figure 1.2). The liquid is disintegrated into a collection of liquid droplets in the atomization zone. The droplets spheroidize and solidify into powders during their free-fall. Depending on the particular design, there are generally two types of melt feeding configurations that are used in low and moderate pressure gas atomization. They are often known as: 1) open or free-fall, and 2) closed, confined-feed, or close-coupled [46] (Figure 1.3). The gas flow pattern is designed to be inclined conically and is focused in front of the orifice of the melt delivery tube at an inclined angle. Typically, the atomization gas is supplied through an axisymmetric annular slit, positioned around the exterior of the melt orifice. For applications where fine powder yields are not critical, a free-fall melt configuration is used, because in general, the free-fall nozzle is simple to assemble and use. In free-fall atomization, a hole at the bottom of the crucible delivers the molten stream. The atomization nozzle is positioned about 10-30 cm below the hole to disintegrate the free-falling stream. In this situation, the unconstrained stream of molten metal falls under the influence of gravity from the outlet of the crucible through the atomizing gas. The absence of liquid melt stability and concentricity makes free-all gas atomization unsuitable as an efficient gas atomization technique.
Figure 1.2. General design of gas atomizer nozzle (reproduced from Anderson et al. [5]).

Figure 1.3. Atomizer geometries: (a) free-fall nozzle; (b) confined-feed nozzle (reproduced from Klar et al. [46]).
The fact that gas velocity decays very rapidly from a free-fall atomizer nozzle to the melt has influenced nozzle designers to reduce the gas outlet to melt impact distance. This has led to the design of confined-feed nozzles. In the confined-feed configuration, the melt is directed by the melt tip directly into the atomization zone. This makes the confined-feed a more efficient configuration to transfer the kinetic energy of the atomizing gas to the melt stream for producing finer powders. Therefore, the desire to achieve a greater yield of ultrafine powders with improved efficiency at high pressure seems to promote the use of a confined-feed atomization nozzle.

One may distinguish confined-feed nozzles in two nozzle categories: 1) annular-slit nozzle; and 2) discrete-jet nozzle (see Figure 1.4). Annular-slit nozzles usually have a parallel-walled gas passage for the conical gas outlet. On the other hand, discrete-jet nozzles use a ring of discrete jets as the gas outlet. The latter nozzle design may be more cost efficient to manufacture than the first, because the multi-holed configuration is more easily manufactured to high tolerance compared to the difficulties in manufacturing a high tolerance sub-millimeter melt path.

Figure 1.4. (a) a central cross section view of two types of general confined-feed atomization nozzles: b) annular-jet, and c) discrete-jet, in bottom view.
annular-slit orifice. The annular slit atomizer typically operates at a moderately high gas pressures and requires excessive gas consumption. Thus, additional benefit can be found in the reduction of gas consumption when using a discrete jet nozzle compared to an annular slit nozzle. The design of the Ames HPGA nozzle (also known as HPGA-I nozzle) [3-6] is an example of confined-feed, discrete-jet atomization nozzle.

The efficiency of the confined-feed HPGA process, in terms of yields of ultrafine powders, should play an essential role in overcoming current processing barriers in the rechargeable Ni-MH battery industry and in a number of other emerging technologies including metal injection molding, and ultrafine solder and brazing powder pastes. Unfortunately, the state of commercial gas atomization technology, almost exclusively linked to annular slit nozzles, produces only a limited yield of ultrafine powders [31,32,47,73]. However, before the HPGA technology can be implemented successfully as an industrial technique in processing hydrogen storage battery material, the nozzle design should be optimized to promote a maximum yield of ultrafine powder.

This dissertation is divided into two parts. The first part of this work will address our results in HPGA development using imaging and computational techniques. In addition, a design concept was developed to assist the development of new HPGA nozzles. From this design concept a new HPGA-III nozzle geometry was designed. Gas-to-melt mass flow ratio, and atomized powder size distribution, and gas atomization efficiencies were measured for the completed HPGA-III nozzle for stainless steel powder production and compared to previous HPGA results. The second part of this thesis will address the phase selection in gas atomized AB$_5$ alloys using an X-ray diffraction technique. The hydrogen absorption characteristics, and microstructure observations using scanning electron microscope will be presented. Heat treatment as a post-processing step was examined as a means to achieve desired hydrogen absorption properties. From this, thermodynamic constants for interdiffusion were estimated for tin diffusion in a Sn-substituted LaNi$_5$ alloy.

1.2 Objectives

Numerous researchers have studied the material properties of AB$_5$ intermetallic compounds using an alloy substitution approach with conventional cast and crush particulate processing techniques. While valuable to the understanding of metal hydride effects, the previous work nearly ignored the potential for alternative direct powder production methods, like gas atomization. Thus there is a need to understand the relationship between gas atomization processes, powder particle solidification microstructures, and hydrogen absorption properties of ultrafine atomized powders with high surface area for enhanced performance.
Concurrently, development of a gas atomization nozzle that is more efficient than all current designs is needed to increase the yield of ultra fine AB$_5$ alloy powder for further processing advantage.

In order to increase the yield of ultra fine powders, and to maximize the atomization mechanism by enhancing the disintegration of the melt droplets, the following objectives have to be achieved. The first part of this thesis is to investigate and characterize the gas-only flow of HPGA process in an effort to understand the contributions of high velocity compressible gas flow to the atomization process dynamics. This may shed light on the gas jet geometry and operation conditions most likely to yield the desired gas flow patterns in the atomization region. In particular, this dissertation will investigate whether an aerodynamically designed miniature convergent-divergent jet used in rocket science, with its minimal energy loss, would be more effective and efficient than the simple straight-bored jets used in an initial version of the HPGA (HPGA-I) nozzle for the production of fine powders. Further, in order to proceed with development of a new gas atomization nozzle, a design concept has to be advanced. Based on this design concept, new generation of efficient gas atomizer nozzles will be produced and tested.

The second part of this thesis is to investigate and characterize phase selection in gas atomized powders of the AB$_5$ rechargeable battery alloy in an effort to understand the benefits of rapid solidification on the as-atomized phases. In particular, the effect that rapidly solidified phases have on hydrogen absorption characteristics of the alloy will be explored. Further, relaxation time in heat treated AB$_5$ powders will be examined in order to explore heat treatment as an option for post-processing the as-atomized powders as a mean to achieve the desired hydrogen absorption properties. Based on these observations, using X-ray diffraction patterns, thermodynamic properties of substitutional interdiffusion may be obtained. Therefore, by understanding the benefits of rapid solidification of AB$_5$ and with the advancement of gas atomization technology, the information may be useful to develop a simplified model of RSP of the AB$_5$ that may serve as a basis for future investigations of low cost production of multicomponent nickel-metal hydride alloys.
PART I. GAS ATOMIZATION NOZZLE DEVELOPMENT
CHAPTER 2. LITERATURE REVIEW

The most widely used processes for large scale tonnage production of alloy powders are atomization and chemical reduction [41]. Of the two processes, atomization, however, is the most versatile technique. Melt atomization permits direct production of powders of a broad range of alloys with effective control over many physical and metallurgical properties of the powders. Gas atomization is the process of the disintegration of a liquid mass into a collection of liquid droplet by the impact of a high velocity gas flow. Following atomization of liquid metal, the droplets spheroidize, cool and solidifies into metal powder particles which typically range in diameter from 1 μm to 1 mm.

An understanding of the breakup mechanisms that govern droplet formation during atomization is necessary to advance atomizer design and to determine some of the more important parameters of the atomization processes. Hence, numerous research activities into the mechanisms of droplet formation during atomization has been conducted for the past three decades [16,30,47,52,53,114,116]. The atomization of bulk liquid into droplets relies on the physical disturbances which the gas flow imposes on the liquid. Although, there are numerous gas atomizer designs and there are numerous processing variables involved, there are considerable similarities in the mechanisms of droplet formation [56].

A review of various proposed atomization mechanisms of liquid metals shows that droplet formation involves two fundamental processes: 1) the formation of an initial disturbance wave in the liquid brought about by the interaction of the liquid sheet and the impinging gas at the gas-melt-coupling zone, and 2) the breakup of the disturbed liquid sheet when the wave amplitude reaches a critical size forming unstable ligaments limited by surface tension effects. The ligaments subsequently minimize surface energy and spheroidize into droplets. A classical but somewhat oversimplified sketch of droplet formation was proposed by Dombrowski and Johns (see Figure 2.1) [30] showing 3 stages of melt breakup. See and Johnston [101] proposed an atomization mechanism that is essentially similar to the three stage breakup of a liquid proposed by Dombrowski and Johns [30].

According to the mechanism proposed for free-fall gas atomization of liquid metal, three important stages are identified from their experimental observations. In the first stage, primary atomization occurs, when the liquid melt first enters the regions of high velocity gas. As the dynamic gas pressure increases, disturbed material separates from the bulk liquid. See and Johnston argued that this primary atomization occurs before the maximum velocity is attained. In the second stage, the droplets formed from primary atomization enter a higher relative velocity regime, such that a droplet may undergo further breakup if the dynamic
pressure due to the gas stream velocity exceeding the restoring force of the surface tension. This condition is known as the maximum stability criterion [10], and is given by

\[
\frac{1}{2} \rho_g (\Delta v)^2 = c \frac{\sigma_m}{d_m}
\]

where \(\rho_g\) is the gas density, \(\Delta v\) is defined as the difference in velocity between the gas stream and the molten metal, \(c\) is an empirical constant whose value depends on the atomization condition, \(\sigma_m\) is the surface tension force of the melt, and \(d_m\) is the maximum stable droplet size. In the third stage, solidification of the droplets occurs, where the final shape of the particle of liquid metal falling depends on the competition between spheroidization and solidification.

Although, this model was proposed for a free-fall atomization process, the mechanism of secondary atomization is also applicable for particle breakup in a confined-feed atomization process, because the particle stability criterion is based upon the aerodynamic and material properties of the two fluids and not on the physical geometry of the atomization system. Thus from the maximum stability criterion, the improvement in droplet refinement, \(d_m\), is directly related to the difference in velocity between the two “fluids” involved, the gas and the molten metal, \(\Delta v\). Supporting observations by See and Johnston, Lefebvre [56] has recently
examined the factors influencing the mean droplet size in twin-fluid atomization, and concluded
that gas velocity, more specifically the relative velocity between the two "fluids" is the principle
factor governing mean droplet size.

The next important factor is the gas-to-melt mass flow ratio during atomization. This
conclusion was reached by Lubanska [60] where he correlated particle diameter to both relative
velocity and melt-to-gas mass flow ratio,

\[ d_m = d_0 k \left( \frac{v_m}{v_g We} \left( 1 + \frac{\dot{m}_m}{\dot{m}_g} \right) \right)^{1/2} \quad 2.2 \]

where \( We = \frac{(\Delta v)^2 \rho_m d_0}{\sigma_m} \)

is the Weber number representing the ratio of inertial force and the surface tension of the liquid
melt, \( d_m \) and \( d_0 \) is the mean particle diameter and metal melt stream diameter respectively, \( k \) is
a constant that must be determined for a particular atomizer, \( v_m \) and \( v_g \) are kinematic viscosity
of the molten metal and atomizing gas respectively, \( \dot{m}_m \) and \( \dot{m}_g \) are mass flow rates of molten
metal and atomizing gas respectively, \( \Delta v \) is the relative velocity between the melt and the gas.
Material parameters such as density and viscosity vary very little in a gas atomization process
[129]. On the other hand, gas velocity and melt flow rate are the most commonly used
variables in controlling the gas atomization process in terms of particle size yields and size
distributions. Of the two variables, high gas velocity, giving high relative velocity and Weber
number is more effective than melt flow rate, because \( \Delta v^2 \) in Weber number is more effective
than melt-to-gas flow ratio on lowering \( d_m \). Therefore, a high gas velocity, or Weber number,
is essential to achieve an efficient atomization process for increased yields of fine powders.

It has been shown that increasing the relative velocity between the gas and the droplet
will decrease the particle size, and increasing the quench capacity of the gas (helium versus
argon) will increase the solidification rate [25,38]. Therefore, an interest in improving the
efficiency of gas atomization processes has led to several models showing that an increase in
gas kinetic energy associated with increased gas pressure is in part responsible for improved
powder size refinement [16,30,103]. But gas pressures much above 1.0 MPa gave little
velocity advantage for the converging annular slit nozzle used in current atomizers, although, it
may allow the density of gas at impact to be higher, achieving some incremental particle
refinement. In practice, despite some work on the use of gas pressures up to 20 MPa [59,86],
firm evidence of any benefit is minimal. It has been observed that gas pressures above 0.15
MPa allow sonic velocities and pressures above 7.0 MPa allowed only marginal increases in velocity and minimal gain in fine powder yield [73]. Under such high operating gas pressure, improvement in gas consumption can be found by using discrete jets, i.e., HPGA-I uses straight-bored discrete jets. While a high gas velocity promotes finer particles in every theoretical model [60], no other research work has ever been done to improve the performance of HPGA nozzle by using discrete miniaturized convergent-divergent jets (CDJ) from rocket technology. Therefore, there is a need to determine whether an aerodynamically designed CDJ used in rocket science, with its minimal energy loss, would be more effective and efficient than common annular-slit convergent ‘jet’ used in an gas atomizer nozzle for the production of ultrafine powders.

2.1 Aspiration Base Pressure

Although confined-feed nozzles are generally acknowledged as the most efficient gas atomization configuration for fine powder production, the operation of a confined-feed nozzle is regarded as a difficult “art”. As a consequence, the industrial application of confined-feed nozzles is limited to a few practitioners of high technology in atomization, e.g., the producers of superalloy powder for aircraft engines [129].

A characteristic of the confined nozzle design is that subambient pressure near the melt orifice is created. In confined-feed gas atomization, the gas jets impinge on the pour tube tangentially prior to merging at a focal point located in front of the orifice of the pour tube [115] (see Figure 2.2). The rapidly flowing gas passing the periphery of the melt tip produces an overambient/subambient pressure region in front of the delivery tube orifice often known as the aspiration base pressure. The aerodynamic force of this aspiration significantly alters the flow of the molten metal stream by causing the melt to pre-film the delivery tube. The molten metal leaving the delivery tube is stretched into a film that flows to the edge of the melt tip. The important characteristic of the confined feed especially in pre-filming mode is that the atomization jets are then essentially normal to the flow of the molten metal. This atomization configuration gives confined feed higher atomization efficiency due to the enhanced Weber number relative to that associated with free-fall atomizers.

Confined-feed atomizers, however, are extremely sensitive to metal freeze-up, a condition that occurs when the liquid metal at the end of the delivery tube solidifies as a result of the combined effect of pre-filming and rapid heat extraction that occurs at the orifice of the delivery tube. Another problem can arise in high pressure gas atomizer operation when the aspiration base pressure is near or above ambient pressure at the melt tube orifice. Unless this pressure is offset by a high metallostatic head or a pressurized crucible bath, a positive pressure
at the melt-orifice can allow a back flow. Under high pressure conditions, the stability of the melt tip can better be controlled if the atomizer nozzle and the melt tip are designed to experience a subambient pressure at the melt orifice under normal atomization condition. Operating in this intrinsic aspiration regime, the subambient pressure at the orifice should provide for a more stable melt feed operation by drawing the melt stream towards the atomization zone.

![Diagram of gas liquid flow patterns in an annular-slit gas atomizer showing the presence of negative pressure zone in front of the melt orifice and the pre-filming of the liquid prior to atomization.](reproduced from Unal [115]).

Figure 2.2. Gas liquid flow patterns in an annular-slit gas atomizer showing the presence of negative pressure zone in front of the melt orifice and the pre-filming of the liquid prior to atomization (reproduced from Unal [115]).

Therefore, melt orifice aspiration has generally been used as an indicator for evaluation the atomization stability of a gravity-fed confined-feed nozzle. Although Unal [113-116] has demonstrated that pressurized inverted-melt-fed atomization can overcome overambient aspiration base pressures, his pressurized melt chamber setup limits the atomization to a batch-wise powder production process. For a more robust nozzle application, there is a need to design nozzle that can operate in gravity-fed configuration and produce stable aspiration pressure at the melt orifice ensuring a stable atomization. To fulfill this objective, knowledge of this gas atomization aspiration phenomenon is a necessary step, so as to improve our
understanding of the HPGA nozzle. A fundamental theory is needed for the aspiration phenomenon to advance the development of gas atomization technology.

2.2 Gas Atomization Nozzles

The majority of the nozzles currently used in production of metal powders belong to the HPGA category, having annular-slit or discrete-jets. This category of nozzle contains the basic flow characteristics seen in truncated plug nozzle studied by Sule and Mueller [105] for "altitude-compensating" operation (see figure 2.3). The optimum operation of the HPGA nozzles usually occur at high atomization pressures, exceeding 5.51 MPa (800 psi) [2]. This is done in order to achieve "wake-closure". Anderson reported [5] that enhanced recirculation in the wake encourages pre-filming of the melt, and that second stage atomization is encouraged by the full development of an intense Mach shock disk formed after a transition from "open-wake" to "wake-closure" gas flow condition. The transition from "open-wake" to "closed-wake" can be understood on a phenomenological basis by observing the behavior of ordinary underexpanded jets. The underexpanded flow generated by a circular convergent nozzle operating at high pressure is shown in a schematic Figure 2.4a. Placing a large cylindrical blunt body in the center of this nozzle will produce a separation wake that is similar to the flowfield formed by the HPGA. If the wake size is large compared to the gas jet diameter, the Mach disk will be forced open by the reflection of the internal shocks off the wake boundary. If the pressure increases to a critical value, normally at 5.51 MPa for HPGA nozzles, the internal shock will elongate and cross once again giving rise to "wake-closure" [67].

Anderson and Figliola [3] showed that the design of the melt tip geometry was proved to be important to HPGA operations. The HPGA nozzle considered in their study, had 18 straight-bored gas jets fed from an annular manifold around a melt tip to produce an apex angle of 45 degrees. The melt orifice aspiration base pressure for argon-only flow showed that a matching melt tip produce subambient aspiration condition over wide range of elevated gas pressures (see Figure 2.5). This matching geometry was preferred over a straight fully retracted tip (melt tip located next to the gas exit) and a melt tip of 63 degrees apex angle.

Eventually a nozzle was developed by Anderson et al [5,6] (see Figure 2.6) that required considerably lower gas inlet pressure to achieve the same atomization performance as the ultrasonic gas atomization nozzle (USGA) (see Figure 2.7) [2,11,25,61,85,120]. The ultrasonic gas atomization is a technique that has been used in the atomization of fine powders and in spray deposition. The primary difference in the HPGA design is the simple geometry of the gas jets with the improved HPGA nozzle replacing the inefficient criss-cross passage of the USGA. The criss-cross passage of the USGA nozzle creates high pressure losses between the
Figure 2.3. Schematic showing the plug nozzle flow at high operation pressures (reproduced from Sule et al. [105]).

Figure 2.4. Schematic of gas flow fields produced by (a) simple under-expanded converging nozzle, (b) “open wake” operation, and (c) “closed wake” operation (reproduced from Mates et al. [67]).
Figure 2.5. Static aspiration pressure tests using (1) retracted tip, (2) extended square tip, (3) tapered tip having 63° apex angle and (4) tapered extended tip having 45° apex angle (reproduced from Anderson et al. [5]).

Figure 2.6. Nozzle designs shown with HPGA melt tube feed tip: (a) USGA nozzle with manifold; (b) Ames HPGA nozzle with manifold (reproduced from Anderson et al. [5]).
manifold and jet exit. A result of this change allowed HPGA to operate at considerably lower gas inlet pressure. The reduction of flow resistance with the simplified gas jets, permitted the HPGA to achieve the same aspiration effect a half the atomization pressure as in USGA. This low gas consumption resulted in increased atomization efficiency as measured by the decrease in gas-to-melt mass flow ratio.

Figure 2.7. Static aspiration pressure test comparison between USGA and Ames HPGA nozzle with tapered extended melt tip with 45° apex angle (reproduced from Anderson et al. [5]).

Due to the flow complexity in a narrow criss-cross passage, the mechanism of supersonic gas flow from an ultrasonic atomizer remains unclear. One mechanism was proposed by Veistinen et al. [120] to explain the flow behavior associated the ultrasonic nozzle based on gas flow mechanism of a De Laval tube. They argued that the growth of a boundary layer in the exit section of the ultrasonic jet reduces the effective area by creating a throat in the constant cross-section duct, a phenomenon known as the vena contracta effect (see Figure 2.8), although no evidence has ever showed that the ultrasonic jet ever behaved like a contoured rocket nozzle. It is also believed that the atomization gas formed by the ultrasonic atomizer carry shock waves with frequencies beyond the audible range (i.e., 20-100 kHz) [11,25,61,85,120]. The principle of ultrasonic atomization is that the shock waves are tuned to increase the efficiency of the molten metal breakup, although there is no general agreement as to the benefits of this approach [49,89].
Figure 2.8. Resonance cavities and effective throat and vent areas in USGA nozzle (not shown to scale). Reduction in throat area, yielding an effective $A_t$, is shown slightly exaggerated (reproduced from Veistinen et al. [120]).

The configuration of several designs of the gas atomizer nozzles are summarized below in Table 2.1. Table 2.2 compares the reported gas velocities that are associated with various types of atomizers utilized for gas atomization of molten metals. Majority of the nozzles employed straight-bored geometry in either discrete or annular (ring) configuration. The design of NIST is essentially similar to the patent by Anderson [6] except the NIST uses two less jets. It is believed that this design represents a large class of nozzle currently used to produce metal powders. The dimensions of the delivery tube diameter (melt orifice) are found within the range given in Table 2.1. This is because most melt flow rate of the different technique are below 10 Kg.min$^{-1}$ [129]. In addition, commercial systems rarely exceed a mass flow ratio of 2.0 [129], this then determines the gas jet diameter, and number of the discrete jets or the gap in the annular-slit configuration in the nozzles. Duplicating melt stream is then often the method of increasing production output.

Of all the tabulated gas atomizer designs, the annular-slit atomizers designed by Unal [113-117] used the convergent-divergent De Laval design for their gas jet configuration. A straight conical taper was used for the divergent section of the gas jet. It is noted that the nozzle has divergence on only the outer side, with the inner side parallel (see Figure 2.2). Since it is not properly contoured, the exit flow will never be perfectly expanded and shock waves will form at all pressure ratios. In addition, because the apex angle is zero (not
Table 2.1 Parameters of various gas atomizers

<table>
<thead>
<tr>
<th>Atomizer</th>
<th>Type</th>
<th>Number of jets</th>
<th>Gas jet gap or diameter (mm)</th>
<th>Melt orifice diameter (mm)</th>
<th>Apex angle (°)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST</td>
<td>closed</td>
<td>18</td>
<td>0.8</td>
<td>2.5</td>
<td>22.5</td>
<td>[88]</td>
</tr>
<tr>
<td>GE-CCN</td>
<td>closed</td>
<td>ring</td>
<td>0.5</td>
<td>3.8</td>
<td>22.0</td>
<td>[88]</td>
</tr>
<tr>
<td>DJ-CF</td>
<td>USGA</td>
<td>18</td>
<td>0.74</td>
<td>4.75</td>
<td>22.5</td>
<td>[59]</td>
</tr>
<tr>
<td>Ames</td>
<td>HPGA</td>
<td>20</td>
<td>4.5</td>
<td>4.4</td>
<td>27.4</td>
<td>[5]</td>
</tr>
<tr>
<td>See</td>
<td>Free-fall</td>
<td>4</td>
<td>4.5</td>
<td>4.4</td>
<td>34.5</td>
<td>[100]</td>
</tr>
<tr>
<td>See</td>
<td>Free-fall</td>
<td>4</td>
<td>4.5</td>
<td>4.4</td>
<td>34.5</td>
<td>[100]</td>
</tr>
<tr>
<td>IN3/ON7</td>
<td>Unal</td>
<td>ring</td>
<td>1.4</td>
<td>4.0</td>
<td>0.0</td>
<td>[115]</td>
</tr>
</tbody>
</table>

NIST, atomizer at National Institute of Standard and Technology, Gaithersburg, MD, USA; GE-CCN, General Electric, Schenectady, NY, USA, close-coupled nozzle; DJ-CF, discrete jet confined-feed atomizer; USGA, ultrasonic gas atomizer; HPGA, high pressure gas atomizer; Ames, atomizer designed in Ames Laboratory, Ames, IA, USA; Unal, De Laval nozzle designed by Ali Unal, Imperial College of Science and Technology, UK; See, a free fall nozzle.

Table 2.2 Atomization gas velocity determined for various atomizer designs

<table>
<thead>
<tr>
<th>Atomizer</th>
<th>Design</th>
<th>Measurement technique</th>
<th>Atomization pressure (kPa)</th>
<th>Maximum gas velocity (m/sec)</th>
<th>Mach number</th>
<th>Atomization gas</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>INEL</td>
<td>De Laval</td>
<td>-</td>
<td>120</td>
<td>490</td>
<td>-</td>
<td>Ar</td>
<td>[68]</td>
</tr>
<tr>
<td>IN3/ON7</td>
<td>Unal</td>
<td>-</td>
<td>2120</td>
<td>-</td>
<td>2.6</td>
<td>N₂</td>
<td>[113]</td>
</tr>
<tr>
<td>IN3/ON7</td>
<td>Unal</td>
<td>-</td>
<td>3200</td>
<td>-</td>
<td>3.0</td>
<td>Ar</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td>USGA</td>
<td>Pitot tube</td>
<td>7600</td>
<td>560</td>
<td>1.7</td>
<td>N₂</td>
<td>[59]</td>
</tr>
<tr>
<td>Osprey</td>
<td>subsonic</td>
<td>Pitot tube</td>
<td>1040</td>
<td>85</td>
<td>-</td>
<td>N₂</td>
<td>[59]</td>
</tr>
</tbody>
</table>

INEL, atomizer design at Idaho National Engineering Laboratory, Idaho Falls, ID, USA; USGA, ultrasonic atomizer; IN3/ON7, De Laval nozzle designed by Ali Unal, Imperial College of Science and Technology, UK; - not reported

converging) in Unal’s nozzles, the nozzles appear to operate in open-wake mode, thus the nozzles are unable to take full advantage of pre-filming by strong recirculating gas during closed wake operation, described previously.

The gas velocity associated with gas atomization nozzle reported in Table 2.2, shows that greater gas velocity can be achieved using convergent-divergent De Laval jets than with criss-crossed straight-bored jets in the USGA design. But no nozzle have ever been designed with contoured convergent-divergent discrete jets. Therefore there is a need to investigate a gas atomization nozzle with discrete aerodynamically designed gas jets that would be more effective straight-bored jets, having an apex angle that would take advantage of the pre-filming benefit in closed-wake operation. The lack of contoured miniature supersonic jets, with jet dimensions like those described in Table 2.1, is due to the lack of knowledge and research of the effect of boundary layer formation that may interfere with laminar supersonic flow in such small dimensions. Boundary layer formation is inevitable to confined gas flow phenomena. The formation of an attached quiescent boundary layer is due to gas friction against the nozzle wall. It has been the common belief of aerospace engineers and mechanical engineers alike that it is
impossible to develop a viable miniature supersonic nozzle because the thickness of the boundary layer would become significant relative to the total available flow cross-sectional area. It is therefore believed that this would impede the efficient generation of supersonic gas flow in the convergent-divergent jets.

2.3 Gas Dynamics of Micro-Jets

The general structure of the gas flowfield of a discrete convergent jet (CJ) is well known [29]. For very high pressure ratios, the same operating pressure as HPGA systems, the gas-only flow from a discrete CJ, is dominated by a very strong normal shock in the first cell immediately near the jet exit. The normal shock is surrounded by intercepting oblique shocks emanating from the corners of the jet exit, this shock pattern is commonly known as a "barrel" shock. The name comes from the shape the shock pattern produces. The major flow patterns down stream away from the normal shock are characterized by a high velocity core surrounded by a region in which mixing between the jet and ambient gas takes place, see Figure 2.9. Several jet diameters down stream the mixing region dissipates the core. Within the high velocity core a series of Prandtl-Meyer (P-M) waves are formed. The Prandtl-Meyer

![Diagram of gas flowfield](image)

Figure 2.9. Structure of the gas-only flowfield of discrete (a) straight-bored jet and (b) convergent jet.
waves are made up of expansion and compression oblique shock waves. These P-M wave patterns exist for maintaining pressure equilibrium along the edge of the free boundary in the gas stream.

A straight-bored jet behaves identically to a CJ in terms of the general structure of its gas flowfield, as a comparison of Figure 2.9a and 2.9b will show; therefore we will refer to a straight-bored jets as a CJ for the purpose of this document.

The physics of the gas flowfield features of a convergent-divergent jet (CDJ) are also well understood [10,91,131] and they can be described using isentropic compressible gas dynamics. This type of jet is typically shaped like the profile in Figure 2.10a and is physically distinguished by its ratio of the exit area to the throat area. Furthermore the observed flow features are determined solely by the operating pressure ratio, \( P/P_o \), where \( P \) is the receiving pressure (atomizer chamber pressure) and \( P_o \) is the inlet stagnation pressure (nozzle gas supply manifold pressure) or pressure up stream of the converging section of the CDJ. One can determine the pressures, Mach numbers and the gas flow features for a discrete CDJ over several pressure ratios as illustrated in Figure 2.10. The gas flow through the CDJ is initiated when the pressure ratio, \( P/P_o \), is less than one. This pressure ratio corresponds to an increase in atomizer nozzle manifold pressure above the pressure of the chamber that is typically maintained at ambient pressure. When the pressure ratio is above point 2 (Figure 2.10b), the jet has subsonic flow throughout (Figure 2.10c). At pressure ratios between point 1 and 2 in the figure, the gas velocity initially increases in Mach number until its maximum value at the throat of the jet. The Mach number then decreases in the divergent section of the CDJ.

For a pressure ratio represented by point 2, the throat of the jet becomes sonic (Mach number of one). This isentropic condition is also known as ‘choked’ flow condition (or ‘First Critical’). During ‘choked’ flow condition, the velocity of the gas flow in the throat reaches terminal sonic velocity. At this point, any further increase in nozzle manifold pressure will not increase the velocity in the throat. This brings up a common fallacy in the area of gas atomization research, that is the belief that an increase in the inlet pressure beyond the choked flow condition “does not cause any further increase in the mass flow rate of the gas through a converging nozzle [throat]” [51,120]. On the contrary, in a high pressure gas atomization process, a further increase in nozzle manifold pressure, corresponding to a drop in pressure ratios, will enhance the static pressure but will not increase the sonic velocity in the throat. This will result in an increase in mass flow rate at the throat, but not in the velocity flow rate.

Another isentropic condition exists at a pressure ratio at point 6, where the gas flow is devoid of features (or ‘Third Critical’ point). Between the pressure ratios represented by point 2 and point 4 (or ‘Second Critical’ point), a nonisentropic solution exists because a single
Figure 2.10. Schematic of (a) a convergent-divergent jet contour, (b) the pressure ratios and (c) the Mach speed at the exit pressure ratios. The right side of the figure shows the gas features from a convergent-divergent jet at some corresponding pressure ratios (reproduced from Saad [91]).
normal shock will develop inside the jet causing an increase in entropy and a decrease in gas velocity across the shock. For the pressure ratios lower than point 4, the flow inside the jet up to the exit is completely supersonic. Adjusting the pressure ratio from above point 4 to a pressure ratio between point 4 to point 6 transforms the normal shock, within the divergent section of the jet into a system of oblique shocks outside of the jet. This transformation adjusts the exiting gas pressure and matches the ambient chamber pressure. Flow features are represented in Figure 2.11a. With pressure ratios between point 4 and 6, the exiting gas flow is supersonic and the jet is over-expanded (the exiting gas pressure is less than the chamber pressure). The exiting gas first experiences compression by two oblique shocks, followed by a series of Prandtl-Meyer expansion-compression waves. Oblique shocks are weaker than normal shocks, and the angle between the oblique shock and the flow direction is related to the strength of the shock. This angle and the shock strength becomes smaller as the pressure ratio is decreased from point 4 to the design pressure ratio, at point 6. At the design pressure ratio point 6, the shock disappears and the flow becomes isentropic (Figure 2.11b). In an aerodynamically designed CDJ, the gas experiences a controlled expansion in the divergent section of the jet where it generates supersonic velocity within the confines of the jet itself so that the gas flow emerges in a roughly parallel stream with uniform supersonic velocity, see Figure 2.11b. At this design condition of the CDJ, the supersonic core is absent of normal or oblique shocks that can reduce gas kinetic energy and velocity. Thus the strong supersonic core can be extremely long and stretches very far down stream. When the pressure ratio is below the design pressure ratio of point 6, the jet is under-expanded (the exit pressure is greater than the ambient pressure) and a series of P-M expansion and compression waves occur outside the jet. Under expanded flow features are represented in Figure 2.11c.
Figure 2.11. Gas flow features for CDJ under three operating conditions: (a) over-expanded (below design condition), (b) design and (c) under-expanded (above design condition).
CHAPTER 3. GAS ATOMIZATION NOZZLES

3.1 Gas Atomization Nozzle Design

The discrete convergent jet HPGA (HPGA-I) and the discrete convergent-divergent jet HPGA (HPGA-II) nozzles tested consist of a gas atomization nozzle with 20 discrete-jets positioned about a 10.4 mm (0.408 inches) central hole at an apex angle of 45° as shown in Figure 3.1a and 3.1b. The discrete jet design of HPGA-II nozzle uses convergent-divergent jets (CDJ), differing from the HPGA-I nozzle that uses straight-bored jet (CJ). This difference in jet design and other differences that were developed in the melt tip angle will be described in the following section. The atomization gas of the discrete-jets are fed from an annular nozzle manifold that is supplied from a single pressurized gas inlet line. A melt feed-tube is positioned within the nozzle center hole to direct the melt from the crucible. This melt feed-tube consists of an outer stainless steel sleeve enveloping an inner ceramic feed tube made of a refractory material, e.g., alumina or yittria-stabilized zirconia. In this melt feed tube design, there exist a minimal air gap of 0.127 mm (0.005 inches) between the stainless steel sleeve and ceramic tube. The air gap provides a barrier to thermal conduction between the hot ceramic feed tube, that carries the molten metal, from the subambient temperature atomizing gas. This thermal barrier prevents the ceramic tube from experiencing a large thermal gradient, causing thermal shock and fracture of the ceramic tube.

3.1.1 Convergent Jet Design of a Gas Atomization Nozzle

The discrete convergent jet of the HPGA-I nozzle has a straight-bored internal geometry [2]. It was machined using a drill number 69 (English unit) which gave a bore diameter of 0.737 mm (0.029 inches). This bore diameter can also be termed the throat diameter of this type of discrete jet. In the HPGA-I nozzle, the length of the jet was designed to be approximately 8.26 mm (0.325 inches).

The terminology of convergent jet and straight-bored jet are used interchangeably in this thesis as mentioned in the previous section. This is because we are concerned with the gas flow field of the two jets rather than the physical geometry of the jets.

Individual CJ test model parts is of the same dimensions mentioned above were machined as shown in Figure 3.2. These individual jets were used for schlieren imaging for the purpose of examining the isolated gas flow patterns of each CJ.
Figure 3.1. Nozzle designs shown with melt feed tip: [a] HPGA-I with convergent jets; [b] HPGA-II with convergent-divergent jets.
3.1.2 Convergent-Divergent Discrete Jet Design of a Gas Atomization Nozzle

The major uncertainty in using an assembly of discrete miniature CDJs in HPGA technology is whether each CDJ can maintain its described supersonic flow characteristics. The CDJ used in the HPGA-II nozzle was designed with the method of characteristics. The method of characteristics [91] is a classical computational method that allows one to solve the equations of fluid or gas motion graphically using characteristic lines, in a step by step process. Along these characteristic lines, the governing partial differential equations which describe the motion reduce to ordinary differential equations permitting an analytical solution to be generated. More details can be found elsewhere [91]. In summary, the method of characteristics provide a means of computing the flow through a supersonic jet. It also provides a mean of determining the contour of the supersonic jet in such a way that the velocity at the end of the jet is uniform and parallel across the entire cross-section at the jet exit. Proper consideration should be made for boundary layer growth in the throat of a miniature discrete CDJ, since this is the most constricted portion of the CDJ. Significant boundary layer thickness will block the throat and render the jet incapable of generating efficient supersonic flow.

When boundary-layer growth and friction losses are likely to be objectionable, there is an obvious advantage in using the shortest possible jet design. On the other hand, the longer the jet, the less critical its design is, in terms of producing a uniform final velocity. If the expansion angle is small enough, almost any smooth curve connecting the throat to the exit will produce a reasonably uniform final velocity. Boundary layer growth and practical machinability may become problematic for a jet of excessive length. Therefore, to achieve the shortest jet length with high efficiency, it may be a conservative “best” design practice to use an

Figure 3.2. Schematic drawing of the straight-bored jet (also known as convergent jet).
expansion angle between one-half to two-thirds of $\Theta_{\text{max}}$ (the Prandtl-Meyer angle, corresponding to the final desired Mach number) for the divergent section of the jet [85].

For the Mach 3.09 CDJs used in Ames-HPGA-II nozzle, the maximum expansion angle for the divergent section is 13.2 degrees. This transition occurs immediately in the divergent section of the CDJ. The CDJ was designed for argon gas, with an axisymmetric convergent-divergent geometry that has a throat diameter of 0.737 mm (0.029 in) and an exit diameter of 1.306 mm (0.051 in) (see Figure 3.3a). The contour of the CDJ is shown in Figure 3.3b. The length of the throat section is 0.254 mm (0.010 inches) to minimize the boundary layer formation at this most constricted section of the CDJ. The isentropic design operating pressure of the CDJ for shock-free gas flow was calculated to be 3.606 MPa (523 psi). At this pressure the jet will efficiently accelerate the atomizing gas to a calculated Mach number of 3.09 with minimal loss of kinetic energy.

Individual CDJs with the divergent contour shown in Figure 3.3b were machined for schlieren imaging of the gas flow patterns.

3.2 Materials and Methods

3.2.1 Schlieren Imaging

The gas-only flow visualization experiments for the individual test models of the CDJ and CJ and for the full HPGA-I and HPGA-II nozzles were performed using schlieren imaging techniques. The Schlieren images of each gas flow field were studied as a function of operating gas pressure with the manifold pressure ranging over 0.689 to 8.274 MPa (100 to 1200 psi). For the schlieren imaging technique, a 30 mW He-Ne laser source is used in a straight single-pass configuration with a 46.5 mm (1.95 inches) diameter field of view (see Figure 3.4). The gas streams of the individual jets and the HPGA nozzles flowed perpendicular to the schlieren configuration shown. The schlieren images are projected on to a white matted board 1.5 meters from the knife edge and are recorded on 35 mm ASA 400 TMAX film using a 35 mm SRL camera. The contrast in a schlieren image is sensitive to the first spatial derivative of the gas index of refraction which is a measure of the density gradient of the gas flowfield [76]. Thus, the schlieren image of a gas flow feature such as a shock or a shear layer having a significant density gradient will be visible. While the interpretation of the images may be complicated by imposing a three-dimensional flow on a two-dimensional photograph, nevertheless, prominent features of the gas flowfield will remain intact.
Figure 3.3. Schematic drawing of an individual test model of a convergent-divergent jet and (b) the coordinates of its divergent contour.
3.2.1.1 Study of Gas Flow Adjacent to the Melt Tip

In order to examine the gas behavior as it immediately exits each discrete jet from an atomization nozzle assembly, the individual CDJ and CJ are retrofitted externally with an interference-surface. This interference-surface is 4.8 mm (0.189 inches) high and is located adjacent to the jet exit, see Figure 3.5. The 'interference-surface' simulates the side-wall of the stainless steel sleeve (Figure 3.1) in a confined-feed gas atomizer found in the two HPGA nozzle configurations. In this experimental configuration, the high velocity gas exiting the individual jets will seek to expand and will be forced to interact with the adjacent interference-
surface. The flow visualization of this interaction will allow us to observe how the gas flowfield of each isolated discrete-jets behaves as it exits against a melt tip to evaluate the atomization potential of each jet design. This study is a necessary part of developing an understanding of the discrete jets to know the flow pattern of the gas prior to its impingement upon the melt in the atomization process. The ability of the gas jets to develop a high velocity gas stream that couples well with the melt is essential to having an efficient gas atomization nozzle design.

3.2.2 Static Pressure Tests

It is critical that a subambient (aspiration) pressure be observed in the melt orifice region of a feed-tube tip to ensure stable atomization nozzle operation. Static aspiration pressure measurements were made during gas-only atomizer nozzle operation by attaching a pressure transducer to true size melt tip model (see Figure 3.6). The pressure transducer was air-tight fitted into the feed-tube model to ensure a pressure reading only from the melt orifice of the model. The electrical output of the pressure transducer is observed and recorded on a personal computer running collection software obtained from LabView. The reported pressures corresponded to the steady state pressure during a test run. Several feed-tube tip geometries were examined on the HPGA-II nozzle with tip apex angles ranging from 60° to 22° (inclusive angle); while the melt tip base diameter was fixed at 6.60 mm (0.260 inches) (see Figure 3.7). These geometries were examined for aspiration in the HPGA-II nozzle over a wide operating pressure range, 0.689 to 8.274 MPa (100 to 1200 psi). This experimental

![Figure 3.6. Schematic of the positioning of the pressure transducer in the aspiration pressure setup.](image-url)
Figure 3.7. Schematic of some selected melt tip apex angles and melt tip lengths used with HPGA-II nozzle aspiration studies. Apex (full inclusive) angles of (a) 60, (b) 45.5 and (c) 22 degrees are shown. (units in mm).
setup permitted the testing of different feed tube configurations for aspiration potential without requiring multiple melt atomization attempts.

The standard configuration of the HPGA-I nozzle uses a melt tip design that protrudes 2.28 mm (0.09 inches) beyond the discrete jet exits. The apex angle of the melt tip is 45° (total inclusive angle), matching the discrete jet apex angle of HPGA-I nozzle. This optimized melt tip configuration was based upon previously published works [5], and the static aspiration pressure measurements were repeated for this study.

3.2.3 Particle Refinement Study

The powder size yield of the two different high pressure gas atomizing nozzles HPGA-I and HPGA-II are compared directly using the Ames Laboratory high pressure gas atomization system. The powder size yield from a melt atomization experiment enabled us to evaluate the atomization efficiency of using the CDJ over that of the CJ in an atomizer nozzle. An improved atomization efficiency will be demonstrated by a larger yield of fine powder particles per unit volume of atomization gas, because greater surface area per unit volume of the melt has to be generated in creating more fine particles [108]. The description of the atomization system at Ames Laboratory US DOE can be found elsewhere [7].

The design of a high pressure gas atomization (HPGA) system, shown in (Figure 3.8), has provided Ames Laboratory with the capability for production of a wide variety of pure metal and alloy powders. The HPGA system has an atomizing volume capacity equivalent of approximately 4.5 kilogram of metallic melt per atomization run. The HPGA system consists of essentially two chambers, the melt chamber and the atomization chamber. The melt chamber on the top contains the crucible having a refractory nature that is inert to the molten metal. A melt feed tube connects the two chambers and feeds the melt to the atomization nozzle located just below the crucible. The distance between the bottom of the crucible and the HPGA nozzle is made as short as possible to prevent the melt from losing too much of its heat during its passage down the melt tube. Thus, the atomization nozzle resides at the very top of the atomization chamber. In this atomization chamber configuration, the atomized droplets solidify as they cool and free fall down the length of the chamber with the flow of gas and eventually are filtered in a cyclone and collected in a container at the end of the atomization chamber.

A high melting iron-aluminide based alloy was used for this particle refinement study. The melting temperature of this material is 1525°C, as determined by differential thermal analysis. The composition of this alloy was Fe-18.3 at.%Al-3.3 at.%Si alloy (Fe- 8.0 wt % Al- 1.5 wt % Si).
Figure 3.8. Schematic design of the Ames HPGA system.
A 4.5 kilogram charge of this alloy was prepared at Ames Laboratory, DOE, Material Preparation Center. The material for the alloy was heated in an argon atmosphere from room temperature to 1560°C in a Norton alumina crucible (type An299, Alundum, 99.95% purity). The melt was then bottom-poured into a copper chilled mold to form the ingot charge for atomization run.

The crushed iron-aluminide ingot was melted in the atomizer crucible within an induction furnace after the melting chamber was evacuated to $10^4$ atmosphere and then back-filled with high purity argon gas to 1.1 atmosphere. The atomization melt composition was not altered from the original ingot composition (this was determined from chemical analysis of the atomized powder). The melt was heated to a temperature of 1725°C in a Norton alumina crucible. Upon raising the alumina stopper rod, the melt was supplied to the atomization nozzle via a zirconia pour tube conduit.

The Fe-Al-Si alloy is atomized using high purity argon gas supplied to the atomization nozzle at a regulated inlet pressure of 7.57 MPa and 3.61 MPa for HPGA-I and HPGA-II nozzles, respectively. The atomization pressure of 7.57 MPa for the HPGA-I nozzle was determined [5] to be the optimum atomization condition. The atomization pressure of 3.61 MPa for the HPGA-II nozzle is the designed pressure of the CDJs and, thus, was assumed to be optimum for atomization efficiency with this CDJ nozzle. Each powder sample was prescreened to less than 106 μm to remove large metallic flakes, collected and size analyzed using a particle size analysis machine a “Microtac II” model (from Leeds and Northrup) to measure each particle size distribution.

### 3.2.4 Computational Modelling

A commercially available computational fluid dynamic software intended for compressible flow from Fluent Inc., Lebanon, New Hampshire, was used in this study to provide a form of comparison to the gas flow features observed with the schlieren imaging technique mentioned earlier. A set of equations for mass, momentum and energy have been solved using a general solution procedure based on the SIMPLE algorithm [72]. The differential equations are formulated using the “control volume” approximation. An additional conservation equation for turbulent kinetic energy and its dissipation rate are also solved using Sarkar’s “dilatation dissipation” method [96]. The thermodynamic properties of the gas are related through the equation of state of the perfect gas.

In this computer modelling, an annular slit convergent-divergent HPGA nozzle geometry was studied. The manifold pressure of the nozzle in the computer model is varied, while the melt tip taper angle and melt tip protrusion length remain constant. For these
calculations at the various manifold pressures, the melt tip taper angle and melt tip protrusion length were 15 degrees and 14.28 mm (0.5621 in) respectively. Fifteen degrees melt tip angle was chosen because at this geometry the prominence of the aspiration curve fluctuations is significantly greater than the background noise. This will be discussed a later section. The gas operating pressure was set at the gas manifold just upstream from of the throat of the jet. The throat and the exit width is chosen to be 0.737 and 1.306 mm, respectively (0.029 and 0.0514 inches) (see Figure 3.9). These width dimension were chosen to be identical to that of the diameters of the CDJ geometries used in the HPGA-II nozzle. By having similar geometric dimensions, the computational models can be used readily to give qualitative information about the HPGA-II nozzle, such as the size of the gas flow field and the estimated aspiration pressure at the melt orifice.

Figure 3.9. Schematic of the annular-slit convergent-divergent HPGA-II nozzle geometry used in the computer modelling.

3.3 Results

3.3.1 Schlieren Imaging

Schlieren images taken of an individual discrete CJ gas-only flow pattern are shown in Figure 3.10. In Figure 3.10a and 3.10b, the gas flowfields behave as described by previous researchers [40,43] and is shown in Figure 2.1. The schlieren images for CJ gas-only flowfield show the presence of the normal Mach disc located immediately near the jet exit. The Mach disc is observed to move down stream as the gas pressure is increased (see Figure 3.11). The gas-only flow patterns of an individual CDJ over a range of operating pressures from 0.689 to 8.963 MPa (100 to 1300 psi) are shown in Figure 3.12. Here we see that the gas flowfield is absent of a normal Mach disc as observed in discrete CJ.

Selected enlarged schlieren images of Figure 3.12 are shown in Figure 3.13. These
and [b] 7.57 MPa (1100 psi) of manifold pressure.

Figure 3.10. Schlieren images of gas-only flowfield of C1 operated at [a] 3.78 MPa (550 psi) and [b] 7.57 MPa (1100 psi) of manifold pressure.
Figure 3.11. Location of the normal shock disk from an individual CJ.
Figure 3.12. Schlieren images of gas-only flowfield of CDJ operated at (a) 3.61 MPa (525 psi) and (b) 7.57 MPa (1100 psi) of manifold pressure.
Figure 3.13. Schlieren images of discrete convergent-divergent jet operating in (a) over-expansion condition at 1.21 MPA (175 psf), (b) design condition at 2.41 MPA (350 psf) and (c) under-expansion condition at 6.21 MPA (900 psf). PM represents Prandtl-Meyer wave.
enlarged images were used to study the gas flow features of the CDJ. When operating at a manifold pressure between 2.24 to 2.58 MPa (325 to 375 psi), the images of the gas flow were essentially devoid of oblique shocks and expansion-compression waves (Figure 3.13b). This was attributed to the fact that this operating condition allowed for perfect expansion of the gas from the manifold such that the pressure of the exiting gas matches the pressure of the ambient air, i.e., the jet reached the “design” condition illustrated in Figure 2.11b. The faint oblique shocks that are visible are typically attributed to minor machining flaws in the nozzle and do not affect this experimental determination of the design or third critical condition. The apparent design condition at about 2.41 MPa is displaced from the intended value of 3.61 MPa for reasons that will be discussed in a following section. Below 2.24 MPa, in the over-expanded operating condition, oblique shocks are present (see arrow in Figure 3.13a) at the jet exit, followed by a series of Prandtl-Meyer expansion-compression waves shown as dark and light shades in succession in Figure 3.13a. Above 2.58 MPa, in the under-expanded operating condition, the series of Prandtl-Meyer expansion-compression waves, shown as dark and light shades in succession, are visible at the jet exit (see arrows in Figure 3.13c). The over-expanded and under-expanded conditions are illustrated schematically in Figure 2.11a and 2.11c, respectively.

Computer image analysis techniques were used on digitized schlieren images to locate and measure the position of all visible oblique shock nodes and Prandtl-Meyer waves from the jet exit. Results of these measurements are plotted in Figure 3.14. The gas flow features such as oblique shocks and P-M waves are observed to move downstream away from the jet exit at higher manifold pressure. A normal shock pattern was observed only at manifold pressures higher than 7.75 MPa (1,125 psi). Eight regions were distinguished from the Figure 3.14. Regions 1 and 2 denotes the presence of oblique shocks in over-expanded operating condition. Regions 3, 4 and 5 denote the presence of the 1st, 2nd and 3rd Prandtl-Meyer waves, respectively. Each of these three regions is composed of the expansion wave followed by the compression wave, as depicted schematically in Figure 2.11a. In region 6, no clearly distinguishable gas flow features can be identified. The schlieren gas flow images in region 6 lacked the density gradient with the surrounding atmosphere to resolve any features because the gas is ideally expanded to atmospheric pressure. Thus no feature measurements are made for pressure region between 2.07 to 2.76 MPa (300 and 400 psi). Therefore, 2.41 MPa (350 psi), located in region 6, is experimentally determined to be the apparent “design” operating pressure for the CDJ. Regions 7 and 8 are representative of the 1st and 2nd Prandtl-Meyer waves, respectively, in the under-expanded operating condition. Once again, the expansion and compression waves form within the flow field in order to adjust the exiting gas pressure to
Figure 3.14. Oblique shock node distance from the jet exit as a function of manifold pressure. There are three operating conditions for the discrete jet; over-expanded condition: (1) region of 1st oblique shocks (2) region of 2nd oblique shocks (3) region of 1st Prandtl-Meyer waves (4) region of 2nd Prandtl-Meyer waves (5) region of 3rd Prandtl-Meyer waves. Design condition: (6) featureless region devoid of shocks and Prandtl-Meyer waves. Under-expanded condition: (7) region of 1st Prandtl-Meyer waves (8) region of 2nd Prandtl-Meyer waves and (9) location of normal shock formation (reproduced from Ting et al. [110]).

ambient pressure. Label 9 marks the location of the normal shock formations in this highly under-expanded operating pressures.

Using schlieren techniques on the full atomizer nozzle assembly, the gas stream profile for the HPGA-I and the novel HPGA-II can be seen in Figures 3.15 and 3.16, respectively. The HPGA-II produces strong laminar flow pattern over an extended distance compared to the HPGA-I. Whereas, the HPGA-I produces high velocity gas that quickly is dissipated by the formation of the normal (that is only indicative by the narrowing of the gas flowfield) and oblique shocks. Both nozzles produce gas flowfields that exhibit P-M waves in the unified gas flow. This is noted by the “diamond” shock formations in the unified flowfield.
Figure 3.15. Schlieren images of gas-only flowfield of HPGA-I nozzle with 45° melt-tip at (a) 3.78 MPa (550 psi) and (b) 7.57 MPa (1100 psi) of manifold pressure.
Figure 3.16. Schlieren images of gas-only flowfield of HPGA-II nozzle with 22° melt-tip at (a) 3.61 MPa (525 psi) and (b) 7.57 MPa (1100 psi) of manifold pressure.
3.3.1.1 Interference Surfaces

It is observed from Figure 3.17 that the gas flowfield of discrete CJ deflects off the ‘interference-surface’. This is a result of the rapid external gas expansion adjacent to the ‘interference-surface’. The external gas expansion of the CJ can be seen in Figure 3.10 in the previous section. Figures 3.18 a and 3.18b show the schlieren images of the CDJ gas-only flow field with ‘interference-surface’ at 3.61 MPa and 7.57 MPa respectively. One can readily note that at 3.61 MPa, at design pressure, the gas flowfield is almost parallel to the ‘interference-surface’. This is indicative to the fact the gas is properly expanded in the divergent section of the CDJ such that the gas exits the jet parallel to the CDJ exit wall. Likewise, very little gas flow deflection is seen in Figure 3.18b, at 7.57 MPa.

From the schlieren photographs, Figure 3.17 and 3.18, we can measure the deflection angle of the discrete jets with respect to change in the operating pressure. This is seen in Figure 3.19.

3.3.1.2 Annular-Slit Convergent-Divergent Nozzle

An annular-slit HPGA nozzle with convergent-divergent geometry was built to evaluate the computer model described earlier in section 3.2.4. Schlieren images of the annular-slit convergent-divergent HPGA nozzle were compared to the computational results. This will be presented in section 3.3.4. Selected schlieren images over a range of operating pressures from 0.689 to 7.584 MPa (100 to 1100 psi) are shown in Figure 3.20. At each gas manifold pressure increment we observe a change in the gas flow features adjacent to the edge of the melt tip, as described Figure 2.11 in Section 2.3. When operating the manifold pressure at 3.447 MPa (500 psi), the first Prandtl-Meyer expansion wave was observed at the corner of the melt tip (Figure 3.20a). At an incremental higher operating manifold pressure of 4.482 MPa (650 psi), the compression wave has moved down stream to a position immediately adjacent to the melt tip corner (Figure 3.20b). At an operating manifold pressure of 5.516 MPa (800 psi), in the under-expanded condition, a compression wave is the dominant gas feature at the corner of the melt tip (Figure 3.20c). Further increase in the operating manifold pressure to 7.584 MPa (1100 psi) showed the dominant gas feature to be the expansion wave of the first Prandtl-Meyer wave in the under-expanded condition (Figure 3.20d). These gas flow features adjacent the melt-tip can be correlated to aspiration curve measurement for the annular-slit convergent-divergent HPGA nozzle. This will be discussion in section 3.4.2.2.

It is also observed from the schlieren images in Figure 3.20 that the gas flow field is asymmetrical about the centerline of each images. This is primarily the result of an unevenly pressurized nozzle manifold. As described previously, the annular-slit convergent-divergent
Figure 3.17. Schlieren images of gas-only flowfield of CJ operated with ‘interference-surface’ at (a) 3.61 MPa (525 psi) and (b) 7.57 MPa (1100 psi) of manifold pressure.
Figure 3.18. Schlieren images of gas-only flowfield of CDJ operated with 'interference-surface' at [a] 3.61 MPa (525 psi) and [b] 7.57 MPa (1100 psi) of manifold pressure.
Figure 3.19. Discrete jet deflection angle from the 'interference-surface' versus operating pressure.
Figure 3.20. Schlieren images of annular-slit convergent-divergent HPGA nozzle at operating manifold pressure of (a) 3.45 MPa (500 psi), (b) 4.482 MPa (650 psi), (c) 5.516 MPa (800 psi) and (d) 7.57 MPa (1100 psi) (The pressure gradient of the gas flow field tends to distort the image). PM stands for Prandtl-Meyer wave.
HPGA nozzle has a single pressurized gas inlet feeding the annular manifold of the nozzle. The schlieren results showed that for an annular-slit nozzle which consumes considerably more gas [73] one must invest a greater effort in designing the gas manifold so that the chamber is evenly pressurized. This will ensure an even gas flow field from the annular-slit jet for uniform atomization velocity.

3.3.2 Static Pressure Tests

3.3.2.1 Discrete Jet Convergent-Divergent HPGA-II Nozzle

Static aspiration pressure of the HPGA-I was repeated to form a base line for this study agreed well with published results on the HPGA-I nozzle [5]. The static aspiration pressure was measured based on previously mentioned melt tip geometry. The HPGA-I nozzle experiences an initial overambient pressure between 1.5 to 2 MPa of manifold pressure, after which the aspiration pressure drops to a minimum of 40 kPa at a manifold pressure of 6 MPa (see Figure 3.21). Then the aspiration pressure is observed to rise at pressures above 6 MPa. The statistical fluctuation of the aspiration pressure measurement diminished at higher manifold pressure, above 4.5 MPa. This is an indication that the gas from the 20 discrete jets may have begun to form an organized flow field down stream near the melt tip. This reasoning would be in agreement with observed gas flow field described by Anderson et al. [5] using HPGA-I type nozzles. At pressure between 5 to 6 MPa, the recirculation zone of the nozzle is observed to diminish in size and length [5,67]. The phenomenon is known as “wake closure” [105]. This is often followed by the formation of a normal shock at the wake front of the

![Figure 3.21. Static aspiration base pressure of HPGA-I with argon using a matching 45 degrees melt tip.](image)
recirculation zone as manifold pressure is increased. Because the formation of a normal shock requires a stable gas flow field for it to exist, the presence of this stable gas flowfield helps explains the observed diminishing data fluctuation that occurs at the high manifold pressures.

In order to prevent the melt from back flowing \cite{5} we need to generate aspiration pressures at the melt tip to stabilize the melt flow from the crucible to the atomizer nozzle. Our research showed that a melt tip with an apex angle of 45°, used in the HPGA-I, created a positive backpressure of 33.7 kPa above the ambient pressure at the melt orifice, when used in the HPGA-II operating at 3.61 MPa (the design pressure of the CDJ) (see Figure 3.22). When this melt tip is replaced with another having a 30° apex angle, an aspiration of 10.3 kPa pressure is measured at the orifice for the same operating pressure. Further decrease in the melt tip apex angle to 22° was found to generate a deeper aspiration pressure of 18.6 kPa (see Figure 3.7).

Another static aspiration pressure study with the HPGA-II nozzle was performed varying the melt tip length, while having the melt tip apex angle fixed 40°. A melt tip with a total inclusive apex angle of 40° was positioned, within the nozzle central hole. This melt tip angle was chosen to induce a mild mismatched angle that with the proper melt tip length was expected to generate an enhanced subambient aspiration without a large sacrifice in gas kinetic energy, as described in the results section. A detailed study on the static aspiration was carried out for the 40° melt tip at several tip lengths on the HPGA-II nozzle. This was done by machining away length increments of 0.127 to 0.508 mm from the 40° melt tip starting at an

![Graph showing aspiration pressure measurements for HPGA-II with several melt tip angle configurations.](Figure 3.22. Aspiration base pressure measurements for HPGA-II with several melt tip angle configurations (reproduced from Ting et al. [109]).)
initial length of 9.144 mm (0.360 in) and ending at a final length of 1.524 mm (0.060 in). At each incremented length, aspiration base pressures were measured for the HPGA-II nozzle over an atomization gas supply pressure range from 0.689 to 8.274 MPa (100 to 1200 psi).

Sensitivity of static aspiration pressure to this 40° melt tip length was examined. Static aspiration base pressure measurements for the HPGA-II nozzle are shown in Figure 3.23 for 3 selected lengths of the 40° melt tip. Aspiration base pressures were observed to rise and to fall, at a given nozzle manifold pressure, as the melt tip lengths were changed. High overambient aspiration base pressure of 135 kPa (~20 psia) was observed as a maximum when using a long melt tip length of 6.86 mm (0.270 in.). A drop in the maximum overambient aspiration base pressure was observed with a shorter melt tip length 3.81 mm (0.150 in.). In Figure 3.23b, deep subambient base pressure of 70 kPa (~10 psia) was observed with a manifold pressure above 5 MPa, indicating a very stable gas atomization condition. However, further shortening of the melt tip to 2.03 mm (0.080 in.) again raised the overall trend of the base pressure. The current work contradicted the prediction that extended melt tip geometries will promote subambient base pressures [72], especially not for HPGA nozzles that have discrete convergent-divergent micro-jet configurations. Rather, an optimum length for a melt tip should exist.

### 3.3.2.2 Annular-Slit Convergent-Divergent HPGA Nozzle

For the annular-slit convergent-divergent HPGA nozzle, deep subambient and high overambient aspiration base pressures were observed (Figure 3.24). A maximum subambient base pressure occurred at a manifold pressure of 4.0 MPa (~580 psi) followed by a continuous rise towards a maximum overambient base pressure occurring at 5.5 MPa (~800 psi). At operating manifold pressure of just over 5.5 MPa, the aspiration base pressure drops abruptly. A steady decrease in aspiration base pressure, below ambient pressure, is observed with further increase in operating manifold pressure. It is interesting to note that although the gas flow features are non-uniform around the melt tip (see Figure 3.20b and 3.20c) the static aspiration pressure data fluctuates very little (see Figure 3.24). This is because a non-uniform flow field does not necessarily mean an unstable flow field [74]. An unstable flow field will give rise to significant data fluctuation in the aspiration measurement. It can exist a case where there is a stable yet non-uniform flowfield around a melt tip giving rise to stable (minimal data fluctuation) static aspiration measurement, such is the case shown in Figure 3.24.
Figure 3.23. Variation of aspiration base pressure with manifold pressure for HPGA-II using 40° melt tip at three melt tip lengths of (a) 6.86 mm (0.270 in) (b) 3.81 mm (0.150 in) (c) 2.03 mm (0.080 in). Grey bars show pressure rising; cross-hatched bars show pressure dropping; and solid bar show subambient base pressure. (reproduced from Ting et al. [110]).
Figure 3.24. Experimental aspiration base pressure of an annular-slit convergent-divergent HPGA nozzle, showing corresponding positions on the curve where the schlieren photographs in Figure 3.20 are observed (reproduced with modification from Ting et al. [110]).

3.3.3 Particle Refinement Study

The atomized Fe-Al alloy powder was collected and screened to exclude particle debris larger than 106 μm (140 mesh) and size analyzed. Two atomization runs with the HPGA-II nozzle and one run for the HPGA-I nozzle were conducted.

The powder size refinement results for the HPGA-I nozzle, using a 45° apex angle melt tip, and for the HPGA-II nozzle using a 22° melt tip with taper length of 4.6 mm (0.180 inches) are compared in Figure 3.25.

For the particle size distribution for the HPGA-I nozzle, about 50 weight % of the particles were less than 28 microns in diameter, about 16 weight % of the particles were less than 13 microns in diameter and about 84 weight % particles were less than 50 microns in diameter.

For the particle size distribution for the HPGA-II nozzle, about 50 weight % of the particles were less than 32 microns in diameter, about 16 weight % of the particles were less than 15 microns in diameter and about 84 weight % particles were less than 62 microns in diameter.

By comparing the cumulative percentage at the average diameter, d50 particle size, the particles produced using the HPGA-I nozzle are finer than particles produced using the HPGA-II nozzle (see Figure 3.25). The gas-to-metal ratio consumed in the gas atomization process
Figure 3.25. Summary of powder size refinement studies for HPGA-I and HPGA-II Nozzles (reproduced from Ting et al. [110]).

showed that the HPGA-I and HPGA-II consumed a ratio of 1.934 and 1.176, respectively. This showed that HPGA-II consumed one third less argon gas than HPGA-I nozzle, approximately.

Most gas atomized powders follow a log-normal size distribution [51,129] as shown in Figure 3.25. This distribution can be shown mathematically by a variation of the Gaussian probability function. Then, the standard deviation of the powder yield can be calculated using the ratio of particle diameter measures at 84 over 50 weight percent yield (d84/d50) [51,129]. Even though the particle size yield was different between the two atomizer nozzles, it is apparent that the standard deviations of 1.85 and 1.91, for the particle size distribution of HPGA-I and HPGA-II atomization runs, respectively, were similar. These standard deviations results are representative of standard deviations of published atomization runs [129]. Further evaluation of the particle refinement results should also take into account the fact that the atomization pressure of the HPGA-I run was at 7.57 MPa. This is more than twice the atomization pressure of the HPGA-II run, at 3.61 MPa.

3.3.4 Numerical Modeling of an Annular-Slit Convergent-Divergent Gas Atomization Nozzle

For the annular-slit convergent-divergent HPGA, the numerically calculated aspiration base pressure results were compared to the measured static orifice pressures over the same range of operating pressures as in Figure 3.24. The calculated orifice pressure in Figure 3.26
was obtained by averaging the static pressure along the entire melt feed tube orifice, which had a constant diameter of 3.17 mm (0.125 in). A drastic change in aspiration base pressure occurred between 3.45 and 4.83 MPa (500 and 700 psi) in the calculated results of Figure 3.26 which compared very closely to the measured results in Figure 3.24.

The computational flow field showing velocity vectors for selected pressures are shown in Figure 3.27. These gas flow fields have features that are identifiable from the velocity vector density in these figures. The areas with a high velocity vector density correspond to areas of P-M compression waves. Similarly, areas with low vector density correspond to areas of P-M expansion waves. For all the numerical results a recirculation zone occurred adjacent to the melt tip. This is identifiable by the reversal in the gas vector from the “right-flowing” (away from the melt tip) to the “left-flowing” direction (towards the melt tip orifice).

![Figure 3.26. The numerical results showing the aspiration base pressure for the annular-slit convergent-divergent HPGA nozzle (reproduced from Ting et al. [110]).](image)

3.4 Discussions

3.4.1 Schlieren Imaging

Shearing of molten melt by high velocity gas is one primary mechanism for gas atomization. A stable laminar gas flow field will provide the maximum shearing momentum for primary melt breakup in the atomization process. From Figures 3.15 and 3.16 we can conclude that the HPGA-II nozzle produces laminar flow features over a wide range of operating pressures compared to HPGA-I nozzle. Although the HPGA-II nozzle is not operating in its most efficient configuration using a 22° melt tip, the ability of the HPGA-II nozzle to generate subambient aspiration pressure over a wide range of manifold pressures may permit us to fine tune for desirable particle sizes by simple varying the operating pressures.
Figure 3.27. Numerical results showing the velocity vector of the gas flow field for an annular slit convergent-divergent HPGA nozzle at (a) 2.76 MPa (400 psi) (b) 4.83 MPa (700 psi), and (c) 7.28 MPa (1100 psi).

(b) Compression wave

Anular slit exit
Melt tip

1st Pm wave

(a) Expansion wave

Anular slit exit
Melt tip

Oblique shocks

1st Pm wave
Figure 3.27. (continued)
This is opens up a wide range of operating pressure range for HPGA-II compared to existing HPGA-I that is limited to operate over a restricted range of pressures dictated by the range of aspiration (see Figure 3.21).

Since high shear gas velocity is desirable for efficient gas atomization it would then be useful to know the relative gas velocity in the HPGA nozzles. It has been previously described by Hartmann and Lazarus [43] that the length of the node spacing in the gas flow field of an individual CJ can be qualitatively related to the velocity of the gas flow. Similarly, then, the relative gas velocity of the HPGA-I and HPGA-II nozzles can be qualitatively ranked by measuring the distances between the nodes spacing of the 1st and 2nd oblique shocks formed in the unified gas stream, i.e., see Figure 3.15. Figure 3.28 shows a plot of node spacing in the unified gas stream versus different operating gas pressures for the HPGA-I nozzle using a 45° tip and the HPGA-II nozzle using 45°, 30° and 22° tips. At an exact designed operating pressure for HPGA-II of 3.61 MPa, we find that the gas velocity for the HPGA-II is approximately the same as that for the HPGA-I at 7.57 MPa. This qualitative analysis demonstrates that the HPGA-II nozzle using discrete CDJs can generate the same supersonic gas velocity for atomization at about half of the operating pressure of the HPGA-I nozzle. In addition, the HPGA-II gas stream is considerably more laminar and uniform as seen from the straight gas streams observed around the melt tip (see Figure 3.16). This is useful for creating an uniform high Weber number (We) between the melt and gas velocities around the circumferential edge of the melt tip, see Eq. 2.2.

Figure 3.28. A qualitative gas velocity comparison between the nodes distances at different operating gas pressures for the HPGA-I and HPGA-II nozzles having different melt-tip geometries (reproduced from Ting et al. [109]).
In close-coupled gas atomization, the melt flows along the melt tip base tangentially (see Figure 3.29) into the high velocity gas stream at the periphery of the melt tip, therefore the velocity of the melt is negligible in this equation [2,51]. The magnitude of the Weber number is then solely dependent upon the velocity of the gas.

The HPGA-II using a 45° melt tip geometry, matching the apex angle of the jets to the melt tip, clearly shows significantly higher velocity over most operating pressures compared to the other two atomizer configurations. The differences in the observed velocities, between the HPGA-II nozzle with a 22° melt tip and the HPGA-II nozzle with 30° and 45° melt tips, over a range of operating pressure is related to the mismatch between the melt tip and the gas jets.

This mismatch leads to altering the direction of the gas flow in the HPGA-II nozzle angle with the 22° melt tip; while no change in gas flow occurred when using the 45° melt tip. The mismatch of the nozzle and melt tip angles creates strong oblique shocks as the supersonic gas attempts to turn at the junction where the miss-matched angle is found. The creation of strong oblique shocks at this location dissipates the kinetic energy of the gas flowfield, by raising the entropy of the gas [131], thereby diminishing the overall gas velocity after the shock formation. Although the HPGA-II nozzle with a 45° melt tip shows greater promise in generating higher velocity than other melt tip geometries, unfortunately, the 45° melt tip geometry cannot be used with the current HPGA-II nozzle because of the high backpressure that is observed in the static aspiration measurement (refer to Figure 3.22).

Figure 3.29. Schematic showing tangential flowing melt as it exits the pour tube orifice.
3.4.1.1 Individual Convergent-Divergent Micro-Jet

The schlieren results for the present CDJ provided evidence for a significant boundary layer effect that lowers the apparent operational Mach number of the “design” condition, when compared to the inviscid isentropic prediction based on area ratio alone. This boundary layer effect can be particularly acute in miniature jets [45,99]. In our individual CDJ, from schlieren imaging, the experimental operating pressure for the “shockless” design condition is determined to be about 2.41 MPa (350 psi) located in the middle of region 6 in Figure 3.14. This indicated that the experimental design operating pressure is lower than the expected calculated design pressure of 3.61 MPa (525 psi) and, thus, the gas velocity is also reduced. The gas velocity at 2.41 MPa can be determined to be equal Mach 2.82 using isentropic calculations. The reduced velocity, Mach 2.82, of the micro-jet is within 10% of the ideal jet velocity, Mach 3.09. This magnitude of velocity reduction between designed and observed is in good agreement with previous work on conventional rocket nozzles [107]. A comparison of the exit area ratios required theoretically for Mach 3.09 and 2.82, using isentropic methods, showed the boundary layer thickness to be about 0.0023 inches (equivalent to an occupation of 17% of the total exit area). A calculation using Blasius approximation [10,131] for a flat boundary layer yielded a thickness of 0.0013 inches, in reasonable agreement with the experimental estimate based on isentropic methods.

3.4.1.2 Schlieren of Interference Surface

It is important that the gas and the liquid melt are in close contact to one another to maximize energy transfer from the high velocity gas to the liquid melt to enhance the shearing mechanism and the Weber number, for particle breakup. The gas flowfield in a discrete CJ was found to be non-ideal for close-coupled atomization, because the high velocity gas flowfield is deflected away from melt tip edge. From the figure we see that the angle at which the gas flowfield of the CJ is deflected increases with increasing manifold pressure. Therefore, the benefit gained in having higher kinetic energy, by operating HPGA-I nozzle at high pressures (greater than 1000 psi), is easily canceled by the high deflection angle, at these pressures, such that the high kinetic energy may not participate in the melt primary breakup process.

Thus, all observations indicate that using the CDJs in an HPGA-II nozzle improves the gas-to-melt close-coupling around the peripheral edge of the feed-tube for the purpose of maximizing kinetic energy transfer during primary breakup in gas atomization.
3.4.2 Static Pressure Tests

3.4.2.1 Discrete-Jet Convergent-Divergent HPGA-II Nozzle

A summary composite plot of results (Figure 3.20) was obtained from superimposing 11 aspiration curves (some are shown in Figure 3.23) grey, cross-hatched and solid bars, representing the rising and falling sections of the aspiration base pressure curves, in into Figure 3.14. From Figure 3.30, the rising sections of an aspiration base pressure curve (gray bars) were found to be located near a Prandtl-Meyer node (solid diamonds in Figure 3.30). This is close in proximity to where compression wave would be located in a free expanding CDJ. Meanwhile, the falling sections and subambient sections of an aspiration base pressure curve (cross hatched bars and solid bars respectively) were located manifold pressure regimes where one would expect to generate Prandtl-Meyer expansion waves adjacent to the melt tip edge. It becomes apparent that a strong correspondence between the rise or fall sections of the aspiration curve with gas flow features that are present at the periphery of the melt tip.

In summary, it was observed that the location of Prandtl-Meyer expansion waves at the periphery of melt tip lowered the aspiration base pressure, while Prandtl-Meyer nodes or compression waves raised the aspiration base pressure. This is because Prandtl-Meyer expansion waves have subambient static pressure and Prandtl-Meyer compression waves have overambient static pressure. In both cases, the aspiration base pressure is directly related to the static pressure of the gas flow feature located at the melt tip corner.

![Composite results: from overlaying base pressure rises (dotted gray bars) and base pressure descends (cross hatched bars and solid bars) from Figure 3.23 on to Figure 3.14. Solid bars show regions of subambient aspiration base pressure (reproduced from Ting et al. [110]).](image-url)
For illustration of this hypothesis a Prandtl-Meyer expansion wave is schematically shown in Figure 3.31b and 3.31d. The low static pressure of the PM wave will reduce the aspiration base pressure by setting-up a radial pressure gradient that favors a velocity flow from the melt orifice radially to the periphery. The undesirable overambient condition occurs when the periphery of the melt tip experiences a Prantl-Meyer compression wave, schematically shown in Figure 3.31a and Figure 3.31c, where the corner experiences a high static pressure. A schematic drawing of a possible aspiration base pressure curve is shown in Figure 3.32, showing the corresponding regions depicted in Figure 3.32.

The rising portions of an aspiration base pressure curve (shown as dotted gray bars in Figure 3.30) are located further away from the jet exit compared to the Prandtl-Meyer nodes of a free-expansion CDJ (shown as solid triangles in Figure 3.30), as anticipated. The aspiration base pressures for an HPGA-II nozzle having jets positioned at a 45° apex angle were measured using a 40° melt tip. This geometry resulted in a very slight mismatched angle with the jet of 2.5°, i.e., the half angle difference. It is documented [131] that a mismatch angle at high Mach velocity will invariably form an oblique shock at the mismatched junction. A schematic drawing of the discrete gas features with mismatched melt tip is given in Figure 3.33. The exiting gas is in an under-expanded condition which will result in the formation of Prandtl-Meyer expansion waves. The supersonic gas, after experiencing the expansion wave, forms an oblique exit shock as it encounters the mismatched junction. This oblique exit shock turns the initial supersonic gas flow direction that is parallel to the micro-jet centerline to a flow direction that is parallel to the melt tip wall by an angle equal to the mismatched angle. The exit oblique shock interacts and deflects the expansion wave further down the gas flowfield (see Figure 3.33b). Thus, for a given operating pressure, the gas features formed from this geometrical mismatch are further away from the jet exit than expected from the matching condition (see Figure 3.33a) or from a free-expansion CDJ (see Figure 3.14). When the melt tip becomes extremely short, around 2.03 mm (0.080 in), the presence of the exit oblique shock promotes a sharp rise in aspiration base pressure. This is due to the increase in the static pressure behind all shock formations. Therefore, an abrupt rise in aspiration base pressures is observed in short melt tip lengths (Figure 3.23c).

Regions of subambient aspiration base pressure are shown as solid bars in Figure 3.30. For the HPGA-II nozzle using a 40° melt tip, the lowest operating manifold pressure for the occurrence of subambient base pressure is observed at a melt tip length of 3.81 mm (0.150 in). This indicates an optimum melt tip length for a stable atomization condition for a mismatched melt tip. This geometrical configuration allows for maximizing available kinetic energy, while
Figure 3.31. Gas flow features at the periphery of the melt tip are shown in different operation conditions. Below design pressure condition (a) PM compression wave and (b) PM expansion wave are located at periphery of the melt tip. Above design pressure condition (c) PM compression wave and (d) PM expansion wave are located at periphery of the melt tip.
Figure 3.32. Schematic drawing of the aspiration curve showing regions corresponding to schematic drawing shown in Figure 3.31.

Figure 3.33. Schematic drawings of gas features for the under-expanded condition from a HPGA-II nozzle having: (a) matching (45° melt tip), and (b) mismatched (40° melt tip) geometries (reproduced from Ting et al. [110]).
sustaining subambient base pressure for a stable atomization process. This is otherwise impossible to achieve in the HPGA-II nozzle using matching apex angle melt tips.

3.4.2.2 Annular-Slit Convergent-Divergent HPGA Nozzle

Strong correlation can be made readily with the gas features in the schlieren images (Figure 3.20) and the slopes in the aspiration base pressure curve (Figure 3.24). At an operating manifold pressure of 3.45 MPa (500psi), a P-M expansion wave produced a drop in aspiration base pressure. At 4.48 MPa (650 psi) a P-M compression wave is observed to cause the rise in base pressure to start. The maximum overambient pressure is observed at 5.52 MPa (800 psi). This occurs towards the end of the P-M compression wave formation causing the aspiration curve to reach a maximum overambient pressure. At higher operating pressure, above 5.5 MPa, the expansion wave became the dominant gas feature adjacent to the melt tip producing the initial drop in base pressure followed by a steady drop in base pressure (Figure 3.20d).

3.4.3 Particle Refinement Study

In gas atomization, a droplet formed by primary disintegration may undergo further disintegration if the gas stream shearing effect on a melt film exceeds the restoring force due to surface tension. Thus gas atomization can be viewed as a process that consumes gas kinetic energy to create particle surface area. The greater a nozzle's ability to convert gas kinetic energy into particle surface energy (creating fine powders), the more efficient is the nozzle. Therefore it is reasonable to evaluate the efficiency of the two different nozzles by comparing powder surface area created per unit mass of atomizing gas consumed in the process (units of, m²/kg) [108]. Simple comparison of the mean powder size or powder particle distribution provides an incomplete picture of the efficiency of atomizing nozzles.

From this studies, see Table 3.1, the gas/melt ratio (kg/mₖg) of the HPGA-II nozzle is two-thirds of that of the HPGA-I nozzle. The standard deviation, dₚ/dₜₜ, is shown to be similar for the two atomizers. The measured surface area per cubic-centimeter of powder from automated size analysis is also tabulated. We calculated the atomization efficiency of HPGA-I and HPGA-II nozzles by considering the gas/melt consumption during atomization, the percentage yield of useful powder, and the surface area of powder per unit volume of powder, see Eq. 3.1. The measurements of powder surface area per unit volume of powder are a direct relation to the powder size distribution. By considering powder size distribution in the efficiency calculation, we can also, without bias, evaluate the efficiency of atomization nozzles that produce bi-modal powder size distributions.
Efficiency = \left( \frac{\text{calculated surface area per unit volume}}{\text{density of metal}} \right) \times \frac{\% \text{ yield of useful powders}}{\text{gas-to-melt mass flow ratio}}, \quad 3.1

The percent yield of useful powder is a weight yield of powder less than 106 μm. This is calculated by taking the weight ratio powder less than 106 μm to the total weight of metal in the crucible. This is a very conservative number for given fact metal atomization have metal residuals in the crucible, transient time in the beginning of atomization, and metal spats again atomization chamber that all reduces the percentage yield of the powders. The units for the parameters for calculating the efficiency of atomization is given below,

$$\left( \frac{m_{\text{metal}}^2}{\text{kg}_{\text{gas}}} \right) = \left( \frac{m_{\text{metal}}^2}{\text{cm}_{\text{metal}}^3} \right) \times \frac{\%}{\left( \frac{1}{\text{kg}_{\text{metal}}} \right)} \times \left( \frac{1}{\text{kg}_{\text{gas}}} \right), \quad 3.2$$

### Table 3.1. Particle refinement results using Fe-8wt.% Al-1.5wt.% Si as the melt medium.

<table>
<thead>
<tr>
<th>Atomizer nozzles</th>
<th>Operating pressure (MPa)</th>
<th>Gas/Melt ratio (kg$<em>{\text{gas}}$/kg$</em>{\text{metal}}$)</th>
<th>Mean particle diameter, (μm, $d_m$)</th>
<th>Standard deviation, ($d_m$)</th>
<th>Calculated surface area per cc of powder (m$^2$/cc)</th>
<th>Efficiency: Area produced per kilo of gas (m$^2$/kg)</th>
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<td>HPGA-II</td>
<td>3.61</td>
<td>1.243</td>
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<td>0.255</td>
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<tr>
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<td>3.61</td>
<td>1.109</td>
<td>37.5</td>
<td>1.901</td>
<td>0.219</td>
<td>17.54</td>
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<tr>
<td>HPGA-I</td>
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<td>1.934</td>
<td>27.7</td>
<td>1.852</td>
<td>0.284</td>
<td>17.27</td>
</tr>
<tr>
<td>Annular-</td>
<td>3.5-4.2</td>
<td>7.7</td>
<td>30.0</td>
<td>1.930</td>
<td>0.308</td>
<td>5.89</td>
</tr>
<tr>
<td>Slit *</td>
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</tbody>
</table>

* Commercial atomization nozzle [73]

Upon first glance, we find that the two atomizers are comparable in efficiency, see Table 3.1, but this conclusion dismisses the very different atomization conditions, i.e., operating pressures and gas-to-melt ratios. The results given in Table 3.1 indicates that the HPGA-II nozzle is a more technologically effective nozzle for powder production because of its ability to produce a similar atomization efficiency (measured in m$^2$/kg$_{\text{gas}}$) as HPGA-I while operating at half the atomizing pressure as that used by HPGA-I. The current industrial gas atomization with HPGA-I can only be achieved using a serially connected ultra-high pressure gas cylinders, that have 6000 psi of gas pressure. This gas atomization duration time in this serially connected set up is heavily limited the to the number and capacity of the pressurized gas cylinders. The HPGA-II nozzle is a more technologically effective nozzle for powder production because the nozzle can works within the limits of pressurization gas pump systems.
These pump systems take evaporated gas from a liquid dewar sources, pressurizes gas up to 4.13 MPa (600 psi), and provides continuous pressurized gas to the atomization nozzle. Therefore the new HPGA-II nozzle using this alternative gas supply technology will liberate the gas atomization process from the pressurized gas cylinders, allowing continuous gas atomization process without compromising the atomization efficiency.

This investigation has clearly demonstrated that the CDJs in the HPGA-II nozzle are indeed more technologically effective for producing finer powders than the CJs in the HPGA-I nozzle. We have also demonstrated in this study that better nozzle atomization efficiency does not mean finer mean powder diameter, \( d_{\text{sp}} \), but rather, the nozzle atomization efficiency measures the ability of the atomizer nozzle to transfer gas kinetic energy to the melt for producing surface area for fine powder particles. If we are to compare atomization nozzles by just giving mean powder diameter, we neglect the significant contribution that gas/melt ratio, powder size distribution (in terms of powder surface area per volume of powder) and percentage yield has on the efficiency of the atomization nozzle. Therefore, it is essential to consider the contribution of these factors upon evaluating of the efficiency the atomization nozzles. Therefore, we hope that the efficiency comparison made in this study will provide an unbiased future reference for the evaluation of different inert gas atomization nozzles.

3.4.4 Numerical Modeling of an Annular-Slit Convergent-Divergent Gas Atomization Nozzle

Numerical results showing the velocity vectors of the gas flow field are given in Figure 3.27 behaved similar to what are observed in schlieren in Figure 3.20. At 3.45 MPa (Figure 3.20) and 2.76 MPa (Figure 3.27) for the schlieren and numerical results respectively, we observe similar distinct P-M expansion gas flow features to pass the periphery of the melt tip, reducing the aspiration base pressure. At 2.76 MPa (400 psi), the dominating P-M expansion flow feature at the melt tip periphery that can be corresponded to region 4 of Figure 2.11a. This P-M expansion wave lowered the aspiration base pressure in both the experimental and numerical results shown in Figure 3.24 and Figure 3.26, respectively. On the other hand, at 5.516 MPa (Figure 3.20) and 4.83 MPa (Figure 3.27) for the schlieren and numerical results respectively, we observe similar distinct P-M compression gas flow feature at the melt tip periphery that can be corresponded to region 13 of Figure 2.11c. This P-M compression waves described above created overambient peaks in the experimental and numerical results shown in Figure 3.26 (at 4.83 MPa) and in Figure 3.20 (at 5.52 MPa), respectively. Also at 4.83 MPa, the computational modeling showed a transition in the gas flow feature was occurring at the corner of the melt tip. It is noted that the presence of the compression wave in
Figure 3.27b and the expansion wave in Figure 3.27c at a location adjacent to the tip edge could be correlated to the aspiration pressure rise and drop, on either side of overambient peak in Figure 3.26, respectively. Similar behavior is also observed in the experimental aspiration and schlieren results shown in Figure 3.24 and Figure 3.20, respectively.

In the numerical calculation at 7.58 MPa (1100 psi), the dominating flow feature represented the expansion wave of the first Prandtl-Meyer wave, analogous to region 11 of Figure 2.11c. This flow feature continued the lowering of the aspiration base pressure that started at around 4.83 MPa. Even though the computation results reported in Figure 3.26 and Figure 3.27 do not model the discrete-jet converging-diverging HPGA-II nozzle in its geometry, nevertheless, the numerical flow field results have demonstrated the strong influence of localized gas flow features on the aspiration base pressure curve.

3.5 Conclusions

The schlieren images confirm that operation of the HPGA-II jet assembly produces a tightly organized collection of individual gas flow streams that merge downstream in a highly streamlined pattern. The aerodynamically designed discrete CDJ has been demonstrated to be effective at producing efficient and uniform supersonic velocity gas such that the entire gas curtain around the periphery of the melt tip, as shown in Figure 3.34, will be closely coupled to the melt for efficient and uniform atomization. The benefit of having HPGA-II generating

(a) HPGA-I discrete jet position

(b) HPGA-II discrete jet position

Figure 3.34. Schematic representation of an unfolded gas flowfield around the circumferential edge of the melt-tube for (a) HPGA-I and (b) HPGA-II nozzles (reproduced from Ting et al. [109]).
uniform supersonic gas velocity, by using CDJs, is that the gas flowfield has a uniform kinetic energy to aid in producing finer powders with a narrow powder size distribution. The HPGA-I nozzle operating at the same pressures with argon gas showed patterns that have a tangled appearance to the collected jets and a more disorganized downstream confluence region. A simple comparison of the gas flow patterns at comparable operating pressures reveals the extensive interference of the jets of the HPGA-I nozzle compared to the HPGA-II nozzle. The flow patterns suggest that the HPGA-II nozzle would have a higher and more consistent shear flow energy available for efficient atomization in the near-exit region where primary atomization occurs.

The benefit of using CDJ is seen in the particle refinement study. The HPGA-II nozzle was demonstrated to be efficient in generating fine powers at lower operating pressures than HPGA-I. We have shown this by comparing the surface area generated per unit mass of gas. This study demonstrated that HPGA-II is slightly more efficient than HPGA-I; and HPGA-I is almost three times more efficient than a commercially available annular slit nozzle, see Table 3.1. Unfortunately we are unable to use the full potential atomization efficiency of the HPGA-II nozzle by using the full kinetic energy of the atomizing gas flow field. In other words, the lack of subambient aspiration for the condition of matching apex angles of the jets and the melt tip, see Figure 3.28, prevents stable atomization at the highest kinetic energy. Therefore, we expect by further research and modification of the HPG nozzle using CDJs, we can expect finer particle size distribution than what we have observed so far in this report.

This study has also demonstrated that understanding of the gas flow features of an atomization nozzle can guide the design of a melt tip for generating subambient base pressure in an HPGA nozzle. Particularly, in confined-feed gas atomization, subambient base pressure plays a critical role promoting stable melt feeding by generating a compatible gas recirculation region at the base of the melt tip. A suitable melt tip length can be estimated by observation of the relevant gas flow features of an individual convergent-divergent micro-jet. Basically, if a strong expansion flow feature is found adjacent to the corner of the melt tip, a drop in base pressure, possibly subambient, can be predicted. In close-coupled gas atomization, the magnitude of the pressure gradient that drives the radially flowing gas along the base of the melt tip determines the strength of the recirculation. The results in this thesis showed that a low static pressure region is created on the periphery of the melt tip when the melt tip’s corner experiences a Prandtl-Meyer expansion wave. This low static pressure will reduce the aspiration base pressure by setting-up a radial pressure gradient that favors a velocity flow from the melt orifice radially to the periphery. An undesirable overambient gas flow field is
one where the melt tip periphery experiences a strong compression wave producing a high static pressure that can reverse the radial flow direction and can cause melt backstreaming.

For a desired operating pressure level, a tip length can be selected to place an expansion feature at the proper position. The melt tip length can influence the static base pressure by being located in the PM expansion or compression region. As the melt tip length changes from length 1 to 3 in Figure 3.35 (in matching condition), the static pressure of the gas stream would change from high static pressure to low static pressure and back to high static pressure. Further evidence of this design principle is provided by computational modeling given in section 3.3.4. This indicates the length of the melt tip has to be selected with careful consideration to the gas flow features. Therefore, an important consideration in designing the melt tip geometry is to allow for a strong Prandtl-Meyer expansion wave at the melt tip periphery within the most desirable range of atomization gas supply pressure.

This study showed that the HPGA-II nozzle having a melt tip with an apex angle of 45° and a melt tip length of 2.286 mm (0.090 inches), creates an overambient base pressure over most operating pressures. However it is possible to generate subambient base pressure at the expense of the kinetic energy by using a 22° melt tip (Figure 3.22). Compared to what can be attained by using a matching 45° melt tip, at 3.61 MPa (523 psi), the disadvantage of using the 22° melt tip is a loss of approximately 28% of the maximum available kinetic energy (Figure 3.28). Therefore, an improved design strategy was needed to maximize the available gas kinetic energy, while sustaining subambient base pressures. The strategy involved design changes in both melt tip length and in jet apex angle. As a starting point, some insight was acquired about how static aspiration pressure is generated in a confined-feed HPGA atomizer. This design concept is presented in the next chapter.
Figure 3.35. Schematic showing the location of 3 different melt tips and the location of the melt tip peripheries in the gas flow features emanating from a CDJ in an HPGA assembly.
CHAPTER 4. A DESIGN CONCEPT FOR GAS ATOMIZATION NOZZLES

A design concept was required to enhance understanding of the melt orifice aspiration phenomenon for close-coupled gas atomization nozzles to enable further development of converging-diverging designed discrete jets to their full performance limits. In the former sections we found that a highly efficient HPGA-II nozzle using a matching 45° melt tip created an over-ambient aspiration that rendered the nozzle inoperable. In order to achieve aspiration and gas atomization stability, a mismatched 22° melt tip was used with the HPGA-II nozzle, but the gas atomization efficiency was reduced and the full potential of the gas kinetic energy was not used.

In order to understand the aspiration phenomenon it is necessary to focus on the gas dynamics occurring in the recirculation zone in which the melt orifice resides. The first step is to represent the recirculation zone using a control volume analysis. This volume will permit us to model the events in the recirculation zone isolating it from the surrounding gas flow fields. The boundary of the control volume is delineated by the physical melt tip base at the top, high shear flow side walls, and a stagnation wake front located at the apex of the control volume, to the bottom, as shown in Figure 4.1. Small turbulent eddies can be generated along the high shear walls to accommodate the velocity mismatch with the merged supersonic gas streams outside the borders of the control volume. In this design concept, we will assume that the turbulent eddies contribute little influence on the aspiration pressure, since the circular vortex of an eddy can be seen as providing an equal exchange of gas in and out of the control volume across a boundary. In general, gas enters the control volume primarily through the stagnation wake front and exits along the peripheral edge of the melt tip base.

Control volume modeling of the recirculation wake permits us to account for all the gas entering and leaving the volume. Because aspiration base pressure is a measure of gas pressure acting against the melt orifice area, it could be assumed that the aspiration base pressure could be decreased by reducing the amount of gas circulating in the control volume. When more gas exits the control volume than enters it, a subambient aspiration base pressure can result.

In the HPGA-II nozzle that we have studied, two dominant parameters appear to regulate the pressure in the recirculation zone. These two dominant parameters are: 1) the gas flow features located adjacent to the edge of the melt tip; and 2) the impinging angle of the discrete jets. The angle is usually predetermined at the early stages of the nozzle design and remains fixed during operation. As we will see later, proper design selection of the impinging angle is crucial to the performance of the nozzle.
Figure 4.1. This schematic shows the location of stagnation pressure at wake front in relation to the recirculation control volume (reproduced from Ting et al. [111]).

The first dominant parameter causing the aspiration phenomenon in our design concept is related to the gas flow features located within the supersonic gas flow outside of the control volume, adjacent to the edge of the melt tip. Gas flow features, such as Prandtl-Meyer (P-M) waves having deep subambient static pressure, will set up a pressure gradient within the control volume that favors a gas flow radially to the edge of the melt tip. This gradient draws gas out of the control volume, lowering aspiration base pressure. Our observations in previous sections support this concept. We were able to observe a decrease in the aspiration base pressure as a result of the melt tip edge experiencing a Prandtl-Meyer expansion wave. On the other hand, strong P-M compression waves having high over-ambient static pressure resulted in an increase of the aspiration base pressure. Therefore, an important consideration in designing the melt tip geometry for stable atomization is to promote formation of a strong Prandtl-Meyer expansion wave pattern at the edge of the melt tip.

The second dominant parameter dictating the melt orifice aspiration phenomenon that we propose is the discrete jet apex angle. The jet apex angle which is set when one designs a new nozzle, can modify the aspiration pressure by affecting the magnitude of the stagnation pressure at the wake front. When the jet apex angle is small, the stagnation pressure at the wake front should be reduced giving rise to lower aspiration pressure. This is because the
magnitude of the stagnation pressure at the wake front dictates the amount of recirculating gas entering the control volume (or recirculation zone). Using a simple geometrical approach illustrated in Figure 4.2, the magnitude of the radial pressure component, $P_{\text{radial}}$, at the stagnation wake front can be related to the free stream pressure, $P_f$, and jet apex angle, $\theta$, by the following relation:

$$P_{\text{radial}} = P_f \sin(\theta/2)$$  \hspace{1cm} 4.1

This equation assumes a direct relationship between pressure and velocity, such that the magnitude of the radial velocity component is a close analogy of the radial pressure component, $P_{\text{radial}}$.

Figure 4.2. This schematic shows the geometrical relationship between stagnation pressure at wake front and radial velocity component of the gas flow (reproduced from Ting et al. [111]).

4.1 Computer modelling

A systematic computer modelling was conducted using the annular-slit convergent-divergent HPGA-II geometry. In this computer study, the computational geometry of the apex angle of the annular-slit convergent-divergent jet and melt tip length (matched apex angle) are varied. The operational parameter, gas manifold pressure, is incrementally stepped from 0.688
to 7.57 MPa (100 psi to 1100 psi) at 0.163 MPa (200 psi) increments. A matrix of this study is shown in Table 4.1 below.

Aspiration base pressure, stagnation pressure and peripheral edge pressure measurements from the computer modelling are given in Table 4.2, Table 4.3, and Table 4.4 respectively. In the analysis of the data generated from the computer models, one has to be aware that some of the operating pressure conditions causes ‘wake-closure’ condition. This ‘wake-closure’ condition affects the shape of the recirculation zone, generally by reducing the recirculation length. In light of this affect, data generated from wake-closure will be removed from the analysis. This is done, because, any alteration of the recirculation zone by ‘wake-closure’ will add unnecessary complexity to our understanding of the effective influence that jet apex angle has on the recirculation zone.

Table 4.1. Annular-slit convergent-divergent HPGA-II geometries used in the computation modelling study.

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<th>Melt tip length (mm)</th>
<th>Melt tip apex angle</th>
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X: Computer modelling was conducted at this given geometry.

Table 4.2. Calculated aspiration pressures (kPa) of the annular-slit convergent divergent HPGA-II nozzle with different geometry.

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<table>
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Table 4.2. (continued).

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Table 4.3. Calculated stagnation pressures (kPa) of the annular-slit convergent divergent HPGA-II nozzle with different geometry.

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Figure 4.3 shows a plot of aspiration base pressure versus edge pressure from the computer simulation data, Table 4.2 versus Table 4.4, one observes a distinct correlation between the aspiration base pressures and the edge pressures. The edge pressure is apparently determined by the gas flow feature at the periphery of the melt tip. This result is in agreement with the experimental observations and design concept described in the previous section, that showed the gas exits the control volume via the periphery of the melt tip. The edge pressure is determined by the static pressure of the gas feature at the melt tip periphery, causing the gas to flow radially from the melt orifice out towards the periphery of the melt tip. Therefore there is relative linear relationship in the two pressure shown in Figure 4.3, for 182 data points. Never the less, this correlation tells us that the aspiration base pressure is distinctly correlated to the gas flow feature located at the periphery of the melt tip.

From computer simulation results in Table 4.3, we observed a general trend between the stagnation wake front pressure and jet apex angle (Figure 4.4) for C-D annular slit HPGA-II nozzles. This relationship shows that the magnitude of the stagnation pressure decreases with decreasing jet apex angle. The stagnation pressure at the wake front can directly influence recirculating gas feeding into the recirculation zone, i.e., high stagnation pressure at the wake front will tend to raise the aspiration base pressure near the melt tip orifice.

![Figure 4.3. Plot showing the relationship between static pressure at the edge of the melt tip and melt orifice aspiration.](image-url)
These computer simulation results have shown considerable agreement to the proposed design concept for a close-coupled convergent-divergent discrete-jet HPGA nozzle. This design concept presents two important parameters influencing the aspiration base pressure. These are: (1) the gas flow feature located at the periphery of the melt tip edge, and (2) the designed jet apex angle of the nozzle. Therefore, it is essential to give strong considerations to the design of the apex angle and to the operation pressures of the nozzle. To take advantage of the high kinetic energy of the CDJs in the HPGA nozzle while generating subambient aspiration pressure for stable gas atomization, one would design the apex angle of the CDJs to be significantly less than that found in current the HPGA-II nozzle. A balance has to be made between reducing apex jet angle that lowers the aspiration by reducing stagnation pressure and maintaining sufficient pressure from the recirculation gas to film the liquid metal as it leaves the orifice. This balance will be achieved by changing the jet apex angle and the length of the melt tip away from the CDJ exits. This design concept was put into practice when a new HPGA nozzle known as the HPGA-III was built. This will be described in the next chapter.
CHAPTER 5. A NEW GAS ATOMIZATION NOZZLE

The need for a highly efficient gas atomization nozzle was the motivation for building the close-coupled HPGA-II nozzle that uses aerodynamically designed convergent-divergent discrete jets [109]. Although the HPGA-II nozzle was measurably more efficient than the HPGA-I nozzle, HPGA-II was unable to operate at its most efficient configuration. Instead, some of the gas kinetic energy of the HPGA-II had to be sacrificed to ensure stable melt orifice aspiration during the atomization process.

A design concept was established to permit development of a C-D discrete jet HPGA nozzle with high kinetic energy transfer capability. This has led to the design of a new gas atomization nozzle, named HPGA-III. The HPGA-III nozzle has 18 discrete C-D jets, positioned at a greatly reduced apex angle compared to that of its predecessor, the HPGA-II nozzle. The reduced apex angle was intended to generate subambient base pressure adjacent to the melt discharge orifice for stable gas atomization. This new design should permit the nozzle to utilize the full kinetic energy of the supersonic gas by allowing matching or near-matching of the apex angles of the C-D jets and the melt tip. In addition, an improved discrete C-D design was used that accommodates boundary layer formation within the divergent section of the jets [110]. This will greatly enhance the ability of the discrete C-D jet to accelerate the gas to supersonic velocity, compared to the HPGA-II jets.

A major feature of the new HPGA-III design is that it has a jet apex angle of 22.5 degrees (see Figure 5.1). Also, an enlarged exit diameter was introduced to the new C-D jet design to accommodate for the boundary layer formed in the divergent section of the jet [110]. The throat and exit diameters of the C-D jets for the HPGA-III nozzle are 0.737 and 1.80 mm (0.029 and 0.071 inches), respectively. The contour of the CDJ in HPGA-III is shown in Figure 5.2. The C-D jet was designed for nitrogen gas using the method of characteristics described in the previous section. The calculated isentropic designed pressure was 5.87 MPa (853 psi). At this calculated pressure, the C-D jet should accelerate the gas to Mach 3.31. However, the actual designed operating pressure should be closer to 3.96 MPa (575 psi) after accommodating for exit area loss due to boundary layer formation [110]. At this designed operating pressure the gas should accelerate to a calculated gas velocity to Mach 3.16, slightly greater than the designed gas velocity of the HPGA-II nozzle.
Figure 5.1. Schematic showing the geometry of the HPGA-III nozzle, fitted with a matching taper angle melt pour tube tip.

Figure 5.2. Contour of the divergent section of the CDJ used in the HPGA-III nozzle.
5.1 Materials and Methods

Schlieren images of the individual new CDJ design and static pressure measurements of the full HPGA-III nozzle were studied. The experimental set up for schlieren imaging and the static pressure were described in previous section.

In the static aspiration pressure measurements of the complete HPGA-III nozzle, several matching melt tip lengths were measured. The melt tips studied were 5.08 mm (0.200 inches), 3.81 mm (0.150 inches), 2.54 mm (0.100 inches) and 1.27 mm (0.050 inches) in length, with a 22.5° apex angle.

This particle refinement study was used to examine the improved HPGA-III nozzle performance in atomization yields compared to that of the HPGA-II nozzle. A four kilogram charge of 316L stainless steel was atomized for each experiment using ultra pure nitrogen gas supplied to the atomization nozzle at the same regulated pressure of 3.13 MPa (450 psi) for both the HPGA-II and the HPGA-III nozzles. Each charge was superheated to 1650°C prior to the atomizing run. The atomized powder was collected from each run, screened to less than 106 μm, and measured with a laser light scattering particle size analyzer to obtain the particle size distribution.

Originally the HPGA-II nozzle was designed for argon. By using nitrogen gas, this shifted the designed pressure for the CDJ to 2.32 MPa (337 psi) and the designed velocity to be Mach 2.69. Thus, the HPGA-II nozzle was operated above designed condition for nitrogen. For HPGA-III, the atomization pressure was lower than the experimentally determined design pressure of 3.96 MPa (575 psi). Although both nozzles were operated off-design pressures, 3.13 MPa (450 psi) was chosen for these comparative experiments to correspond to common commercial practice for nitrogen atomization of this alloy.

5.2 Results

5.2.1 Schlieren Imaging

Selected schlieren images of the gas-only flow pattern of an individual discrete jet of the new C-D design are shown in Figure 5.3, over a range of atomization gas manifold pressures from 0.689 to 8.963 MPa (100 to 1300 psi). We found that operating the individual CDJ of the HPGA-III design at a manifold pressure between 3.44 and 4.47 MPa (500 and 650 psi) produced images of the gas flow that were essentially devoid of oblique shocks and expansion waves, Figure 5.3. Therefore, the design pressure for the new C-D jet was experimentally determined to be about 3.96 MPa (575 psi), at the center this pressure range.

The schlieren image of the full HPGA-III nozzle showed a strong laminar flow pattern over an extended distance, similar to that observed for the HPGA-II nozzle (see Figure 5.4).
Figure 5.3. Schlieren images of a single CDJ, designed for HPGA-III, operated at nitrogen inlet pressures of a) 2.58 MPa (375 psi), b) 3.96 MPa (575 psi), and c) 6.19 MPa (900 psi). The white bar denotes the width of the CDJ exit (reproduced from Ting et al. [111]).
Figure 5.4. Schlieren images of the HPGA-III nozzle operating at (a) 3.09 MPa (450 psi), (b) 4.13 MPa (600 psi), and (c) 6.88 MPa (1000 psi) manifold pressure.
Figure 5.4. (continued).
In addition, from the schlieren images, the total inclusive apex angle of the gas emanating from HPGA-III is 22 degrees approximately. This demonstrated that the CDJ expanded the gas within the divergent section before it exited the jet. Therefore the gas flowed parallel to the matching melt tip without external gas expansion as observed in the HPGA-I nozzle (see Figure 3.15).

5.2.2 Static Pressure Tests

Static aspiration pressure measurements for the full HPGA-III nozzle are shown in Figure 5.5 for selected lengths of a matching 22.5 degree melt tip. When the melt tip length was 5.08 mm (0.200 inches) the aspiration base pressure fluctuated around atmospheric pressure. As the melt tip length is shortened, the aspiration pressure became steadier and subambient in pressure. At a melt tip length of 1.27 mm (0.050 inches), a highly stable subambient aspiration plateau of 90 kPa (13.1 psig) was measured. As Figure 5.5c reveals, this stable aspiration plateau was observed over a wide pressure range from 1.7 to at least 7.6 MPa (250 to 1100 psi).

5.2.3 Particle Refinement Study

In the powder size refinement study, gas atomization of 316L stainless steel was carried out using the HPGA-III nozzle. A matching melt tip apex angle of 22.5 degrees and a melt tip length of 1.27 mm (0.050 inches) was used. This configuration was identical to the setup nozzle [109] and a longer melt tip was used [109]. The atomized 316L stainless steel powders were pre-screened to less than 106 μm to eliminate non-regular particles (see Figure 5.6).

By comparing the weight percentage at the average particle diameter, d₉₀, the powder particles produced by the HPGA-III nozzle are finer than powder particles produced using the HPGA-II nozzle. For the HPGA-II nozzle, about 50 wt.% of the particles were less than 42 μm in diameter, while the HPGA-III nozzle had a d₉₀ of 35 μm. The melt flow rate was observed to be 8 kilograms per minute (17.6 pounds per minute) for the trials of both nozzles. A complete summary of the comparative results is found in Table 5.1. It should be noted that in addition to a finer d₉₀, the HPGA-III nozzle also exhibited a further improvement in efficiency.

5.3 Discussion

5.3.1 Schlieren Imaging

The design pressure for the new C-D jet was experimentally determined to be about 3.96 MPa (575 psi), between 3.44 and 4.47 MPa (500 and 650 psi), where the images of the
Figure 5.5. Aspiration curve for HPGA-III with matching melt tip that has melt tip lengths of a) 5.08 mm (0.200 inches), b) 2.54 mm (0.100 inches), and c) 1.27 mm (0.050 inches) (reproduced from Ting et al. [110]).
Figure 5.6  Particle size distribution of atomized 316L stainless steel using HPGA-II and HPGA-III nozzles (reproduced from Ting et al. [11]).

Table 5.1. Particle refinement results for 316L stainless steel

<table>
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<tr>
<th>Atomizer nozzles</th>
<th>Atomization pressure (MPa)</th>
<th>Average Gas/Melt ratio (kg_gas/kg_metal)</th>
<th>Mean particle diameter, (μm, d_μ)</th>
<th>Standard deviation (d_μ/d_μ)</th>
<th>Calculated surface area per cc of powder (m²/cc)</th>
<th>Efficiency: Surface Area produced per kg of gas (m²/kg_metal)*</th>
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</tr>
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* Formula for efficiency calculation can be found elsewhere [108,109]

gas flow were essentially devoid of oblique shocks and expansion waves, Figure 5.3. This agreed well with our expectations from the design parameters. We were able to accommodate the formation of the boundary layer inside the divergent section of the jet and thereby, to build a C-D jet with the expected design performance.

The schlieren images of HPGA-III (see Figure 5.4) showed a highly organized and uniform gas flow field such that the formation of the oblique shocks are readily distinguished among the adjacent discrete jets as dark bands across the unified flow field. This formation of oblique and P-M shock waves are an indication that the CDJs are uniformly pressurized in the manifold. This enabled the HPGA-III to produce uniform gas flow field around the melt tip compared to the non-uniform flow field exhibited by the annular-slit convergent-divergent
HPGA-II design (see Figure 3.20). This observation demonstrates that using the discrete CDJ design reduces gas consumption compared to annular-slit design in HPGA nozzle, thus allowing for the manifold to pressurize evenly, giving a uniformed and predictable gas flow field around the melt tip.

5.3.2 Static Pressure Tests

Both C-D discrete jet nozzles, HPGA-II and HPGA-III, have similar aerodynamic designs. The main distinction between the two nozzles is in their jet apex angles. The HPGA-II nozzle has a 45 degree jet apex angle while the HPGA-III nozzle has 22.5 degree jet apex angle. As predicted by the design concept, when both nozzles have matching melt tip configurations, the aspiration pressure for HPGA-III was found to be far lower than that for the HPGA-II nozzle over the full range of atomization gas supply manifold pressures. This can be revealed by comparing the 45 degree melt tip result for HPGA-II in Figure 3.21 to any of the three results in Figure 5.5 for HPGA-III. Both nozzles experience a peak over ambient aspiration pressure (a back-pressure condition) occurring at around 5.5 MPa (800 psi) when comparing the same melt tip lengths of 5.08 mm, i.e., Figure 5.5 and Figure 3.22 (45° case). Our computational modelling indicates that this is caused by the influence of a P-M compression wave at the melt tip edge in both cases. With a reduced jet apex angle, as in the HPGA-III nozzle, our geometric analysis of Eq. 4.1 (in Chapter 4) shows that the stagnation pressure at the wake front is also reduced by 49% compared to HPGA-II nozzle. This change would give an overall decrease in the amount of recirculation gas entering the control volume by half. Both of these influences on the recirculation in the control volume would promote a reduced base pressure at the melt orifice in the HPGA-III case, consistent with these results.

At atomization gas supply pressures between 0 and 5.5 MPa (0 to 800 psi), the aspiration curve for HPGA-II (Figure 3.22) with a matching melt tip of 45 degrees shows a steady increase in over-ambient aspiration base pressure. The steady increase in the aspiration pressure can be attributed, according to the design concept discussion, to the increase in the stagnation pressure at the wake front as operating pressure increases. A reduced stagnation pressure at the wake front in the new HPGA-III nozzle, with the same melt tip length (Figure 5.5a) allows one to observe the fluctuating aspiration pressure over the same range of gas inlet pressures. In other words, the masking effect of a large stagnation pressure effect is suppressed in the HPGA-III. In accordance with our previous studies [110], the fluctuations are attributed to the gas flow features that pass adjacent to the edge of the melt tip. We have previously demonstrated that Prandtl-Mayer expansion and compression waves significantly
influence the aspiration pressure because the Prandtl-Meyer expansion and compression waves are composed of subambient and overambient static pressure regions, respectively.

A matching 22.5 degree melt tip with a length of 1.25 mm (0.050 inches), reported in Figure 5.5c, was determined to provide the most stable aspiration pressure for the HPGA-III nozzle. A plateau of subambient aspiration pressure is created over a broad range of operating pressures. This can be explained by the two dominant factors put forth by the design concept. Both factors appear to play a complimentary role to form a subambient plateau pressure. The smaller C-D jet apex angle of the HPGA-III nozzle reduces the stagnation pressure, and aspiration pressure, by lowering the amount of gas entering the control volume. The shorter melt tip in HPGA-III also assures the constant presence of a strong Prandtl-Meyer expansion wave adjacent to the melt tip which pulls gas out of the control volume.

Frequently, melt aspiration that fluctuates with changes in the operating pressure can alter the melt flow rate of the gas atomization nozzles, introducing additional uncertainty into the control of the atomization process. With the HPGA-III nozzle, an aspiration base pressure plateau can be achieved by using a shorter melt tip length. The subambient plateau pressure in the HPGA-III nozzle should maintain a stable melt aspiration effect over a wide range of gas inlet pressures. This may provide an advantage for particle size control because operating inlet gas pressures can be shifted radically, with the HPGA-III nozzle without causing a fluctuating melt flow rate affected by aspiration.

5.3.3 Particle Refinement Study

The powder refinement study demonstrated that the HPGA-III nozzle produced finer 316L stainless steel powder than the HPGA-II nozzle. This can be seen from the finer mean powder particle size, $d_{50}$, in Table 5.1. Also, from the gas atomization efficiency calculation, HPGA-III was moderately more efficient than HPGA-II. The atomization results showed a 40 wt.% yield of particles less than 25 μm for HPGA-III, giving a 10 wt.% increase in yield over that of HPGA-II. This efficiency can be attributed primarily to the ability of the HPGA-III nozzle to use the full kinetic energy of the C-D discrete jets by matching discrete jet and melt tip apex angles.

Gas atomization can be said to involve the transfer of gas kinetic energy into the creation of powder surface area during a particulate breakup process. In atomization, molten metal has to be deformed and disintegrated into fine droplets. From an energy viewpoint, the kinetic energy imparted by the atomization gas to the melt is dissipated in the breakup process to overcome the viscous forces of the melt that resist deformation and to overcome the surface energy barrier that resists free surface creation. Therefore the surface area per unit volume of
powder created during atomization can be used to evaluate the improved performance of the HPGA-III nozzle over the HPGA-II nozzle. From Table 5.1, the calculated surface area per cc of powder is 16.8% greater for HPGA-III compared to the HPGA-II atomization run of 316L stainless steel. Another measure of improved performance for HPGA-III is the reduced gas-to-melt mass flow ratio that can also be found in Table 5.1.

The observed $d_{50}$ for gas atomized Fe-Al-Si (Table 3.1) and 316L stainless steel (Table 5.1) using HPGA-II were 35 μm and 42 μm, respectively. Two explanation for this are possible. The most obvious reason of finer $d_{50}$ in argon atomized Fe-Al-Si compared to nitrogen atomized 316L is that argon atomization was conducted at 4.13 MPa, 25% higher pressure compared to nitrogen atomization at 3.10 MPa. The other not so obvious reasoning is that both materials are essentially made of an Fe-based alloy in composition, therefore the liquid property, such as viscosity, surface tension and density of the two materials should behave quite similar; although it is know [84] that silicon addition to Fe-base alloy can reduce its viscosity and surface tension force. This will attribute to a larger Weber number (see Eq 2.2) and thus create finer droplets during atomization.

5.4 Conclusions

We have used the design concept set forth in this dissertation to build a highly efficient HPGA-III gas atomization nozzle that has matching C-D jet and melt tip apex angles. The nozzle was designed to utilize the maximum available gas kinetic energy of the C-D discrete jets by avoiding the formation of oblique or normal shocks that can result from use of a mismatched melt tip. The HPGA-III was able to produce a stable subambient plateau-like aspiration pressure that should make the nozzle easy to tune to control particle size by directly varying operating pressure.

Using a comparison of surface area created during atomization, we have showed that the HPGA-III nozzle has improved performance over the HPGA-II nozzle by 16.8%. This result demonstrates that HPGA-III using matching jet and melt tip apex angles has improved surface area production, which is directly related to yield of fine particles.

A direct $d_{50}$ powder size comparison, showed gas atomization using the HPGA-III nozzle, at only 3.13 MPa inlet nitrogen pressure and 8 kg per minute melt flow, produced a 40 wt.% yield of less than 25 μm diameter stainless steel powder in a small scale trial using less than the full design pressure. More atomization experiments are needed with higher pressures and extended steady state operation to determine the potential benefits of coupling such high kinetic energy to the melt with the HPGA-III nozzle.
We have demonstrated the ability of producing a high yield of ultrafine powder efficiently and cost effectively, using the new HPGA-III technology. The necessity of producing high yield of ultrafine powders is essential to the development of an improved production process for AB$_3$ alloy particulate for battery applications. This will be discussed in Part II of this dissertation.
PART II. METAL HYDRIDE DEVELOPMENT
CHAPTER 6. LITERATURE REVIEW

After the oil crisis of 1974, the search for alternative energy sources sparked extensive research throughout the world. During this time, hydrogen was proposed as the most promising fuel for a clean and abundant combustion energy system, creating a need for light, compact and safe hydrogen storage methods. Thus, numerous researchers focused on hydrogen storage alloys such as LaNi₅-base alloys because these materials could store larger amounts of hydrogen (1000 cc/cc) per unit volume than liquid hydrogen (784 cc/cc at -273°C) and high pressure tanks (200 cc/cc at 200 ATM.). In addition, in the beginning of the 80’s, social change and consumerism spurred the development of rechargeable battery materials and technologies for producing nickel-cadmium batteries. This was largely driven by the demand and popularization for light and compact cordless portable electronics such as video cameras, cellular phones, lap-top computers, etc. As a result it created a demand for compact, high power, long cycle life and maintenance free rechargeable batteries. By 1990, 1.1 billion Ni-Cd cells were produced. This great demand for Ni-Cd batteries caused a serious shortage of cadmium and rapid rise in price because it was a by-product of zinc processing [94]. Indeed, cadmium has only 1/10 of the available ore deposits of cobalt and 1/100 of the available nickel and rare-earths ore deposits. In addition, the use of toxic Ni-Cd batteries brought about environmental concerns for the future, followed by legal regulation of cadmium in many countries [48].

As we move into the threshold of the new millennium, in the 1990’s, automobiles are one of the major sources of air pollution in urban areas [24]. As the air pollution in heavily populated areas becomes unbearable, the need for cleaner alternatives such as electrical vehicles (EV) will ensure the importance of continual development of rechargeable battery materials for the consumer markets, especially large prismatic cells for EVs. Current battery material in nickel/metal hydride (Ni/MH) rechargeable batteries, based on LaNi₅ alloys, especially small sealed cells for consumer electronics, are steadily replacing Ni/Cd batteries because of their extended rechargeable cycle life, absence of memory effects, enhanced energy storage capacity, and reduced environmental hazard, and also because the hydrogen storage material is recyclable. Thus today, the ABₓ intermetallic metal hydride (MH) compounds have become more than the simple hydrogen storage medium proposed in the 70’s. Rather ABₓ compounds have become promising candidates for rechargeable energy storage material in EV applications because of their ability to react rapidly and reversibly with large quantities of hydrogen at ambient temperature and moderate pressure [15,21,42,65,94].
However, the high performance negative electrode in Ni/MH rechargeable batteries must be constructed from a material which has to meet a number of specific requirements, which are difficult to realize. These are: 1) large hydrogen storage capacity or high hydrogen/metal ratio; 2) full capacity hydrogen absorption-desorption near room temperature, preferably between -25°C and +50°C, and at half ambient pressure; 3) physical and mechanical stability of the hydride; 4) good electrocatalytic activity and chemical stability in corrosive basic solutions; and 5) availability and low cost. The scientific and patent literature contains an extensive number of reports regarding different aspects of the crystal chemistry and hydrogen storage properties of numerous materials, concluding that rare earth intermetallic alloys [94] are preferred for cathode fabrication. However, Ni/MH battery technology is still lacking basic knowledge of how to enhance electrode performance and lower processing complexity and cost of MH powders. Advanced powder processing methods such as gas atomization have not been pursued for technology advancement of hydrogen storage alloys.

The current standard route for manufacturing the AB₅ battery materials utilizes the traditional cast and crush metallurgical techniques. This process involves melting and casting the material into an ingot, heat treating each ingot for several days to eliminate inhomogeneities, crushing the ingot by mechanical grinding, and further pulverizing through hydrogen cycling of the particulate materials. These procedures are laborious and represent a processing cost barrier to widespread commercialization of the Ni/MH batteries for vehicle applications.

Recently, rapid solidification processing (RSP) of LaNi₅ powders by high pressure gas atomization (HPGA) has been suggested as a means to suppress the inhomogeneity effects observed during conventional chill casting of LaNi₅ alloys [8,15]. The production of AB₅ powders directly, eliminating costly long homogenization anneal and grinding steps, may hence be facilitated. However, there is a need to develop an efficient HPGA nozzle that can produce high yields of ultrafine AB₅ powder from cheap inert gas, such as argon, instead of more expensive helium that is currently preferred for the recent atomization studies [9].

Using fine particles have the effective benefit by increasing both the activation rate and the final hydrogen storage content. This is because the smaller particles, which have a larger surface area, are in better contact with hydrogen and will absorb more hydrogen at a faster rate than larger particles [64]. In battery applications, Van Rijswick [119] analyzed the rate determining steps for a LaNi₅-base electrode, and concluded that hydrogen diffusion is the rate determining step for large particles, while charge transfer dominates for small particles. When a charging reaction is limited by the hydrogen diffusion process, hydrogen evolution occurs, reducing charging efficiency. In a prismatic cell, if the hydrogen is not consumed quickly, the gas released causes the electrolyte to dry-out, increasing the internal resistance of the battery
and limiting the cycle life of the cell. Therefore, a small powder size is desired for battery applications.

The higher rate of solidification in gas atomization, compared to ingot castings, is useful to obtain more homogeneous composition and fine powder with smaller grain size to achieve shorter diffusion paths for segregated elements during heat treatment. A rapidly solidified alloy processed by a melt spinning technique was reported by several researchers [75,93] to show an enhanced cycle life for a mischmetal-based AB₅ alloy, MmNi₃.₅Co₀.₇Al₀.₈ (Mm represents mischmetal), a lower decrepitation rate, and a flatter pressure plateau. This was attributed to smaller grain size. In a gas atomization study which produced spherical powders (30-40 µm) having small grain size (10 µm), a higher rate capacity and longer cycle life after a suitable heat treatment was observed, as compared to a sample prepared by a conventional induction melting and casting method [106]. An excessive solidification rate or other aggressive process may form amorphous alloys that are not desirable. Ikeya et al [44] showed that prolonged mechanical grinding of MmNi₃.₅Co₀.₇Al₀.₇ and cobalt powder produced an amorphous alloy with a decreased discharge capacity. Therefore, it seems that post-atomization heat treatment of the powders may be an inevitable processing step to achieve the full hydrogen capacity of the atomized alloys, especially in ultrafine gas atomized powders that may contain amorphous regions. Nevertheless, reducing segregation distance using the RSP of gas atomization is still desirable for the purpose of minimizing the processing time during heat treatment.

The desire to prolong cycle life and lower decrepitation rate has lead research into two areas of battery technology, surface treatment and bulk alloy design. A surface treatment using fluorine-containing aqueous solution has demonstrated great benefit for improved H₂ activation characteristics (initial hydriding reaction) in AB₅, AB₅, A₂B alloys. Fluorinated surface structures found in these alloys are reported to contribute to the long-term storability of the particles by protecting against oxidation or hydrolysis from air or water and poisoning from other impurities [63,64,124-126]. Recently, in bulk alloy design, a lot of attention has been given to a Sn-modified AB₅, LaNi₄.₇₅Sn₀.₂₅, as a candidate for energy storage material in the form of interstitial hydrogen. Tin-substituted LaNi₅ alloys were found to suffer negligible loss in capacity after 10,000 cycles in gas phase cycling [50]. Most current commercial applications utilize AB₅ alloys [128], usually of the type Mm(Ni,Co,Al,Mn)₅, containing typically 10 wt.% Co. Mm denotes mischmetal, a cost-effective mixture of the rare earths, with the presence of La, Ce, Pr and Nd. The large amount of Co (10 wt.% Co) insures a cycle life of approximately 1500 cycles, whereas those with only 7 wt.% normally hold for only approximately 75 cycles (these values refer to sealed cylindrical cells of AA size) [57]. The use
of cobalt in an AB₅ compound reduces corrosion in the alkaline battery environment, however, cobalt substitution reduces the hydrogen storage capacity, thus the energy storage capacity of the battery [118]. This commercial alloy composition may possess a reasonable cycle life, but increases the alloy cost because of the cobalt addition. To insure successful development and production of a cost effective AB₅ alloy, it is necessary to decrease, or completely remove Co without diminishing the cycle life and high rate capacity. It has been shown that gas atomized powders of tin modified LaNi₅, LaNi₄₅₀Sn₀₁₅, having a spherical shape and diameter of less than <25 μm, are resilient to hydride-induced cracking [9], a primary cause leading to material surface corrosion and reduction in battery performance [12,61,62,66,69,128]. This indicates that gas atomization processing, in addition to possible fluorine surface treatment, of a tin-modified hydrogen storage alloy, such as LaNi₄₅₀Sn₀₂₅, may represent a promising way to achieve the goal of complete removal of Co from the alloy while assure reasonable life cycle.

6.1 Properties and Related Microstructure Phases

The crystal structure of LaNi₅-based alloys and their hydrides have been studied extensively [21,77-79,94]. The LaNi₅ compounds exhibit the CaCu₅ crystal structure shown in Figure 6.1, a hexagonal space group P6/mmm [21]. The nickel atoms are found in two different sites, 2c site at \( z=0 \) [Ni(2c)] and 3g sites at \( z=1/2 \) [Ni(3g)]. Upon absorbing hydrogen, the LaNi₅ material first forms the \( \alpha \) solid solution phase LaNi₅H₀.₅ and begins to form the \( \beta \) hydride phase LaNi₅H₆ by absorbing more hydrogen at an isobaric pressure of two and a half atmospheres, at room temperature. The pressure-composition isotherm phase diagram is given in Figure 6.2. The generally accepted location of the hydrogen atoms in the LaNi₅Hₓ phase are in an octahedral and a tetrahedral sites. An octahedral site \( D(1) \) is composed of two La, two Ni(2c) and two Ni(3g) atoms. The tetrahedral site \( D(2) \) is composed of two La and two Ni(3g). The hydrogenated LaNi₅Hₓ alloy can store three H atoms at the \( D(1) \) sites and three H atoms at the \( D(2) \) sites. This causes both the a-axis and c-axis of the lattice to expand by about 7.5% (\( \Delta a/a \) and \( \Delta c/c \)), resulting in a total cell volume change (\( \Delta V \)) of 24.3%. The crystal lattice parameters of the CaCu₅-type hexagonal unit cells for the \( \alpha \) and \( \beta \) phases have been defined as: \( a=5.02, c=4.00 \) Å, and \( a=5.4 \) and \( c=4.3 \) Å, respectively. The large lattice expansion (24.3 vol.%) of LaNi₅ during hydrogen absorption-desorption cycling causes cracking of the brittle intermetallic alloy, damaging the protective surface layer and continuously forming oxides on the freshly exposed surfaces in a corrosive 6 KOH battery electrolyte. Lambert [50] has reported that during a 1000 cycles of gas absorption-desorption LaNi₅ 200μm powders were pulverized to fine powder averaging 2.6 μm in diameter. Lambert
[50] showed that partial substitution of cobalt for nickel resulted in a considerably more stable hydride electrode that is resilient to hydride fracture. This was a result of a reduction of the volume expansion on hydrogen absorption [118], i.e., the volume expansion ratio decreased from 24.3% for LaNi$_5$ to 15.1% for LaNi$_{2.5}$Co$_{2.5}$. The volume expansion ratio decreased especially in the c-axis from 7.5% for LaNi$_5$ to 2.1% for LaNi$_{2.5}$Co$_{2.5}$. The lattice expansion
along the c-axis is believed to have more influence on fracture because the alloys have a layered structure with an ABAB stacking sequence. The same anisotropic effect of lattice expansion accompanied by stability improvement was reported also for Si substitution for Ni [69].

Gas phase hydrogen absorption plateau pressure, however, remains one of the most important criterion for electrode alloy designs. This is because the plateau pressure obtained by gas method (Siervert's method) for LaNi$_{5-x}$M$_x$ (M= Cu, Cr, Mn, Al) electrodes showed excellent agreement with the electrochemical plateau pressure in battery half-cells [122]. Thus a direct correlation can be made. If the plateau pressure for hydrogen desorption is too high, the charging efficiency of hydrogen decreases, leading to lower storage capacity and hydrogen evolution. If La is replaced by smaller size mischmetal element such as Ce, Pr, Nd, or Sm, the cell volume decreases, causing an increase in the hydrogen plateau pressure. Since the usual mischmetal (Mm) is composed of La 20-30%, Ce 40-50%, Nd 10-20% and Pr 5-10%, MmNi$_5$ has a hydrogen pressure plateau higher by an order of magnitude compared to LaNi$_5$. An analysis of earlier work reveals that lanthanum is the principle element in the mischmetal that can reduce the hydrogen plateau pressure (see Figure 6.3). A summary of hydrogen plateau pressures versus composition of each element in the mischmetal, using data from Liu and Huston [58], showed that only increasing lanthanum fraction in the mischmetal decreased hydrogen plateau pressure. Other mischmetal elements increased hydrogen plateau pressure with increasing composition in the mischmetal. A high hydrogen plateau pressure can be lowered also by substituting the nickel element in AB$_3$ with specific transitional and non-transitional elements [28,70,71,102,118].

It was observed by Sakai et al [92] that substitution of the nickel element in AB$_3$ had not only lowered the hydrogen absorption pressure but had also increased the mechanical stability of the particle to resist fracture upon hydrogen absorption. This behavior is believed to be closely related to ductile properties of the LaNi$_5$-based alloys. Sakai et al [92] found that the decrepitation rate decreased with decreasing Vickers hardness in the order of M= Mn > Cu > Cr > Al > Co for LaNi$_{5-x}$M$_x$, thus increasing the cycle life of the alloys. The importance of mechanical properties is supported by the fact that such ductile metals a Pd and TiNi are not decrepitated during charging-discharging cycles [94].

For the practical use of AB$_3$ alloys in hydrogen absorption/desorption cyclic applications, any change in hydrogenation properties, or intrinsic microstructure degradation, may be a very important effect. Busch [20] and Sakai [94] have suggested that the intrinsic degradation of LaNi$_5$ could be due to microphase separation at the surfaces. This leads to the formation of a stable LaH$_2$ phase through the disproportionation reaction given below:

\[ \text{LaNi}_5 + H_2 \leftrightarrow \text{LaH}_2 + 5\text{Ni} \]
Figure 6.3. Individual rare earth from the mishmetal composition, (a) Cerium, (b) Lanthanum, (c) Praseodymium and (d) Neodymium, in MmNi_{x} alloys are plotted with respect to hydrogen absorption plateau pressure. The plots reveal Lanthanum to be the dominant influencing factor for lowering hydrogen absorption pressure [Data from Liu et al. [58]].
Other researchers have proposed that a disordering in the bulk of the hydriding particle changes the environment of the lattice for hydrogen occupation, which would result in permanent loss of the reversible hydrogen absorption capacity [23,37,95]. From a thermodynamic viewpoint, the disproportionation is reasonable because the hydrides of alternative La-Ni intermetallics are more stable than LaNi₅ hydrides. As shown in Figure 6.4, with increasing La/Ni ratio, the stability of these hydrides increases [20].

Alternatively, the stability of the hydride phase may be increased with increased cell volume of the alloy [22]. The nickel can be replaced by numerous transition metals and non-transition metals [28,70,71,102,118] to suppress the disproportionation of the intermetallic hydride during hydrogen cycling. The hydrogen absorption properties for many substituted intermetallics LaNi₅₋ₓMₓ, with both transition and non-transition metals, are reported in literature: with M replaced by Pt, Pd, Ag, Cu, Co, Fe, Cr, Ge, Si, Ga, B, Mn [71], Al [28,70], Sn, and In [70,71,102,118]. Percheron-Guegan et al. [81] reported that Al and Si replaced the Ni atoms only at the 3g sites, lowering the hydrogen plateau pressure.

Unfortunately, substitution for the Ni 3g sites also distorted the D(2) hydrogen occupation site causing a decrease in hydrogen storage capacity. Wasz et al. [127] showed that Sn substituted for Ni also at the 3g sites, and decreased the hydrogen storage capacity of the LaNi₅₋ₓSnₓ alloys. They reported that the storage capacity decreased linearly with increasing tin concentration, and attributed this decrease to increased occupation of 3d band by electrons donated by tin solutes [127], filling up holes where hydrogen would normally donate its electron [39].

Figure 6.4. Specific enthalpy of formation of La-Ni hydrides vs. intermetallic composition (reproduced from Busch et al. [20]).
Bucur and Lupu also noted that these substituted intermetallics have a hexagonal CaCu$_5$-type structure like the parent compound LaNi$_5$ and that the unit cell volume changes continuously with the substituent [19]. The change in the free energy per mole, $\Delta G$, of hydrogen desorbed from $\beta$ hydrides of LaNi$_{5-x}M_x$ systems at 313 K is plotted in Figure 6.5 against the fraction $x$ of nickel substituted. As can be seen in Figure 6.5, all the substituents, except for platinum and palladium, strengthen the metal-hydrogen bond compared to that observed for pure LaNi$_5$.

It was noted that 3d transition metals (except manganese) have a smaller effect than non-transition metal substituents [19]. In this proposed research, non-transition substituents of Sn and Si have been selected as the most promising candidates for gas atomization processing of modified AB$_5$ materials. Silicon and tin both belong to the non-transition Group IV elements, showing a large change in free energy of formation upon hydriding. The compositions of silicon and tin modified LaNi$_5$ will be determined by the necessary concentration of each element to lower the hydrogen absorption pressure to at least ambient pressure and preferably to half an atmosphere. The noticeable difference between silicon and tin is in their atomic radius, which may affect microphase segregation in the RSP. The benefit

![Figure 6.5. The dependence of the change $\Delta G$ in the free energy due to formation of the $\beta$ hydride on the concentration $x$ of the substituents in LaNi$_{5-x}M_x$ at 313K (reproduced from Bucur et al. [19])](image)
of using non-transition Group IV elements is in the steeper free energy slope of silicon and tin addition, which will enable the design of a more stable hydride with a minimum of alloying addition, which may otherwise diminish the hydrogen storage capacity of the AB\textsubscript{5} alloy.

It has been shown for some time that small additions of tin to LaNi\textsubscript{5} not only decrease the plateau pressure for hydrogen absorption, but also reduce the hysteresis in the pressure plateau for hydrogen absorption and desorption [70]. Tin most probably decreases the hydrogen plateau pressure by expanding the LaNi\textsubscript{5} lattice since plateau pressure has been shown to vary strongly with LaNi\textsubscript{5} unit-cell volume [70]. Lambert et al showed that tin-substituted LaNi\textsubscript{5} alloys suffer negligible losses in capacity after 10 000 cycles in a gas phase cycling [50]. This enhanced performance was attributed to preferential site occupation by the tin. The tin atom occupies only the 3g nickel sites in LaNi\textsubscript{5} [127], which blocks lanthanum migration in the hydride [37]. It has recently been determined that lanthanum migration is linked to the disproportionation of LaNi\textsubscript{5} to nickel and a LaH\textsubscript{x} phase that seems to arise after thermal cycling [14,42].

6.2 Tin and Silicon Modified LaNi\textsubscript{5} Phase Diagram

The first systematic study on the La-Ni phase diagram was done by Vogel [121]. Recently, a more complete phase diagram was presented by Zhang and Gschneidner (Figure 6.6) [130]. There are two eutectic reactions occurring at about 56 and 93 at.\% Ni and an unusually a large homogeneity region for LaNi\textsubscript{5} at high temperature. The Ni solubility limit for the intermetallic phase for the LaNi\textsubscript{x} region is temperature dependent [21], showing solubility range, x, of 4.85 to 5.40 at 1 200°C, 4.90 to 5.10 at 1100°C, and 4.95 - 5.05 at 1000°C.

No complete phase diagrams have been reported for either the La-Ni-Sn or La-Ni-Si systems. A partial phase diagram of La-Ni-Sn (Figure 6.7) by Wasz et al [127] shows a stoichiometric solubility of Sn in the LaNi\textsubscript{5}Sn\textsubscript{y} intermetallic compound, with the maximum tin solubility determined to be y=0.44. A similar ternary phase diagram can be assumed for the La-Ni-Si system by inferring from the Ce-Ni-Si ternary phase diagram [90] (Figure 6.8). In this study, hydrogen absorption properties will be correlated with the phases present in the La-Ni-Sn and La-Ni-Si microstructures. It is hoped that relationship can be found between the system phases and the hydrogen absorption capacity. This would then provide some guidance to explore heat treatment as an option for post-processing the as-atomized powders as a mean to achieve the desired hydrogen absorption capacity.
Figure 6.7. Schematic diagram of the nickel-rich corner of the La-Ni-Sn ternary phase diagram (modified from Wasz et al [127]).

Figure 6.8. Ce-Ni-Si composite isothermal section at 800°C (0-33 at.% Ce) and 400°C (33-100 at.% Ce) (reproduced from Rogl [90]).
CHAPTER 7. MATERIALS AND METHODS

7.1 Gas Atomization

Gas atomization was studied on the processing of the \( \text{AB}_5 \) (LaNi\(_5\)-based) alloy materials. Three stoichiometric and one off-stoichiometric \( \text{AB}_5 \) alloy compositions were studied in this thesis. Tin and silicon were used as substitutive elements for nickel in the LaNi\(_5\) alloy compositions. The gas atomization process is described in section 3.2.3. The gas atomization nozzle that was used in this study was HPGA-I. This nozzle was selected for the atomization runs over the HPGA-II and HPGA-III nozzles because of our extensive experience base and confidence in the reliability of the HPGA-I. The two atomization gases used in this study were helium and argon. It is expected that because of the significant difference in thermal properties between He and Ar, different rapid solidification behaviors may arise from atomization of the same alloy. The composition of the alloys and the atomization runs are given in Table 7.1.

<table>
<thead>
<tr>
<th>Atomization gas</th>
<th>Atomization pressure (MPa)</th>
<th>Sn modified LaNi(_5)</th>
<th>Si modified LaNi(_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>7.23</td>
<td>LaNi(<em>{4.75})Sn(</em>{0.25})</td>
<td>LaNi(<em>{4.6})Si(</em>{0.4})</td>
</tr>
<tr>
<td>Helium</td>
<td>5.51</td>
<td>LaNi(<em>{4.85})Sn(</em>{0.15})</td>
<td>LaNi(<em>{4.6})Si(</em>{0.4})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LaNi(<em>{4.75})Sn(</em>{0.25})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>LaNi(<em>{5.5})Sn(</em>{0.3})</td>
<td></td>
</tr>
</tbody>
</table>

An alloy charge of 4.5 kilogram was used for each gas atomization run. Each alloy was pre-cast at the Ames Laboratory Material Preparation Center. Each alloy was heated in an argon atmosphere from room temperature to 1560°C in a Norton alumina crucible (type An299, Alundum, 99.95% purity). The melt was then bottom-poured into a copper chill mold to form the ingot charge for atomization.

The HPGA-I nozzle can be used with either helium or argon gas because it was not aerodynamically designed for any specific gas. Helium and argon atomization runs were performed at 800 and 1050 psi respectively. The value for the helium atomization pressure was chosen to be the highest operation pressure that maintained a stable subambient aspiration pressure (see Figure 7.1). The gas atomized powders were classified into size fractions in an inert atmosphere glove-box to prevent surface oxidation of the powders that may retard hydrogen absorption.
7.2 Hydrogen Absorption Isotherms

A Sievert's apparatus (see Figure 7.2) was used to characterize the hydrogen storage capacity of the atomized AB₅ alloy powders. The experiment is performed under isothermal conditions. The stainless steel sample chamber that holds about 1.5 grams of powder material is immersed in a thermostatic bath to maintain constant temperature throughout the experiment. Coolant at 20°C is pumped around the sample chamber to absorb heat and maintain a uniform temperature in the sample bed. Data is taken after more than 5 times of repeated hydriding-dehydriding cycling at 20°C. The pressure change is measured by an electronic pressure transducer with a digital voltmeter.

The experimental procedure chosen for this study was the step-wise method that allows one to measure incremental hydrogen absorption, (Figure 7.3) [123]. The hydriding reaction proceeds from a starting higher pressure Pₒ to Pᵣ or from nₒ, a hydrogen concentration at the point where reaction was started, to nᵣ, the final concentration of the run. Pₒ is the initial pressure and Pᵣ is the final equilibrium pressure. The concentration nᵣ in turn becomes the next starting concentration. Each run can be continued by changing the pressure in the gas reservoir to a higher level than the equilibrium pressure of the previous run.

Most AB₅ alloy samples must be “activated” before reliable hydrogen absorption data can be measured. This normally means that the surface oxide of the sample has to be reduced to permit easy access for hydrogen in and out of the surface of the sample. The activation procedure begins with opening all valves and closing valve #1 and #2 (see Figure 7.2). This
Figure 7.2. Schematic diagram of the Sievert’s apparatus.

Figure 7.3. Schematic diagram showing the experimental procedures for determining the hydrogen absorption isotherm (reproduced from Wang et al. [123]).
evacuates the whole system to a baseline vacuum of 0.1 milli-torr. Then, the sample chamber is connected to valve #2 with a CAJON D-N-316 VCR nickel gasket having a nickel filter of 5 μm. This filter prevents the fine particles from back flowing and contaminating the Sievert's apparatus. Valve #2 is slowly opened to evacuate the sample chamber. The sample chamber is heated under vacuum up to 400°C using a resistance furnace made of chromel wire. Dwell time at 400°C is 5 minutes. This step drives away moisture by decomposing the La(OH)$_3$ into La$_2$O$_3$ and H$_2$O vapour. At 400°C, hydrogen is introduced into the reservoir chamber #1 by closing valves #2, #3 and #4 and opening #1 and #2. As the sample cools to room temperature, one can usually observe the onset of absorption as an abrupt drop in reservoir chamber pressure. After several hours, the stabilized hydrogen pressure is recorded. The above procedures are repeated 5 times to ensure full activation of the AB$_5$ alloy. Activation is complete when the difference in the stabilization pressures becomes less than 0.1 psi.

Hydrogen isotherm measurement of the powder is done only after activation of the sample is complete. This activation usually involves 5 complete saturation of hydrogen, during absorption, and desaturation of hydrogen, during desorption cycles. The hydrogen isotherm is measured at 20°C. The procedure to measure a hydrogen isotherm begins with pressurizing reservoir #1 to a chosen hydrogen pressure by opening valve #1 briefly, and closing valves #2, #3 and #4. Valve #2 is, then, opened to pressurize the sample chamber. The equilibrium pressure of the chamber pressure is recorded before the above procedures are repeated. The mass of absorbed hydrogen can be calculated from the pressure of hydrogen gas added into the chamber during each pressurization cycle by using the ideal gas law.

Surface poisoning with carbon monoxide can entrap hydrogen in the powder particles. This is done after the powder sample is saturated with hydrogen so that crystallographic lattice determination can be made using X-ray diffraction techniques, this will be discussed in a later section.

### 7.3 Rapid Heat Treatment

The desire to be able to utilize the as-atomized hydrogen-storage powder directly after atomization has fallen short of expectations. Previously, [15] annealing 4 hours at 950°C was shown to fully remove Sn-rich segregation phase at the cellular boundaries of the argon gas atomized LaNi$_{4.75}$Sn$_{0.25}$ sample. Therefore, post atomization heat treatment appear necessary to homogenize the composition of the gas atomized hydrogen-storage powder for optimum hydrogen sorption characteristics.

Post atomization annealing parameters of the powders were examined. This thesis expanded on Bowman's study [15] to examine what is the minimum annealing temperature and
time to fully homogenize gas atomized AB₅ alloy powders. The range of annealing temperatures were chosen between 650 to 950°C, having 50°C temperature increments. The dwell time at each annealing temperatures was 5 minutes.

Helium atomized LaNi₄.₈₃Sn₀.₁₅ was used in this rapid heat treatment study. This alloy was used primarily because, the helium atomization produced a high yield of ultrafine powders, about 84 weight percent of the powders are less than 22 μm, and that the hydrogen isotherm was known to be just below the ambient pressure. As will be shown later, powder particle size of less than 25 μm resisted hydrogen induced fracture. Thus atomized powders screened to less than 25 μm were used.

The LaNi₄.₈₃Sn₀.₁₅ powder was sealed in 5 mm diameter quartz tube with inert helium atmosphere. About 4 grams of LaNi₄.₈₃Sn₀.₁₅ powders were annealed at each targeted heat treating temperature. The quartz tube was placed into the furnace chamber for a total of 5 minutes, this included the transient time required to heat the sample from room temperature up to the target temperature. The transient time usually took 90 seconds. Immediately after heat treating the sample, the quartz tube was quenched in ice water to arrest further homogenization.

7.4 SEM Imaging

The typical metallographic techniques using scanning electron microscopy (SEM) and microprobe were used to examine the phase segregation in as-atomized powders of the different compositions. The SEM technique allows the fine detail in the solidification microstructure of the powders and the distribution of the segregation to be characterized. The compositional determination of the matrix and the segregated phase can be characterized by microprobe.

Secondary electron imaging (SEI) mode of the SEM was used to examine the powder surface morphology of as-atomized and hydrogen-cycled powders. Particulate fracture morphology was examined after hydrogen cycling was conducted on rapidly heat treated powders. The post heat treated samples were metallographically mounted for backscatter imaging technique using SEM.

7.5 X-Ray Powder Diffraction

X-ray diffraction (XRD) was the primary method that was used to examine the crystal structure of phase products resulting from rapid solidification of AB₅ alloys. The lattice spacing of the matrix phase was also determined using the diffraction patterns. XRD was utilized for structural characterization of the powder so as to determine a minimum annealing time required for particle homogenization.
An XRD spectrum analysis program was used to determine the lattice parameter of selected crystal structures in the atomized powders. This program was used instead of the Rietveld least-squares analysis because the typical atomized AB₅ alloy tended to have multiple phases of the same crystallographic structure. Rietveld least-squares is typically used for single phase crystal structure determination. This XRD spectrum analysis program determined lattice parameters by first determining the intensity, Bragg angle, and full width at half maximum of the diffraction peaks using Lorenzian and Gaussian fitting functions. Then, a minimizing function was imposed on the observed lattice spacing and calculated lattice spacing from the Bragg equation. From this the lattice parameters can be calculated providing one has prior knowledge of the crystallographic structure of the phase in question.
CHAPTER 8. RESULTS

8.1 Hydrogen Absorption Isotherm

The as-atomized alloy LaNi$_{4.85}$Sn$_{0.15}$ powders of less than 10 μm and 10 to 25 μm size ranges showed an elevated hydrogen absorption pressure of approximately 2 atmospheres at room temperature (see Figure 8.1). This result was an indication that the rapid cooling in the He gas atomization process was not rapid enough to quench in some tin inhomogeneities into the AB$_5$ alloy composition. After a 5 minute anneal at 900°C, the hydrogen absorption isotherm shifted to just below atmospheric pressure, as anticipated in fully annealed alloy powders of this composition. This indicated that rapidly solidified powder has segregated Sn-rich phases. Further evidence from SEM indicating Sn-rich segregation in as-atomized powder will be discussed later.

Hydrogen absorption-desorption behavior of the LaNi$_{4.79}$Sn$_{0.25}$ and LaNi$_{4.6}$Si$_{0.4}$ powders is shown in Figure 8.2 and 8.3, for both as-atomized and annealed powders. The as-atomized absorption data of a 38-45 μm LaNi$_{4.6}$Si$_{0.4}$ powder sample shows an overambient pressure trend in Figure 8.2, but the isotherm is almost flat at 1.9 ATM. Figure 8.2 shows the results for LaNi$_{4.6}$Si$_{0.4}$ powders and illustrates that an ideal plateau-like isotherm was achieved by only 5 minutes of annealing at 900°C. This is consistent with observations of LaNi$_{4.85}$Sn$_{0.15}$ annealing treatments. The as-atomized absorption and desorption data in Figure 8.3 for a 38 μm to 53 μm size range LaNi$_{4.75}$Sn$_{0.25}$ powder shows a subambient absorption and desorption

![Figure 8.1. Hydrogen absorption isotherm of LaNi$_{4.85}$Sn$_{0.15}$ powder of size range less than 25 μm (reproduced from Ting et al. [112]).](image-url)
Figure 8.2. Hydrogen absorption isotherm of LaNi$_{4.6}$Si$_{0.4}$ (reproduced from Ting et al. [112]).

Figure 8.3. Hydrogen absorption and desorption isotherm of LaNi$_{4.75}$Sn$_{0.25}$ (reproduced from Anderson et al. [9]).
trend, as desired, but has an enhanced slope [15]. Again, this suggests that the phase segregation in the solidification microstructure of the as-atomized powder provides more resistance to the transport and exchange of hydrogen [9]. Annealed LaNi$_{4.75}$Sn$_{0.25}$ powders produced by the HPGA method have gas phase hydrogen storage capacities and equilibrium pressures similar to materials prepared from annealed ingots [61].

The hydrogen absorption isotherm of a 900°C, 5 minute annealed, LaNi$_{5.5}$Sn$_{0.3}$ powder sample exhibits a plateau pressure below atmospheric (see Figure 8.4). The isotherm of this off-stoichiometric alloy was observed to rise above atmospheric pressure at around 4.5 H/AB$_5$. The stoichiometric alloy of LaNi$_{4.75}$Sn$_{0.25}$, with slightly less Sn rose above atmospheric pressure at around 5.5 H/AB$_5$. Both alloys have similar plateau pressure of about 0.45 atmospheres. It is typically expected [65], that alloys with higher tin composition, i.e., LaNi$_{5.5}$Sn$_{0.3}$ would have lower plateau pressure.

![Figure 8.4. Absorption isotherm of annealed LaNi$_{5.5}$Sn$_{0.3}$ along with isotherms of LaNi$_{4.85}$Sn$_{0.15}$ and LaNi$_{4.75}$Sn$_{0.25}$ from Figure 8.1 and 8.3 respectively.](image)

### 8.2 SEM Imaging

The gas atomized powders of Sn and Si-modified LaNi$_5$ are generally spherical in shape and have a fine cellular microstructure with a significant segregation of a second phase to the cellular boundary as determined by SEM. The fine scale, uniform solidified microstructure of Argon gas atomized LaNi$_{4.75}$Sn$_{0.25}$ powders consists of a cell interior phase that is depleted in Sn, and a cell boundary phase that is enriched in Sn, compared to their nominal
compositions (see Figure 8.5. Similar observations were seen for LaNi$_{4.85}$Sn$_{0.15}$ (see Figure 8.6) and for LaNi$_{4.75}$Sn$_{0.3}$ (see Figure 8.7).

Electron microprobe of a cross-section of a LaNi$_{4.75}$Sn$_{0.25}$ powder particle provided a semi-quantitative characterization of the effect that annealing has on the Sn- segregation in Sn-modified AB$_5$ (see Figure 8.8). This is consistent with the fact that excess Sn solute is rejected during the RS process of gas atomization with both Ar and He, in spite of the difference in cooling rate. Microprobe results on an unannealed Ar-atomized LaNi$_{4.75}$Sn$_{0.25}$ particle showed the Sn varied in an opposite manner to Ni and La compositions (Figure 8.8). Results on an annealed particle of this alloy, given in Figure 8.9, indicate that high temperature diffusion at 950°C for 4 hours produced a homogeneous composition across the full particle diameter.

Similar SEM microphase segregation was observed in helium and argon as-atomized LaNi$_{4.6}$Si$_{0.4}$ powders as was noted for LaNi$_{4.75}$Sn$_{0.25}$. As-atomized LaNi$_{4.6}$Si$_{0.4}$ powders consist of a cell interior phase that is depleted of Si, and a cell boundary phase that is enriched in Si, compared to the nominal composition (see Figure 8.10). Electron microprobe of the LaNi$_{4.6}$Si$_{0.4}$ particle microstructure cross-sections provided a semi-quantitative characterization of the phase segregation effect (see Figure 8.11), showing that Si and Ni varied together and in an opposite manner to the lanthanum content. This result differs from La(Ni,Sn)$_5$ alloys, where the modifying element Sn varied opposite to nickel composition. The observed composition variation between the two alloys will be discussed in later sections.

Particle surface morphology of annealed LaNi$_{4.6}$Si$_{0.4}$, LaNi$_{4.85}$Sn$_{0.15}$ and LaNi$_{4.75}$Sn$_{0.25}$ was examined using SEM after at least 5 repeated hydrogen charge-discharge cycles. Secondary electron SEM imaging of the particle surface shows that annealed LaNi$_{4.75}$Sn$_{0.25}$ particle of 38 to 53 μm size range fracture intragranularly as indicated by the cleavage mode fracture, as shown in Figure 8.12b, while particles of less than 10 μm were not affected (Figure 8.12a). Similar observations were made for annealed LaNi$_{4.6}$Si$_{0.4}$ particles. It showed intragranular cleavage mode fracture to be the fracture mechanism in the two alloy compositions. Particles of 5 μm to 10 μm size range were resilient to fracturing during hydrogen cycling and retained their spherical powder morphology, as shown in Figure 8.13a; while particles of 38 μm to 45 μm showed significantly less fracturing (Figure 8.13b) as those observed in LaNi$_{4.75}$Sn$_{0.25}$ (Figure 8.12b). A more extensive study was performed on the as-atomized LaNi$_{4.85}$Sn$_{0.15}$ alloy composition, where the upper size limit of particles that resisted fracture upon hydrogen cycling was around 25μm (see Figure 8.14). Surface morphology of hydrogen cycled particles using SEI shows fracture on the particle surface occurred (see, Figure 8.15) across the grain, verifying intragranular fracture.
Figure 8.5. Backscatter SEM micrographs of Ar as-atomized LaNi$_{4.75}$Sn$_{0.25}$ of a) 38 μm to 53 μm and b) less than 10 μm particles.
Figure 8.6. Backscatter SEM micrographs of Ar as-atomized LaNi$_{4.85}$Sn$_{0.15}$ of (a) 10 to 25 μm and (b) less than 10 μm particles.
Figure 8.7. Backscatter SEM micrographs of Ar as-atomized LaNi$_{5.5}$Sn$_{0.3}$ of (a) less than 25 μm and (b) 38 to 53 μm particles.
Figure 8.8. Electron microprobe of argon as-atomized LaNi$_{4.75}$Sn$_{0.25}$ powders of size ranging from 38 - 53 µm. Arrowhead lines show nominal composition of the alloy.

Figure 8.9. Electron microprobe of heat-treated LaNi$_{4.75}$Sn$_{0.25}$ powders (Ar atomized) of size ranging from 38 - 53 µm. The sample was heat treated for 4 hours at 950°C. Arrowhead lines show nominal composition of the alloy.
Figure 8.10. Backscatter SEM micrographs of Ar as-atomized LaNi$_{4.8}$Si$_{0.4}$ of a) 38 to 53 μm and b) 5 to 10 μm particles.
Figure 8.11. Electron microprobe of argon as-atomized LaNi$_{4.6}$Si$_{0.4}$ powders of size ranging from 106 - 150 µm. Arrowhead lines show nominal composition of the alloy.
Figure 8.12. Secondary electron imaging of powders samples annealed 4 hours at 950°C of LaNi$_{4.75}$Sn$_{0.25}$ (Ar-atomized), having hydrogen cycled 5 times, (a) less than 10 μm and (b) 38-45 μm size particles.
Figure 8.13. Secondary electron imaging of powder samples annealed 5 minutes at 900°C of LaNi$_{4.8}$Si$_{0.4}$ (Ar-atomized), having hydrogen cycled 5 times. (a) 5 to 10 μm and (b) 38 to 45 μm in particle size.
cycled 5 times, (a) less than 10 μm, (b) 10 to 25 μm, and (c) 25 to 38 μm size particles.

Figure 8.14. Secondary electron imaging of as-grown, LANT®-SN 15, Sn 15% having hydrogen.
Figure 8.14. (continued).
Figure 8.15. Secondary electron imaging of the particle surface showing intragranular cracking in (a) LaNi$_{4.5}$Sn$_{0.15}$ of 25 to 38 µm annealed at 850°C for 30 minutes and (b) LaNi$_{4.5}$Si$_{0.4}$ of 38 to 45 µm annealed at 900°C for 5 minutes.
Backscatter electron imaging of 5 minutes heat treated $\text{LaNi}_{4.89}\text{Sn}_{0.15}$ showed diminishing cellular boundary phase as temperature increase from 650 to 950°C (see Figure 8.16). The cellular boundary phase almost completely disappeared in the 5 minutes, 950°C heat treated powders. The disappearance of the light coloured cellular boundary phase is shown to be replaced by a dark coloured secondary phase dispersed primarily where the prior cellular boundary phase existed. Even though this alloy had stoichiometric AB$_5$ composition, using EDS the second phase was determined to be nickel with tin in solid solution. This finding was verified by XRD and it will be discussed in a later section.

LaNi$_{5.5}$Sn$_{0.3}$ powder having 5 minutes of heat treatment at 900°C, indicated significant nickel-tin solid solution phase along the cellular boundary (see Figure 8.17) compared to as atomized particle (see Figure 8.7). The amount of nickel-tin second phase was significantly greater than that observed in heat treated LaNi$_{4.89}$Sn$_{0.15}$. This was expected for the LaNi$_{5.5}$Sn$_{0.3}$ composition, because, this alloy is an non-stoichiometric AB$_5$ phase that is enriched in B elements.

The chemistry of each alloy composition was determined for as-atomized powder for each alloy composition. This is given in Table 8.1. Interstitial elements such as carbon, oxygen and nitrogen are also measured in the powder chemistry, because interstitials such as carbon can poison the material that would inhibit hydrogen absorption [96].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Formula (wt%)</th>
<th>Chemistry (wt.%)</th>
<th>Chemistry (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LaNi}<em>{4.89}\text{Sn}</em>{0.15}$ (He)</td>
<td>31.5 64.5 4.0</td>
<td>La 30.2 Ni 64.6 Sn 4.09</td>
<td>C 353 N 22 O 610</td>
</tr>
<tr>
<td>$\text{LaNi}<em>{4.75}\text{Sn}</em>{0.25}$ (He)</td>
<td>31.0 62.2 6.6</td>
<td>La 29.2 Ni 61.0 Sn 7.50</td>
<td>C 180 N 151 O 777</td>
</tr>
<tr>
<td>$\text{LaNi}<em>{5.5}\text{Sn}</em>{0.3}$ (He)</td>
<td>27.9 64.9 7.2</td>
<td>La 27.0 Ni 63.6 Sn 7.36</td>
<td>C 157 N 33 O 417</td>
</tr>
<tr>
<td>$\text{LaNi}<em>{4.8}\text{Si}</em>{0.4}$ (Ar)</td>
<td>33.1 64.3 2.7</td>
<td>La 30.4 Ni 65.5 Sn 2.1</td>
<td>C 436 N 600 O 486</td>
</tr>
<tr>
<td>$\text{LaNi}<em>{4.8}\text{Si}</em>{0.4}$ (He)</td>
<td>33.1 64.3 2.7</td>
<td>La 30.0 Ni 63.5 Sn 1.75</td>
<td>C 180 N 511 O 184</td>
</tr>
</tbody>
</table>

He: helium atomization; Ar: argon atomization.

### 8.3 X-Ray Powder Diffraction

XRD patterns of the Sn-modified LaNi$_5$ alloys all showed peak broadening that can be readily seen on the base of each Bragg peaks (see Figure 8.18, 8.19 and 8.20). This is caused by tin segregation to the cellular boundary during rapid solidification, resulting in Sn-enriched La(Ni,Sn)$_5$ phase that has the same hexagonal crystal structure as the matrix. The off-stoichiometric Sn-modified AB$_5$ alloy composition, LaNi$_{5.5}$Sn$_{0.3}$, exhibited a cubic crystalline phase segregating in large as-atomized particles and in annealed powders (see Figure 8.20). No fcc phase was found in atomized powder of the two stoichiometric Sn-modified AB$_5$ alloys.
Figure 8.16. Backscatter electron imaging of rapidly heat treated LaNi$_{4.85}$Sn$_{0.15}$ for 5 minutes at (a) 650°C, (b) 700°C, (c) 750°C, (d) 800°C, (e) 850°C, (f) 900°C, and (g) 950°C, for powders less than 25 μm. Arrows show examples of the second phase.
Figure 8.16. (continued).
Figure 8.16. (continued).
Figure 8.17. 5 minutes heat treat of LaNi$_3$Sn$_x$ powders, of less than 25 μm, at 900°C. Arrows show examples of second phases.
Figure 8.18. XRD patterns of helium as-atomized and annealed LaNi$_{4.85}$Sn$_{0.15}$ powder of various sizes.
Figure 8.19. XRD patterns of helium as-atomized $\text{LaNi}_{4.75}\text{Sn}_{0.25}$ powder of various sizes.
Figure 8.20. XRD patterns of helium as-atomized and annealed LaNi$_{5.3}$Sn$_{0.3}$ powder of various sizes. Arrows indicating fcc Ni-Sn solid solution phase.
Structural characterization of the powder by XRD was utilized to determine a minimum annealing time required for particle homogenization. Five minute rapid heat treatment were carried out over the range of temperature between 600 to 950°C (Figure 8.21) at 50°C increments. A short 5 minute anneal at 950°C for the gas atomized LaNi$_{4.85}$Sn$_{0.15}$ alloy was shown to completely homogenize the micro-segregation in the powder. This is indicated by identical lattice parameters observed between 5 minutes and 4 hours anneal at 950°C (see Figure 8.22). In addition, the sharpest Bragg peaks were observed in 5 minutes, 950°C heat-treat sample, showing distinct Cu $K_\alpha$ and $K_\beta$ peaks at high diffraction Bragg angles, indicating complete homogenization. One notes that the Bragg peaks in all observed diffraction planes shifted to a lower Bragg angle. This is an indication of Sn diffusing into the cellular from the cellular boundaries and caused the crystallographic lattice to expand, resulting in the observed downward shift in Bragg angles at each Bragg peaks.

Heat treatment at 800°C and 950°C was conducted over several annealing times, this is presented in Figure 8.23 and 8.24, respectively. A 950°C anneal showed that less than 10 minutes was sufficient to achieve full homogenization by observing the sharp appearance of the Cu $K_\alpha$ peaks at high diffraction angles. A 800°C anneal showed that the Bragg peaks to broaden at 5 minutes anneal, but full homogenization was achieved at an annealing time of 60 minutes.

XRD patterns of helium and argon gas atomized Si-modified LaNi$_3$ powders showed peak broadening that can be readily identified at the base of each Bragg peaks (see Figure 8.25 and 8.26). Si-modified AB$_3$ behaves similar to Sn-modified AB$_3$ alloys, in that, the peaks broaden at the shoulder of the main Bragg peaks. However, the direction in which the peaks broaden differs between the two group of AB$_3$ alloys. Si-modified AB$_3$ broadens asymmetrically towards larger Bragg angles, while Sn-modified AB$_3$ broadens towards smaller Bragg angles. In addition, Si-modified AB$_3$ showed the occurrence of a minor hexagonal phase to be the weakest in large particles and the strongest in the smallest particles. Another distinction between the two alloys is that there exists a weak Bragg peak occurring at approximately 38.3 degrees, in Si-modified but not in Sn-modified alloys, that do not correspond to hexagonal phase (see Figure 8.25 and 26). This anomalous peak has a peak intensity that varies in opposite manner to the presence of peak broadening at the shoulder of each hexagonal Bragg angles. The anomalous peak intensity is the highest when the particle is the largest and the intensity disappears in smaller particles. The anonymous peak intensities from helium and argon atomized powders where found to be different for the same particle size range. The intensity was suppressed in helium gas atomized powders possibly because helium has higher cooling rate than argon.
Figure 8.21. XRD of 5 minute and 4 hours heat treatment of LaNi$_{4.85}$Sn$_{0.15}$ powders less than 25 μm at target temperatures.
Figure 8.22. XRD of as-atomized, and 5 minute and 4 hours annealed $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ powders of size less than 25 $\mu$m. Arrows indicating Ni-Sn solid solution fcc phase.
Figure 8.23. XRD patterns of LaNi$_{4.85}$Sn$_{0.15}$ heat treated at 800°C at various times, for powder size of less than 25 μm. Arrows indicating Ni-Sn fcc solid solution phase.
Figure 8.24. XRD of 950°C heat treated LaNi$_{4.85}$Sn$_{0.15}$ powders of size less than 25 μm.
LaNi$_{4.6}$Si$_{0.4}$; He as-atomized

10-25 $\mu$m; Anneal 5 min @ 900$^\circ$C;  
$a=5.0067(3)$,  $c=3.9920(5)$

25-38 $\mu$m; $a=5.0092(3)$,  $c=3.9895(5)$

38-45 $\mu$m; $a=5.0090(2)$,  $c=3.9929(2)$

45-53 $\mu$m; $a=5.0088(2)$,  $c=3.9900(2)$

53-106 $\mu$m; $a=5.0112(3)$,  $c=3.9891(3)$

106+ $\mu$m; $a=5.0109(4)$,  $c=3.9913(3)$

Figure 8.25. XRD patterns of helium as-atomized and annealed LaNi$_{4.6}$Si$_{0.4}$ powder of various sizes. Arrow indicating a non-hexagonal second phase.
Figure 8.26. XRD patterns of argon as-atomized and annealed LaNi$_{4.6}$Si$_{0.4}$ powder of various sizes. Arrow indicating a non-hexagonal second phase.
XRD of hydrogenated $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ particles are also measured and are shown in Figure 8.27. The volumetric expansion upon full hydrogenation was 20.1% for $\text{LaNi}_{4.85}\text{Sn}_{0.15}$. 
Figure 8.27. XRD of annealed and hydrogen saturated LaNi$_{4.85}$Sn$_{0.15}$ powders of less than 25 μm.
CHAPTER 9. DISCUSSION

9.1 Hydrogen Absorption Isotherms

Rapid heat treatment for the as-atomized powders at 900°C for 5 minutes was found to efficiently homogenize the tin and silicon segregation in LaNi_{5.5}Sn_{0.3} and LaNi_{5.2}Si_{2} alloys, respectively. This is reasoned from the fact that the hydrogen isotherms exhibited a plateau pressure that is indicative of homogeneous composition in AB₃ alloys. Therefore, the sloped hydrogen isotherm of as-atomized LaNi_{4.75}Sn_{0.25}, as shown in Figure 8.3, is indicative of existing compositional phase variations. As-atomized absorption and desorption curves of LaNi_{4.75}Sn_{0.25} were shown to occur above and below the isotherm of that of the fully annealed alloy. The absorption curve of as-atomized powder occurring above the annealed powder desorption curve is an indication of the presence of Sn-depleted phases that form upon solidification. The portion of the absorption curve for as-atomized powders that is below the annealed powder absorption curve indicates the presence of Sn-enriched phases that have tin composition exceeding the nominal tin composition in the alloy. Further evidence of these phases is validated using XRD that will be discussed in a later section.

Even though the off-stoichiometric LaNi_{5.5}Sn_{0.3} alloy was expected to have lower plateau pressure than the stoichiometric LaNi_{4.75}Sn_{0.25} alloy because of the presence of more Sn in the alloy composition, both alloys were found to have similar plateau pressures in the annealed state. We believe the plateau pressure was the same, for the two alloys, because of mechanical strain pinning [37,82] from the excess nickel segregated within the off-stoichiometric LaNi_{5.5}Sn_{0.3} particle causing the hydrogen absorption pressure to rise.

Significant nickel segregates were observed in SEM micrographs (see Figure 8.17) in annealed LaNi_{5.5}Sn_{0.3} particles. The matrix phase of the off-stoichiometric alloy has an AB₃ composition and it will absorb hydrogen causing the particle to expand. However, the segregated nickel, which does not absorb hydrogen, will restrain the matrix and prevent it from expanding. The excess nickel adds additional coherent strain to the already existing hydrogen induced lattice strain to cause further rises in the measured hydrogen absorption pressure. Not to mention also the volume percent of AB₃ phase is reduced because of the excess nickel phase. The rise in plateau pressure due to mechanical strain and the stress that it creates has been documented by Petersen et al. [82]. The shift to lower hydrogen capacity per unit cell is also indicative of the significant strain field around the excess nickel phase making hydrogen absorption difficult.
9.2 SEM Imaging

The gas atomized powder of Sn- and Si-modified LaNi₅ alloys showed significant amounts of substitutional element segregation to the cellular boundary. In the Sn-modified AB₅ alloys, the Sn-rich segregates are seen as light areas in the BEI micrographs (see Figure 8.5, 8.6 and 8.7) compared to the matrix phase. The opposite is observed for Si-modified AB₅ alloy. The Si-rich segregates in the Si-modified AB₅ alloy are observed as dark areas in the BEI micrographs (see Figure 8.10). This is because BEI intensity is sensitive directly to the atomic weight of the elements. Lighter elements, as is silicon, will scatter less electrons compared to heavier elements, as in tin, so silicon will appear darker compared to its surroundings.

Microprobe results (see Figure 8.8 and 8.11) confirmed what is seen in the BEI micrographs, described above, indicating Sn- and Si-enriched phases located on the cellular boundary of the grains in the powder particles. What is observed is that Sn varied in opposite manner to La and Ni in Sn-modified AB₅ alloys, and Si and Ni both varied in opposite manner to La in Si-modified AB₅ alloy. Nickel and silicon formed a cubic phase in the cellular boundary, this will be discussed in the next section. This cellular boundary phase is also responsible in the forming of the anomalous phase observed at 38.3 degree in the LaNi₅₆Sn₀₄₋ₓ XRD patterns.

The XRD patterns for the stoichiometric Sn-modified AB₅ alloys show no other major crystallographic phases other than the hexagonal structure. The microprobe results (Figure 8.8) showed significant tin segregation up to as much as 25 weight percent at some cellular boundaries. This indicates that the highly segregated tin phases in stoichiometric AB₅ formed only the AB₅ hexagonal crystalline structure. Microprobe showed that a composition of LaNi₅₆Sn₁₂₂ formed is significantly higher in tin than documented stoichiometric La(Ni,Sn)₅ composition [127]. Wasz et al showed that the maximum equilibrium Sn, y, in LaNi₅ₓSn₁₋ₓ was 0.44. Therefore, the presence of these phases can only be attributed to be metastable. Although these are metastable hexagonal phases and can be eliminated by rapid annealing, it has been documented before by Notten et al. [77-79], that it is possible to form equilibrium off-stoichiometric single phase having formula up to AB₆ with copper. Thus it is not without merit to assume that we have rapidly solidified a hexagonal phase with La(Ni,Sn)₆ formula, approximately. The construction of the AB₆ phase will probably have the extra nickel occupying the Lanthanum sites. The La replacements are in the form of nickel dumbbell pair oriented along the c-axis [77,127]. The depletion of La in the hexagonal lattice is verified by the microprobe, showing depleted La composition in the cellular boundary where the AB₆ phase forms. Another plausible explanation for the observed microprobe results is that rapid
solidification formed lanthanum depleted alloy compositions at the segregated boundary. From observing the La-Ni phase diagram with the enhanced solubility for the LaNi$_5$ phase at high temperatures, one can form AB$_5$ phases with either nickel or lanthanum defects depending on the composition of the final solidified liquid whether it has composition on the left or right side of the enhanced solubility range, respectively. Therefore, it can be reasoned that the final solidifying liquid at the segregation boundary is enriched in tin and depleted in lanthanum. Thus the formation of the lanthanum depleted alloy compositions arose from the formation of AB$_5$ phases having lanthanum defects solidifying from the right-hand side of the enhanced solubility region.

In the stoichiometric alloy of Sn-modified LaNi$_5$ composition of LaNi$_{4.85}$Sn$_{0.15}$, SEM images of hydrogen cycled powders showed that powders having spherical size of less than 25 μm, produced by gas atomization, are resistant to gaseous hydrogen-induced cracking (Figure 8.14). The improved resistance to cracking can be suggested to cause by the improved uniform isotropic hydriding expansion of these fine spherical particles and the improved mechanical ductility with the addition of tin [61]. Spherical shaped objects are known to provide the best geometry to withstand hoop stress induced from internal pressures, i.e., designs of pressurized gas storage containers. Even so, there appears to be an upper limit to the particle size beyond which particle fracture becomes inevitable. It has been suggested that particle fracture occurs during hydrogen desorption [13]. Hydrogen absorption of this alloy expands the material up to 20 percent of its original volume (see Figure 8.27). This induces a tremendous amount of hoop stress near the particle surface. Volumetric contraction on the surface occurs during hydrogen desorption, aggravating the hoop stress on the surface. This is because the surface layer is the first to shrink back into alpha phase. As it does, it experiences tension stress, because the underlying core is still in the hydrogenated beta phase. Particle fracture begins to occur when this surface tension is likely to dilate pre-existing cracks and surface flaws. Larger particles are more likely to fracture, because the particles are more likely to have a core of beta-phase, dilating the contracted alpha-phase near the surface. On the other hand, smaller particles have a shorter diffusion distance from their core to their free surface. The rapid hydrogen diffusion through a small particle quickly eliminates the beta-phase at the center, and reduces the tension stress at the surface (see Figure 9.1), thereby avoiding particle fracturing.

9.3 X-Ray Powder Diffraction

Bragg peak broadening observed in Sn-modified LaNi$_5$ alloys is caused by segregation of the tin during rapid solidification (see Figure 8.18, 8.19 and 8.20). Hexagonal LaNi$_5$ was
Figure 9.1. Schematic of hydrogen particles of large and small during hydrogen desorption. Large particle has a core of hydrogenated beta-phase during desorption. Hydrogen diffusion distance is shorter for small particle such that the beta-core is quickly eliminated during desorption.
identified as the primary crystallographic structure of the alloys, as expected. The primary peak from each diffraction plane (indicated in Figure 8.18) arises from the matrix phase (see Figure 8.5, 8.6, 8.7), representing the dominant phase in the as-solidified powder. The minor peaks occurring at the base of each diffraction plane show asymmetrical Bragg peak broadening toward lower Bragg angles. These minor peaks are the multiple minor phases from the rapid solidification process (RSP) (see Figure 9.2a). They have the same crystallographic hexagonal structure as the primary matrix phase but with differing tin composition. As observed from the electron microprobe, the cellular boundary is Sn-rich. The Sn-rich phases are created during rapid solidification when the larger tin atoms (in relation to nickel) are redistributed to the cellular boundary. Even though the addition of a larger atom such as tin would increase the strain energy in the matrix crystal lattice, the primary solidified matrix phase is found to have some excess tin in its microstructure. This is indicative of solute entrapment due to RSP. Therefore, from a mass balance point of view, the minor phases that exist at the cellular boundary should have high degrees of solute entrapment forming the Sn-rich hexagonal phases. These phases are highly metastable with respect to the Sn-depleted matrix phase, due to the high lattice strain caused by the large entrapment of tin in the cellular boundary hexagonal lattice.

These entrapped Sn-rich phases are seen as the asymmetrical peak broadening. Close examination will show that the lowest Bragg angle from the asymmetrical broadening are smaller than the Bragg angle of a fully annealed alloy of the same composition (see Figure 9.3). This shows that some of the metastable hexagonal phase regions have higher Sn composition than the nominal alloy composition. Interestingly, this is suppressed at smaller particle sizes due to rapid quenching in the RSP in gas atomization. The hydrogen absorption isotherm in Figure 8.3 also shows that as-atomized powder has lower absorption pressure over lower H/AB₅ ratios. This can only occur if there exists a minor phase or phases that have higher tin composition than the nominally annealed tin composition. Thus gives further evidence of tin segregation forming multiple Sn-rich minor phases with hexagonal crystallographic structure. It was found that Bragg peaks of as-atomized Sn-modified LaNi₅ showed sharper Bragg peaks as particle size is decreased. This is indicative of enhanced rapid solidification of the alloys in smaller particle, due to the larger surface-to-volume ratio in smaller spherical particles [2]. The minor phases in the smaller particles are suppressed compared to the larger particles. The rapid solidification is particularly acute in LaNi₅,Sn₀.₃ (see Figure 8.20). The off-stoichiometric AB₅ alloy with excess nickel showed segregated peaks for fcc phase appearing at ~44 and ~51 degrees (see Figure 8.20). But the rapid heat extraction associated with smaller particles appears to have suppressed the nickel segregation.
Observed XRD pattern

Nominal composition phase

As-atomized major phase

Minor phases

Sn-enriched phases

Sn-depleted phases

Bragg angle of nominal composition

(a)

Minor Bragg peaks grew as tin migrates to nominal composition

Sn-enriched phases

Sn-depleted phases

Bragg angle of nominal composition

(b)

Observed Bragg peak of fully annealed powder

Sn-enriched phases

Sn-depleted phases

Bragg angle of nominal composition

(c)

Figure 9.2. Schematic showing minor Bragg peaks superpositioning to form the observed XRD pattern about the observed major diffracted phase. (a) Observed XRD pattern formed by major and minor hexagonal phases, (b) Bragg peak broadens upon annealing, and (c) observed Bragg peak of nominal composition.
Close examination of the XRD patterns for heat-treated $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ temperature revealed significant Bragg peak broadening to occur at about 750°C and 800°C during the rapid 5 minutes heat-treat (see Figure 8.21). This phenomenon is a result of tin migration within the observed Bragg planes in the hexagonal crystallographic structure. The large tin atoms that migrate upon annealing can be seen to occur as broadening of the Bragg peaks measured at full-width-quarter-maximum (FW1/4M) (Figure 9.4). Bragg peak broadening due to atomic migration is not typically observed in XRD patterns because of lack of atomic size difference between the solute and the solvent atoms. In our study, FW1/4M peak width is chosen to enhance the sensitivity of the angular two-theta measurement. At FW1/4M, the breadth of the Bragg peak is located well above the background signal. This Bragg peak broadening is caused by the migration-induced strain of tin atoms in the diffracted Bragg plane. Thus, the magnitude of peak broadening observed in the XRD patterns can be viewed as a relative comparison of the ease of tin diffusion in a particular crystallographic plane. A direct relationship can be derived between lattice strain due to tin diffusion and peak broadening because Bragg angle is related to the distance in a lattice plane, $d_{\text{hkl}}$. But the diffraction broadening observed in the XRD patterns for $\text{LaNi}_{4.85}\text{Sn}_{0.15}$ is asymmetrical unlike that from particle size broadening. The observed XRD pattern is not due to particle size beam...
Figure 9.4. Full width quarter maximum, FW$^{1/4}$M, of XRD Bragg peak of LaNi$_{4.85}$Sn$_{0.15}$ after 5 minute annealing at temperatures from 650 to 950°C.
broadening, rather it is due to compositional beam broadening from superpositioning of many smaller peaks of differing phase compositions. These peaks are transitional minor hexagonal phases with various compositions of Sn-enrichments that exist (see Figure 9.2b).

The minor hexagonal phases with Sn composition greater than the nominal composition (or lower Bragg diffraction angle) disappear during annealing. The asymmetrical beam, left of the fully anneal peak, migrates to a larger Bragg angle (lower tin composition). At the same time, the asymmetrical beam, right of the fully annealed peak, migrates to a lower Bragg angle (higher tin composition) (see Figure 9.2b and 9.2c). All the while, the maximum peak height shifts lower in Bragg angles, towards the fully annealed Bragg peak (see Figure 8.23).

Since Bragg peak broadening of a given diffraction plane is caused by the lattice dilation of the transitional minor phases present during tin diffusion, then one can possibly determine the preferred crystallographic plane for tin diffusion by the magnitude of the shift peak broadening during the rapid 5 minutes heat treat. This means, one will observe tin to migrate on crystallographic planes of the hexagonal lattice that has the least resistance to Sn diffusion. An increased resistance to the migration of tin may be provided by the presence of La atoms for which tin does not substitute. The path of least resistance would be planes for which tin substitution for nickel is preferred. These are the nickel 3-g sites on the {002} crystallographic planes [127]. From observing the beam broadening at FW$^{1/4}$M, it was found that the preferential migration paths for Sn in La(Ni,Sn)$_5$ alloy were along the {002} and {202} planes (see Figure 9.4) in agreement to what was assumed. Tin is a substitution atom for nickel in LaNi$_5$, therefore the two planes, {002} and {202}, consisting of all nickel atoms, would naturally be the preferential migration planes for the diffusing tin atoms. Other planes such as {001}, {112}, and {311} were found to be more active, i.e., a wider FW$^{1/4}$M, when annealing temperature was increased from 750°C to 800°C. Crystallographic planes such as {110} and {200} were found to be less-desirable diffusion planes because of the presence of lanthanum atoms on these planes. Therefore, less lattice strain is observed in these Bragg diffraction planes, resulting in reduced Bragg peak broadening.

In observing the XRD patterns, other parameters such as X-ray atomic scattering factor, f, should also be acknowledged to influence our collected XRD patterns. The crystallographic plane {001} is a sub-set of the {002} plane. Although the atoms on two crystallographic planes differ, one would expect Bragg peak of {001} plane should observe peak broadening effect occurring at {002}, because of Bragg diffraction. The reason we do not observe the same effect occurring at {001} as we do in the {002} plane is because the Bragg angle of {001} planes has a reduced scattering factor that contribute to a reduced Bragg peak intensity. Typically we assume the scattering factor, f, of any element is usually
considered to be independent of the wavelength of the scattering radiation. This is not quite true for many cases, when the incident wave length $\lambda$ is nearly equal to the wavelength $\lambda_K$ of the K absorption edge of the scattering element. In these circumstances, the atomic scattering factor of that element may be several units lower than it is when $\lambda$ is much different than $\lambda_K$. In our case, it is not the incident wave that is causing the effect, but rather, it is the diffracted wave belonging to the \{001\} plane that is affected. A calculation of an equivalent wavelength, $\lambda_{\text{equivalent}}$, for diffracted \{001\} plane for this hexagonal crystallographic structure of LaNi$_{4.85}$Sn$_{0.15}$ will reveal that it is similar to the K absorption edge of nickel atoms. The equivalent wavelength was 1.526 Angstroms and the absorption wavelength for nickel is 1.66 Angstroms (conservatively using $\lambda_K = \alpha_K$), giving a ratio of $\lambda_{\text{equivalent}} / \lambda_K$ is 0.918. Typically, when the ratio is less than 0.8, the correction to $f$ is negligible. But when $\lambda_{\text{equivalent}}$ is near $\lambda_K$, as in our case, the form factor is reduced. This phenomenon is also known as anomalous dispersion [27]. This does not alter our conclusion discussed previously, but it does help explain why Bragg peak of \{001\} planes do not broaden as much as that observed in \{002\} planes.

In homogenization it is often interesting to calculate the time for an inhomogeneous alloy to reach complete homogeneity. For example, the purpose of determining the time required to eliminate segregation in castings can have great value in the commercial world. Atomization techniques are a rapid solidification process that can produce microsegregation (in micron scale) that are three or more orders of magnitude smaller than the macrosegregation (in mm scale) found in castings. Using the relationship that diffusion distance squared is proportional to diffusion time, then the annealing time for complete homogenization is six or more orders of magnitude shorter in powder than in castings.

In the La(Ni,Sn)$_3$ alloy system, it is well documented that Sn substitutes for Ni at the 3-g sites in the hexagonal crystal structure [77,127]. This is the \{002\} crystallographic plane. In the stoichiometric AB$_3$ composition LaNi$_{4.85}$Sn$_{0.15}$, one could assume the lanthanum atom on the lattice site to remain stationary. Thus, we are now left with the substitutional diffusion of nickel and tin atoms in this hexagonal crystal structure. In view of this, tin diffusion in this alloy can be considered as an interdiffusion mechanism in a pseudo-binary alloy, where lanthanum is an invariant. Thus, some of the sites occupied by lanthanum are prohibitive sites for tin and nickel mobility.

It could be possible to infer diffusion constants and activation enthalpy from the XRD patterns of the heat treated powders. The following model is crude because it assumes isotropic diffusion in this otherwise anisotropic crystal lattice. Nonetheless, it may be useful providing some insight on the kinetics of rapid homogenization process. The simple binary diffusion model corresponding to Fick’s 2nd law will be used to solve for diffusion in our
pseudo binary alloy. The simple binary model will still exhibit interdiffusion also known as substitutional diffusion. In substitutional diffusion to remove segregation, the probability to find a vacancy adjacent to any atom comes into play. In addition, the rate at which solvent (A) and solute (B) atom (Ni and Sn in our scenario) can move into a vacant site is not equal. Each atomic species must have its own diffusion coefficient, \( D_A \) and \( D_B \). In this \( \text{AB}_2 \) alloy only the diffusion of nickel and tin will be considered, lanthanum diffusion is neglected. The solution for substitutional diffusion expressed as Fick's second law is given as,

\[
\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x} \left( D' \frac{\partial C_B}{\partial x} \right)
\]

where, \( C_B \) is the concentration of solute B in solvent A, and \( D' = X_B D_A + X_A D_A \) (also known as Darken's equation), where \( X_B \) and \( X_A \) are the atomic fractions of the solvent and solute respectively. Primed variables are used to denote interdiffusion distinguishing them from interstitial diffusion normally cited in literature. One can simplify Eq. 9.1 by assuming the diffusion coefficient \( D' \) is invariant over distance, yielding solution form to Fick's second law of non-steady state diffusion.

\[
\frac{\partial C_B}{\partial t} = D' \frac{\partial^2 C_B}{\partial x^2}
\]

Fick’s equation could be solved via separation of variables, after applying appropriate boundary and initial conditions (see Figure 9.5), that the concentration of B, function of time and distance, is:

\[
C_B(x,t) = \overline{C} + C_0 \sin\left( \frac{\pi x}{\ell} \right) \exp\left( -\frac{t}{\tau} \right)
\]

where, \( \overline{C} \) is the nominal B composition, \( C_0 \) is the initial concentration of B segregation, \( \ell \) is the diffusion distance, and \( \tau \) is a constant called the relaxation time, and it is given as

\[
\tau = \frac{\ell^2}{\pi^2 D'}
\]

Using the relaxation time equation, a 1 \( \mu \)m grain size (depicted in the SEM photographs), and the time for full homogenization at 800°C to be 57 minutes (see Figure 9.6), we predicted the interdiffusion coefficient \( D'_{800} \) (diffusion at 800°C) to be \( 7.4(10^{-12}) \) cm²/sec. During the rapid heat treat study, it took 3 minutes to reach targeted temperature, thus, the annealing time is reduced by 3 minutes. At 950°C, the interdiffusion coefficient was found to be \( 6.03(10^{-11}) \) cm²/sec with annealing time of 7 minutes (see Figure 9.6).
Figure 9.5. The effect of diffusion on the sinusoidal variation of the composition $C_B$.

Relaxation time of the $\{002\}$ Bragg peak was measured for use in Eq. 9.4 because $\{002\}$ planes are the dominant planes for Sn diffusion and they have the greatest peak broadening during rapid heat treatment gave the greatest sensitivity to $FW^{1/4M}$ measurements.

In fact, most grains are polygons in shape. Thus, spherical isotropic diffusion would best model the annealing heat treatment in this study. Diffusion in a sphere with a constant varying surface concentration is given as [26],

$$C = k \left( t - \frac{a^2 - r^2}{6D} \right) - \frac{2ka^2}{D\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^3} \sin \frac{n\pi r}{a} \exp \left( -\frac{Dn^2\pi^2 t}{a^2} \right)$$  

9.5

Figure 9.6. Change in full width quarter maximum, $FW^{1/4M}$, of $\{002\}$ Bragg peak at 800°C and 950°C anneal with time.
where, $k$ is constant for surface concentration, $a$ is diffusion distance, $r$ is the radius of a sphere. If we take only the first-order terms, $n=1$, and ignoring high-order terms, the relaxation time in spherical particle is also expressed as approximately an exponential term.

$$C = k\left( t - \frac{a^3 - r^3}{6D} \right) + \frac{2ka^2}{D\pi^2 r} \sin \frac{\pi r}{a} \exp \left( -\frac{t}{\tau} \right) ; n=1$$

where the relaxation time is given as, $\tau = \frac{a^3}{\pi^2 D}$.

Then, the time dependence of concentration remains the same regardless of the morphology of the particle.

The above relaxation time was derived for a one-dimensional diffusion model is similar to diffusion in a sphere. Using the relaxation times at two different temperatures we can approximate the interdiffusion coefficients solving the following equation [83] simultaneously for the activation enthalpy, $Q'$, and interdiffusion coefficient $D'_o$,

$$D'(T) = D'_o \exp \left( \frac{-Q'}{RT} \right)$$

If we take only the first-order terms and ignoring high-order terms, the relaxation time in spherical particle is also expressed as approximately an exponential term. Time dependence of concentration remains the same regardless of the morphology of the particle.

Solving for $Q'$ and $D'_o$, we find the values of 152.24 KJ.mol$^{-1}$ and 1.975(10$^{-6}$) cm$^2$.sec$^{-1}$, respectively. The $Q'$ values compare higher for self-diffusion in pure lanthanum, a rare-earth bcc metal (see Table 9.1) [18]. The measured activation enthalpy does compare well with the activation enthalpy in hcp metals, for example, self-diffusion for magnesium has $Q$ of 136 KJ.mol$^{-1}$ (parallel to the c-axis). The measured activation enthalpy, $Q'$, for our pseudo-binary alloy is expected to be greater than a low melting point metal of the same hexagonal crystal structure. This is because there is a rough correlation exits between $Q$ and $T_m$ (melting point temperature). That is, increasing the interatomic bond strength make the process of

<table>
<thead>
<tr>
<th>Class</th>
<th>Metal/Alloy</th>
<th>$T_m$ (K)</th>
<th>$D'_o$ (cm$^2$.sec$^{-1}$)</th>
<th>$Q$ (KJ.mol$^{-1}$)</th>
<th>$Q/RT_m$</th>
<th>$D(T_m)$ (um$^2$.sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rare earth</td>
<td>La</td>
<td>1193</td>
<td>1.3(10$^{-4}$)</td>
<td>102.3</td>
<td>10.4</td>
<td>42</td>
</tr>
<tr>
<td>hcp</td>
<td>Mg</td>
<td>922</td>
<td>1.50</td>
<td>136.0</td>
<td>17.8</td>
<td>2.9</td>
</tr>
<tr>
<td>fcc</td>
<td>Ni</td>
<td>1726</td>
<td>1.90</td>
<td>279.7</td>
<td>19.5</td>
<td>0.65</td>
</tr>
<tr>
<td>hexagonal</td>
<td>LaNi$<em>{48}$Sn$</em>{0.15}$</td>
<td>1623</td>
<td>1.975(10$^{-6}$)*</td>
<td>152.24*</td>
<td>11.3*</td>
<td>0.00243*</td>
</tr>
</tbody>
</table>

* Measured results of this thesis
melting more difficult, giving higher $T_m$. Therefore, the activation energy, $Q'$, of the higher melting LaNi$_5$ intermetallic is greater than similar low melting point hexagonal crystal structured elements and alloys, i.e., magnesium metal and silver-zinc alloy, as anticipated.

We found that activation enthalpy of interdiffusion of tin in La(Ni,Sn)$_5$ was less than the activation energy of self diffusion of nickel ($Q$ is 279.7 KJ.mol$^{-1}$). This is somewhat surprising, because the interdiffusion of tin in LaNi$_5$ involves the substitution of a larger tin atom in place of a smaller nickel atom. The atomic radius of tin is about 21.1% larger than that of nickel. One would expect that this would raise the activation enthalpy of interdiffusion of tin in La(Ni,Sn)$_5$. But one has to consider the fact that nickel has a fcc crystal structure whereas La(Ni,Sn)$_5$ is hexagonal. This makes direct activation enthalpy comparison difficult. For most close-packed metals such as fcc and hcp, the $Q/RT_m$ is approximately 18 [83]. In our measurement, the value $Q/RT_m$ is 11.3 which is closer to the value for bcc rare earth metals. This is interesting, because LaNi$_5$ is predominantly nickel and the activation enthalpy for tin diffusion requires the mobility of nickel. Nevertheless, the activation enthalpy, $Q'$, derived for the interdiffusion coefficient for tin in LaNi$_5$ is well within an acceptable limits observed in literature [18].

The interdiffusion coefficient $D'_o$ is found to be much lower than that generally observed data in literature (see Table 9.2) [17,18]. This can be explained by the fact that tin diffusion in LaNi$_5$ follows particular preferential diffusion paths, or more specifically, diffusion planes. Unlike self-diffusion where the coordination number for migration is large, i.e., close-packed fcc and hcp structures have a coordination number of 12, our pseudo-binary interdiffusion has a low coordination number. The next available site for tin to migrate may not always be a preferred nickel site; that is the nickel 3-g site on the {002} plane. This limited diffusion site availability would naturally reduce the interdiffusion

<table>
<thead>
<tr>
<th>Class</th>
<th>Element 1 (At %)</th>
<th>Element 2 (At %)</th>
<th>$D'_o$ (cm$^2$.sec$^{-1}$)</th>
<th>$Q'$ (KJ.mole$^{-1}$)</th>
<th>Temperature range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc</td>
<td>Ni</td>
<td>Sn (0-7.3)</td>
<td>3</td>
<td>225</td>
<td>1472</td>
</tr>
<tr>
<td>fcc</td>
<td>Au (25)</td>
<td>Cu (75)</td>
<td>6.5(10$^{-3}$)</td>
<td>159.9</td>
<td>823-1173</td>
</tr>
<tr>
<td>fcc</td>
<td>Cu</td>
<td>Al (2.8)</td>
<td>0.4</td>
<td>201.0</td>
<td>1073-1313</td>
</tr>
<tr>
<td>fcc</td>
<td>Cu (13)</td>
<td>Ni</td>
<td>1.5</td>
<td>263.8</td>
<td>1323-1633</td>
</tr>
<tr>
<td>hcp</td>
<td>Ag (0.89)</td>
<td>Zn</td>
<td>$\parallel$ c 0.42</td>
<td>110.1</td>
<td>593-688</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\perp$ c 0.69</td>
<td>117.3</td>
<td></td>
</tr>
<tr>
<td>hexagonal</td>
<td>Ni</td>
<td>Sn (3)</td>
<td>1.975(10$^{-6}$)*</td>
<td>152.24*</td>
<td>1073-1223</td>
</tr>
</tbody>
</table>

* Measured results of this thesis
coefficient $D_{o'}$. However, the simple reduction of coordination number may not cause the several orders of magnitude effect change in $D_{o'}$ observed in our measurements. There has to be a more significant phenomenon in effect here. An interdiffusion coefficient, $D_{o'}$, like the self-diffusion coefficient, $D_o$, is affected by many factors shown in the following equation [83],

$$D_{o'} = \frac{1}{n} \alpha z' v \exp \frac{\Delta S_m' + \Delta S_v}{R}$$

where, $n$ is the number of next available sites, $\alpha$ is the jump distance, $z'$ is the coordination number, $v$ is the jump frequency, $\Delta S_m'$ and $\Delta S_v$ are the entropies of migration and of vacancy formation, respectively, $R$ is universal gas constant.

The change in entropy of migration is a measure of the entropy difference between the initial state to the final state in atomic migration [35,83,104]. Intuitively, equilibrium will be reached when the entropy of the system will reach the maximum value. Or, similarly, we can say maximum entropy is created when the most preferred state of atomic configuration and positioning is achieved in a crystal lattice. In our pseudo-binary alloy, the preferred site for tin is the 3-g site at equilibrium. Therefore, tin migration into other nickel sites, other than 3-g sites, will create mean entropy of migration averaging less than the maximum entropy found at equilibrium state. The diminutive mean entropy of migration created during tin diffusion in numerous other diffusion $\{hkl\}$ planes can therefore conceivably contribute to a reduced magnitude in the interdiffusion coefficient, $D_{o'}$. Since entropy of migration is an exponential term in the above equation, a small change in mean entropy of 13.8 KJ.mol$^{-1}$.K$^{-1}$ can bring about 6 orders of magnitude change in the diffusion coefficient as observed in our measurement.

The low interdiffusion coefficient $D_{o'}$ was found to give rise to low diffusivity at the melting temperature for the LaNi$_{4.85}$Sn$_{0.15}$ alloy. We found the diffusivity to be 0.0024 $\mu$m$^2$.sec$^{-1}$ at the $T_m$ of this alloy. This is significantly lower than literature values by two orders of magnitude. This is due predominantly to low average entropy of migration for tin diffusing in the La(Ni,Sn)$_3$ hexagonal crystal lattice.

As mentioned earlier, that spherical powders of less than 25 $\mu$m, in LaNi$_{4.85}$Sn$_{0.15}$ were resistant to hydrogen induced cracking. This can be attributed also to reduced volumetric variation between the alpha and beta phases. Volumetric expansion in the hydrogenated LaNi$_{4.85}$Sn$_{0.15}$ was measured from XRD determined lattice parameter (see Figure 8.27). A volumetric expansion of 20.1% was determined. This is less by 5 volume percent compared to pure LaNi$_5$ material [61]. The reduced volumetric expansion minimizes the tensile stress (see
Figure 9.1) that is created by the volumetric contraction between the beta and alpha phase. This has enabled the Sn-modified alloy to withstand continuous hydrogen cycling without causing the material to fracture.

A heat treat study of off-stoichiometric LaNi$_{5.5}$Sn$_{0.3}$ alloy has XRD patterns that shows homogenization of Sn in the matrix phase (see Figure 9.7). The lattice parameters of powder sample subjected to a 10 minute anneal at 900°C are 5.0590 Å and 4.0427 Å for $a$ and $c$, respectively. Compared to data obtained by Wasz et al. [127] (see Figure 9.8), the composition for 10 minute annealed powder is found to be approximately LaNi$_{5.3}$Sn$_x$, with $x$ in the range of 0.28. This value for Sn is well within the nominal composition of the alloy. This rapid heat treat apparently achieved a stoichiometric AB$_5$ composition. The lattice parameter of powder samples 30 minutes anneal at 900°C are 5.0671 Å and 4.0500 Å for $a$ and $c$ respectively. From Figure 9.8, the composition of the alloy would be LaNi$_{5.4}$Sn$_x$, with $x$ in the range of 0.32. This is slightly greater than the nominal composition of the alloy. But this result agreed well with the upper limit of Sn found from chemical analysis of the atomized powder which gave a range of chemical formula of LaNi$_{(5.5-5.66)}$Sn$_{(0.3-0.32)}$. The tin concentration in the annealed powder is well within the range of tin concentration determined by chemical analysis.

Bragg peak broadening similar to that observed in Sn-modified alloys are also observed in the gas-atomized LaNi$_{4.5}$Si$_{0.4}$ alloy. Both alloys solidify hexagonal minor phases forming the broadened peak with an enriched substitution element. The main difference between the two alloys is that the asymmetrical peaks broaden in opposite directions. The Sn-modified alloys have peak broadening towards lower Bragg angles because the substitution tin atom is larger than nickel it replaced. This atomic substitution increases the lattice parameters, as described before. Similarly, the atomic radius of silicon is smaller than nickel by six percent, and this atomic substitution would naturally decrease the lattice parameter of the minor phases, thus shifting their Bragg peaks towards higher Bragg angles. The lattice parameter determination of rapid annealed powder sample agrees with the above analysis (see Figure 8.25). The annealed lattice parameters are 5.0067 Å and 3.992 Å for $a$ and $c$, respectively, compared to helium atomized +106 μm particle having 5.0109 Å and 3.9913 Å for $a$ and $c$, respectively. The anomalous peaks was determined to be cubic phase of La(Ni, Si)$_{13}$ having a Fm3c crystal structure (see Figure 9.9) with crystal lattice of 11.278 Å. XRD patterns of La(Ni, Si)$_{13}$ and La(Ni, Si)$_3$ phases from computer simulation showed a consistent identification of all Bragg peaks observed in as-atomized LaNi$_{4.5}$Si$_{0.4}$. The presence of this fcc phase would explain the observed nickel and silicon variation together in the microprobe measurements described earlier (see Figure 8.11). The creation of the minor hexagonal phases are found to
Figure 9.7. XRD patterns of 900°C heat treated LaNi$_{5.5}$Sn$_{0.3}$ at various time for less than 25 μm powder particles. Arrows indicate Ni-Sn solid solution fcc second phase.
Figure 9.8: Lattice parameter of LaNi$_5$Sn$_y$ as a function of tin content y.
Figure 9.9. XRD of experimental LaNi$_{4.6}$Si$_{0.4}$ powders, helium as-atomized. Shown with it is a simulated XRD pattern of the cubic second phase (shown on the top), and the hexagonal primary phase (shown on the bottom).
be in direct competition with this cubic phase that forms the anonymous peak at 38.3 degrees. But, the solidification rate in smaller atomized powder particles was sufficiently rapid to suppress the formation of the cubic phase, but it is not sufficient in larger particles. This is true for both helium and argon gas atomized powders.

As mentioned before that different atomization gas medium will affect the cooling rate of the atomized droplets. The cooling rate of helium and argon are expected to be different because of the heat capacity of helium is an order of magnitude greater than that for argon [25]. We have previously noticed the intensity of the anonymous peak is suppressed to a greater extent in helium than argon atomized particles of the same size range. From the XRD patterns (see Figure 8.25 and 8.26), a semi-qualitative cooling rate difference between the two gases can be inferred taking a ratio of peak intensity of this anomalous peak with respect to a reference hexagonal Bragg peak, say the \{101\} of the hexagonal phase. A plot of this ratio over the various particle size ranges is given in Figure 9.10. The intensity ratios for helium atomized particles are lower than that for argon atomized particles, as expected, demonstrating that helium has a higher cooling rate than argon. In this analysis we expect that the fcc phase is in direct competition with only the minor hexagonal phases and not the as-atomized major hexagonal phase. This assumption has to be made in order that the reference \{101\} peak intensity of the major phase does not change due to minor volume fraction changes stemming from the fcc and hexagonal phase competition. As can be seen from a comparison of Figure 9.9, the lattice parameter determined for various particle sizes does vary with particle size. In fact the lattice parameters increase with increasing particle size. This means that the volumetric phase content of the major as-atomized hexagonal phase changes with particle size, changing the silicon content in the fcc phase. The particle size effect brings additional level of complexity to the cooling rate comparison between argon and helium, that is beyond the scope and will not be addressed in this study. Nonetheless, the cooling rate result is in agreement with the literature [2,25,129] for a general comparison between helium and argon gases only.
Figure 9.10. Relative cooling curves for helium and argon atomized LaNi$_{4.6}$Si$_{0.4}$ alloy by comparing peak height ratio between $\{222\}$ and $\{101\}$ from the fcc and hexagonal phases respectively.
CHAPTER 10. CONCLUSIONS

We have demonstrated that spherical particles of less than 25 μm resisted hydrogen induced intragranular fracture in Sn and Si-modified AB₅ alloys. These powders would be suited for battery material application where hydrogen induced fracture is a main concern.

It is observed from the XRD pattern that only hexagonal phase is rapidly solidified in the gas atomization process of Sn-modified stoichiometric AB₅ alloys of LaNi₄.₇₆Sn₀.₂₅ and LaNi₄.₈₅Sn₀.₁₅. The off-stoichiometric AB₅ alloy of LaNi₅.₃Sn₀.₃ rapidly solidified to a hexagonal phase and an additional minor FCC Ni-Sn solid solution phase. This FCC phase is suppressed in atomized powders of less than 53 μm, approximately.

In the Si-modified LaNi₅ alloy, we also observed solidified hexagonal and fcc phases. The fcc phase was determined to have a crystal structure of F3mc with lattice parameter a=11.278 Å, consistent with data published by Rogl [90]. The fcc phase was removed by rapid heat treatment, but an additional undetermined phase appeared adjacent to the \{200\} Bragg peak at ~41 degrees, approximately (see Figure 8.25). Relative cooling rates effect for He and Ar were investigated, taking advantage of the fcc phase peak height change with particle size. The result showed that helium atomization of LaNi₄.₅Si₀.₅ was indeed more capable of suppressing fcc phase formation than argon atomization. This is demonstrated by the peak intensity ratio (see Figure 9.10). This result also indicates that the fcc phase would most probably be the more stable phase of the two at a lower solidification rate. Thus we observe the benefit of metastable phase selection in a rapid solidification process using the gas atomization technique.

We have shown that a rapid heat treatment of 5 minutes at 900°C is sufficient to remove enhanced Sn and Si segregation from the cellular boundaries. This is primarily due to the refined cellular microstructures that were on the order of one micron in size. It was noted that the cellular size was nearly independent of powder particle sizes, for powder sizes less than 106 μm and greater than 5 μm in both alloy compositions.

We have showed that XRD Bragg peak broadening in La-Ni-Sn can be attributed to a “superpositioning” of multiple hexagonal phases that have varied tin compositions. These hexagonal phases are found to be segregated to the cell boundaries during rapid solidification. The varied tin composition in the hexagonal phases resulted in the sloped hydrogen absorption isotherm for the as-atomized powder seen in Figure 8.3. The portion of the hydrogen absorption pressure below the annealed hydrogen isotherm is a result of the hexagonal phase having higher tin composition than the nominal composition. The higher tin compositions would give rise to lower hydrogen absorption pressure.
A preferential crystallographic Sn diffusion path was observed from the result of the rapid heat treatment of LaNi$_{4.85}$Sn$_{0.15}$ alloys of less than 25 \textmu m. The observed preferential diffusion paths were determined to be along the \{002\} and \{112\} family of planes. This is because these \{hkl\} planes consisted of only nickel atoms for which the alloying element Sn substituted exclusively. Using the relaxation time from heat treating the alloy, we were able to determine the diffusion constants for the assumed pseudobinary, Ni-Sn, ignoring La. The activation enthalpy, $Q'$, and interdiffusion coefficient, $D'_0$, for this interdiffusion system are 152.24 KJ.mole$^{-1}$ and 1.975(10$^6$) cm$^2$.sec$^{-1}$, respectively. The value of the activation enthalpy determined in this thesis is within reasonable agreement in magnitude with other published values of activation enthalpy for similar interdiffusion measurements. However, the interdiffusion coefficient, $D'_0$, for the Ni-Sn interdiffusion system is about 6 orders of magnitude smaller than published work on other binary alloy systems. This can be reasoned from the fact that Sn does not substitute for La in the La-Ni-Sn system. Therefore, a reduced coordination number is available for Sn mobility during diffusion. Unfortunately, the simple reduction of coordination number should not cause several orders of magnitude change in $D'_0$, observed in our measurement. The dominant change in the interdiffusion coefficient probably comes from the entropy of mixing (also known as configurational entropy). In our pseudo-binary alloy, the preferential substitutional site for Sn is in the 3g sites. Therefore, tin migration on numerous other nickel sites during diffusion will create a mean entropy of mixing that averages less than the maximum entropy found at an equilibrium state. The diminutive mean entropy of mixing created during tin diffusion in numerous other \{hkl\} planes can therefore conceivably contribute to a reduced magnitude in the interdiffusion coefficient. Since entropy of mixing is an exponential term in Eq. 9.7, a change in mean entropy of 13.8 KJ.mole$^{-1}$.K$^{-1}$ can bring about a 6 orders of magnitude change in interdiffusion coefficient, as observed in our measurement.
CHAPTER 11. GENERAL CONCLUSIONS

We have studied the relationship between gas atomization processes, powder particle solidification phases, and hydrogen absorption properties of ultra fine atomized powders with high surface area for enhanced battery performance. Concurrently an enhanced gas atomization nozzle was developed to be more efficient than all current designs to increase the yield of ultra fine AB₅ alloy powder for further processing advantages at lower operating pressures.

Miniature convergent-divergent jets (CDJs) based ib rocket nozzle profile were used in designing two new atomization nozzles, HPGA-II and HPGA-III. The HPGA-II had a jet apex angle of 45 degrees, similar to the existing Ames HPGA nozzle that used straight-bored jets, but HPGA-II operated with a mismatched 22° melt tip apex angle. The HPGA-II nozzle was demonstrated to be more efficient in producing fine powders at half the operating pressures of the existing Ames HPGA nozzle that operated at 7.57 MPa. However, measurements of the gas velocity indicated a severe limitation on the possible kinetic energy from the HPGA-II nozzle caused by the extreme tip mismatch required for stable operation. A design concept advanced in this thesis aided in the design of the HPGA-III. The HPGA-III nozzle had CDJs that have an apex angle of 22.5 degrees and was able to form stable subambient melt aspiration with a matching angle melt tip 0.050 inches long. Therefore, the HPGA-III nozzle could make more efficient use of the atomization gas kinetic energy than the HPGA-II nozzle. The HPGA-III was determined to be 16.8% more efficient than HPGA-II, and produced a 40 wt.% yield of <25 µm powders of 316L stainless steel operated at 3.13 MPa. This was a 10% increase in yield over HPGA-II.

We have showed that the design concept set forth in this dissertation enabled development of a highly efficient HPGA-III gas atomization nozzle that has matching CD jets and melt tip apex angles. The nozzle is able to utilize the maximum available gas kinetic energy of the CD discrete jets by avoiding the formation of oblique shocks that can result from the use of a mismatched melt tip. The HPGA-III was able to produce a stable subambient plateau-like aspiration pressure that should make the nozzle easy to tune to control particle size by directly varying operation pressure. The nozzle was demonstrated to produce a high yield of ultrafine powders that is desirable for coupling to the development of AB₅ alloys for battery applications.

Rapid solidification by gas atomization of LaNi₄₋₅SiₓSnₓ and LaNi₄₋₃Snₓ alloys was studied. We observed that small atomized particles (< 25 µm) were resilient to hydrogen induced fracture in gas-phase hydrogen cycling. Quenched-in non-equilibrium phases with different Si and Sn content were observed in the La-Ni-Si and La-Ni-
Sn alloys, respectively, and annealing was necessary to achieve the desired hydrogen absorption properties. Rapid annealing of the gas-atomized AB₃ alloys at 900°C for 5 minutes was sufficient to fully remove the Sn and Si segregations. During annealing, preferential diffusion paths for Sn were observed on \{002\} and \{202\} planes from the XRD patterns. The approximate interdiffusion parameters could be estimated using simple isotropic diffusion model. The activation enthalpy, Q', and interdiffusion coefficient, D', for tin diffusing in La(Ni,Sn)₃ intermetallic are calculated to be 152.24 KJ.mole⁻¹ and 1.975 (10⁻⁶) cm².sec⁻¹, respectively.

Gas atomization processing of the AB₃ alloys was demonstrated to be effective in producing ultrafine spherical powders that were resilient to hydrogen cycling for the benefit of improving corrosion resistance in battery applications. These ultrafine powders benefited from the rapid solidification process by having refined solute segregation in the microstructure of the gas atomized powders which enabled a rapid anneal treatment of the powders. We have demonstrated the ability to produce high yields of ultrafine powder efficiently and cost effectively, using the new HPGA-III technology. Thus, the potential benefits of extended battery cycling life by processing AB₃ alloys using the new HPGA technology would be added to reduction in the manufacturing cost of the nickel-metal hydride particulate. HPGA processing could make the manufacture of AB₃ alloy powders a continuous and rapid production process. These economic and performance gains may thereby encourage the use of nickel-metal hydride rechargeable batteries in electrical vehicle applications in the foreseeable future.

This study has provided a basis for further research on gas atomization processing of AB₃ materials using multicomponent alloying and cheaper mischmetal in place of more expensive element lanthanum. Powder properties for the new atomized powders would have to be investigated for hydrogen absorption pressures and hydrogen storage capacity, prior to battery cell testing. Benefits of RSP and gas atomization on other potential hydrogen storage materials with A and B formulas of A₂B, AB, and AB₂, for rechargeable battery applications should also be investigated.
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