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Centrifugal Atomization of Lanthanide Materials for Cryogenic
Coolers

by

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To my wife, Ann, for her patience, and my
parents, Joyce and Gary, for their support
and guidance.

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ABSTRACT

Many present and future applications require the cooling of magnetic and electronic equipment to cryogenic temperatures. In many cases, a cryocooler utilizing a packed bed, regenerative heat exchanger is used for either direct or indirect cooling of such equipment. Until recently, Pb, in the form of $\sim 200\mu\text{m}$ spheres, was the preferred heat exchanger matrix material used in low temperature (i.e., $<20\text{K}$) cryocoolers; however, the heat capacity of Pb drops drastically below $\sim 15\text{K}$ and new matrix materials based on the lanthanide elements have been developed. These materials, primarily lanthanide intermetallic compounds, magnetically order at low temperatures and the entropy change associated with ordering contributes to the materials' heat capacities. The major drawback to the widespread use of lanthanide intermetallic compounds in cryocoolers has been the difficulty in manufacturing high-quality particulate due to the reactivity and brittleness of these compounds. Most particulate production techniques, such as ingot milling, rotating electrode processing, and gas atomization, have proven to be inadequate in producing solid, spherical particles in the size range of interest ($150\text{-}350\mu\text{m}$).

The purpose of this project was to develop a technique for producing high-quality powders of lanthanide metals and lanthanide intermetallic compounds for use in cryocooler heat exchangers. To accomplish this, a series of atomization experiments was performed using the Ames Laboratory's Centrifugal Atomizer with Rotating Quench Bath (CA/RQB). Er_3Ni , Nd , Nd_3Ni , and $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ were the materials chosen for experimentation based on current cryocooler research and investigation into alternative materials.

Atomization of these materials resulted in particles ranging from mostly spherical to extremely flattened with the majority of the particulate being semi-spherical or slightly flattened. Analyses of size distributions for the experiments indicate that increased atomization disk speed and superheat result in smaller mean particle diameters and narrower size distributions. There is also evidence that increased superheat may allow respherodization of

the atomized droplets prior to solidification, resulting in more spherical powders. Median particle size calculations for the Nd experiments, using an equation experimentally derived for the rotating electrode process, produce values very similar to those found experimentally, indicating that the CA/RQB process can be accurately controlled to produce the desired particle diameters.

Chemical analyses of the atomized powders indicate that the CA/RQB technique produces particulate with much lower interstitial contamination than other techniques, e.g., gas atomization. X-ray diffractometry and differential thermal analysis show that the Er_3Ni and Nd_3Ni powders were predominantly of the desired phase and that the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powder had one major and possibly three minor phases. Optical microscopy of cross-sectioned and etched particles shows that the solidification morphology is typically fine dendritic or cellular with finer microstructure spacings near the particle surfaces.

Low temperature heat capacity measurements on the starting materials and atomized powders indicate that interstitial atom contamination during processing caused the heat capacity peaks to shift in temperature and also to broaden. It is believed that these effects are due to impedementation of the electronic spin alignment by the interstitial contaminants. The Er_3Ni powders were found to have higher heat capacities than gas atomized powders reported in literature. The heat capacity of Nd_3Ni has a tremendous peak which does not degrade dramatically with processing as does the peak for Er_3Ni . While the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ material does not exhibit the characteristic heat capacity peak found in the other materials, it does have a higher heat capacity compared to Er_3Ni , Nd_3Ni , and Nd at temperatures above 10K, making it an interesting prospect as a heat exchanger material for applications between 10 and 20K.

Overall, it appears that any of the powders produced during this research would operate satisfactorily in a cryocooler heat exchanger. It is encouraged that future research involve actual cryocooler testing and the continued experimentation in blending R elements in the R_3Ni (where R = a lanthanide metal) structure in order to develop new materials with optimum heat capacity profiles.

CHAPTER 1. INTRODUCTION

1.1 Cryogenics and Cryocoolers

Since the late 19th century, scientists have strived to produce low temperature environments both for basic research and to improve the operation of temperature influenced systems (e.g., electronics). In the area of applied science, many devices require cryogenic cooling (i.e., less than 120K) for successful operation. Some examples are:

- superconducting magnets in magnetic resonance imagers (MRI)^{1,2} and SQUID magnetometers³
- high-speed (GHz), superconducting Josephson junctions used for extremely rapid electronic switching³
- laser tracking devices³
- infra-red and gamma-ray detectors which are cooled in order to minimize electronic noise and, thus, heighten sensitivity.^{3,4,5}

Possible future applications include magnetic levitation trains¹ and superconducting generators and motors for naval propulsion systems.^{1,6}

Low temperature refrigerators are used in conjunction with devices such as these either to cool directly the device or to maintain the temperature of a coolant (e.g., liquid He). While both cryogenic coolers (cryocoolers) and magnetic refrigerators are used for low temperature refrigeration, cryocoolers are preferred for applications involving superconductivity (see above) since no external magnetic field is involved. This thesis concentrates on heat exchanger matrix materials used in cryocoolers.

The most widely used cryocooler design is based on the Gifford-McMahon (GM) cycle. While the GM cycle is less efficient than other cycles, such as the Brayton or Stirling cycles, it is more dependable, with fewer moving parts and a lower cycle speed.⁷ In general, the GM cycle utilizes gas expansion to cool a transfer gas (usually He). A regenerative heat exchanger is used in the cycle to transfer heat from the high pressure gas to the low pressure gas. A detailed description of the GM cycle is given in Section 2.1.

The principal restriction to the efficiency of the GM or any other cryogenic refrigeration cycle is the heat capacity of the heat exchanger matrix. For many

years, lead was the favored matrix material because of its high specific heat compared to other common metals. However, the heat capacity of solids decreases proportionally to T^3 (see Section 2.2) and the heat capacity of Pb drops drastically below 15K. Some materials, such as lanthanide metals and lanthanide/transition metal intermetallic compounds, have an additional heat capacity contribution from the entropy change during magnetic ordering (see Section 2.3). Since ordering occurs at a specific temperature, there is a "spike" in the heat capacity. Figure 1.1 compares the specific heat of Pb with that of Nd which orders at approximately 8K and 20K (only the lower ordering is shown).

Figure 1.1. Heat capacities of Nd and Pb at low temperatures

Reliability is a very desirable trait in cryocoolers, especially in space applications where maintenance is impossible and excessive equipment weight limits payload. Even for earth-bound applications, maintenance is expensive due to the long start-up and shut-down time associated with cryogenic

equipment. It is therefore beneficial to maximize the efficiency and physical quality of the regenerator matrix. This may be accomplished by using monosized, spherical particles with no internal voids as the heat exchanging matrix. The particles should be monosized (or at least have a narrow size range) since a wide particle size distribution increases packing density which, while decreasing the overall size of the heat exchanger, also decreases the gas flow and thereby decreases efficiency. Nonspherical, angular particles also decrease gas flow and allow shifting of the packed bed. Additionally, angular particles fracture and disintegrate more easily leading to erosion of the gas seals in the cryocooler and subsequent equipment failure.¹ Hollow particles decrease the mass available for cooling and have less physical strength compared with solid particles.

Fabrication of lanthanide intermetallic or lanthanide metal regenerator particulate is not an easy process due in part to the reactivity of molten lanthanides with most materials and the brittleness of lanthanide intermetallic compounds. Also, contamination by interstitial impurity atoms (i.e., O, N, C) reduces the magnitude of the materials' heat capacities and so decreases the cooler's efficiency (see Section 2.3.1). A technique is needed which can produce spherical particles of lanthanide intermetallic or lanthanide materials with minimal contamination and little internal porosity. Production techniques which have been used include crushing of cast ingots, gas atomization, rotating electrode processing, spark erosion, molten salt processing of crushed ingot, low velocity jet atomization, and centrifugal atomization.

Of the production techniques mentioned above, only centrifugal atomization appears capable of producing commercial quantities of lanthanide intermetallic and lanthanide metal powders with low contamination, spherical shape, and little internal porosity.

1.2 Research Proposal

Given the above history and the problems with conventional cryocooler regenerator particulate production techniques, it is obvious that a new production technique is needed in order to economically produce high-quality powders. The objective of this project was therefore to adapt an existing

ambient atmosphere centrifugal atomization apparatus to a form suitable for the production of high-quality lanthanide intermetallic and lanthanide metal materials.

The proposed research began with the adaptation of the existing equipment for use in a controlled atmosphere chamber (Chapter 3). Trial experiments using non-lanthanide, oxygen sensitive materials were conducted to determine if the atmosphere control was sufficient to produce spherical particles (a heavy oxide surface prevents spherodization, resulting in irregular particles). After these successful trials, a search was made to find lanthanide intermetallic compounds and lanthanide metals which exhibit high specific heats at low temperatures. The materials chosen were atomized and the resulting powders characterized by size distribution analysis, scanning electron microscopy, chemical analysis, optical microscopy, x-ray diffractometry, differential thermal analysis, and low temperature calorimetry to determine their potential performance in cryocooler heat exchangers.

CHAPTER 2. LITERATURE REVIEW

Cooling to cryogenic temperatures (below 120 Kelvin) is desirable for many reasons: slowing chemical reactions such as biological tissue degradation; liquefying normally gaseous materials such as hydrogen, oxygen, or methane for transportation and usage; and, most recently, exploiting the superconducting properties displayed by some materials. Superconducting materials can be found in high-speed electronic switching circuits,^{3,8} superconducting motors and generators,^{1,6} and Magnetic Resonance Imaging (MRI) devices,^{1,2} to name only a few. At the present time, commercially utilized superconducting materials must be maintained at low temperatures, possibly as low as 4K, in order to retain their superconducting properties. The materials are generally cooled with liquid He which, in turn, is refrigerated and maintained at low temperature using a cryogenic refrigerator, either a cryogenic cooler (cryocooler) or a magnetic refrigerator. More complete discussions on the history and uses of cryogenics and cryocoolers may be found in Haselden's compilation, Cryogenic Fundamentals,⁹ and Walker's books, Cryocoolers Parts 1 & 2.¹⁰

For the scope of this thesis, we will be concentrating on cryocooler type refrigerators which, in general, cool a system using the expansion of a heat transfer gas. A regenerative heat exchanger is also used in the refrigeration cycle for precooling of the transfer gas. Ideally, the heat exchanger matrix is composed of a material which has a high heat capacity over the entire thermal operating range of the cryocooler. The following sections will provide a literature review of the thermodynamics involved in cryocooler refrigeration, an overview of the Gifford-McMahon refrigeration cycle, heat exchanger matrix materials used in cryogenic coolers, powder production techniques used for these materials, and a brief history of the Ames Laboratory's centrifugal atomizer.

2.1 The Thermodynamics of Cryocooler Refrigeration

The sole purpose of any type of refrigerator is to remove heat from a system. In many instances, such as in the GM cryocooler, the removal of heat

is accomplished by the expansion of a gas from high to low pressure (i.e., Joule-Thompson expansion). Starting with the ideal gas law,¹¹ $PV = nRT$ (where: $P \equiv$ pressure, $V \equiv$ volume, $n \equiv$ number of moles, $R \equiv$ ideal gas constant, $T \equiv$ temperature), we see that, for an infinitesimal pressure decrease in an adiabatic system, there is a proportional temperature decrease (assuming $dV = dn = 0$):

$$d(PV) = d(nRT) \quad \text{Eqn. 2.1}$$

$$\text{or} \quad dP \propto dT \quad \text{Eqn. 2.2}$$

Of course, actual systems are not perfectly adiabatic, so heat will flow from the system to the expanded gas, driven by the temperature gradient between the two. This heat flow constitutes the actual refrigeration of the system.

2.2 The Gifford-McMahon Refrigeration Cycle

As mentioned in Chapter 1, the Gifford-McMahon (GM) refrigeration cycle is the most widely used cycle for cryogenic coolers due to its simplicity and reliability. Figure 2.1 shows a simplified schematic of the GM cycle (adapted from Ref. 7) which we will use to explain how refrigeration is accomplished. The thermal history of a unit of transfer gas is shown in Figure 2.2 for one refrigeration cycle. We begin with the system already in operation.

1. Transfer gas (usually He) at high pressure and ambient temperature, T_1 , enters the system through the valve.
2. The gas passes through the heat exchanger (where the gas cools to T_2 by transferring heat to the packed bed) and into the expansion chamber.
3. The system is vented to low pressure, causing the gas in the expansion chamber to cool to T_3 .
4. The refrigeration load transfers heat to the cooled gas and warms the gas to T_4 .
4. As the gas vents, it passes through the heat exchanger and absorbs heat from the packed particle bed. The gas is now at T_5 .
5. Outside of the system, the transfer gas releases heat to the environment, is repressurized and reenters the system at high pressure and T_1 to begin a second cycle.

Figure 2.1. A simplified schematic of a Gifford-McMahon cryocooler

Figure 2.2. A temperature versus time diagram for a Gifford-McMahon cryocooler (after Ref. 10, p. 248)

Temperature versus time profiles for subsequent cycles would be similar to the one shown in Figure 2.2. Temperatures T_2 , T_3 , and T_4 will decrease with each cycle until steady state conditions are reached at the maximum load cooling.

2.3 Heat Exchangers

Cryocoolers rely upon heat exchangers for precooling the transfer gas before it encounters the refrigeration load. These exchangers may be either recuperative (hot and cold gas flow is through different channels) or regenerative (hot and cold gas flow is through the same channel but alternates with time).¹⁰ In either case, a matrix material, usually fine wires or spheres, is used in the heat exchanger to alternately absorb and reject heat. We will limit our scope to the regenerative heat exchanger since it is used in the GM cryocooler.

2.3.1 Material selection

A heat exchanger's efficiency increases proportional to its heat capacity. For a size-constrained system, this means that the specific heat (heat capacity per unit volume) of the matrix material should be as large as possible. For relatively high temperature coolers (50-100K), copper, brass, bronze, or stainless steel are used. As the temperature (and so the thermal energy) of the system decreases, the heat capacity of the matrix material decreases due to quenching of the lattice vibration and conduction electron contributions to the heat capacity.^{12, 13} Specifically, the lattice vibration and conduction electron contributions decrease as T^3 and T , respectively.¹³ Lead has been used extensively as a low temperature (< 80K) matrix material since its lattice is relatively "soft" (i.e., easy lattice vibration) giving it the highest heat capacity at low temperatures compared to other common metals. However, Pb is only usable to about 10K where its heat capacity becomes comparable to that of helium (the heat capacity of gases increases with decreasing temperature - see Figure 2.3). Alternative materials are therefore needed which have higher heat capacities at low temperatures and also enhanced heat capacity at higher temperatures for initial equipment cooling. As was mentioned above, lattice

vibration and conduction electrons contribute to the heat capacity of most solids. In some materials, Schottky anomalies¹⁴ and magnetic ordering^{12, 14} also contribute to heat capacity. It has been found that, upon cooling, most lanthanide metals and lanthanide intermetallic compounds magnetically order

Figure 2.3. Heat capacities of Pb and He crossing at about 10K (after Ref. 15)

at a critical temperature, either the Curie temperature, T_C , for paramagnetic $\rightarrow$ ferrimagnetic (or ferromagnetic) ordering, or the Néel temperature, T_N , for paramagnetic $\rightarrow$ antiferromagnetic ordering.¹² When ordering occurs in these materials, there is a change in entropy ($\Delta S = S_J$) associated with the alignment of magnetic spins in the material. This, in turn, creates a change in the heat capacity at the critical temperature:

$$C_J = T (\partial S_J / \partial T) \quad \text{Eqn. 2.3}$$

where: ΔS = change in entropy due to magnetic ordering

S_J = magnetic entropy

C_J = magnetic heat capacity

T = temperature.¹⁵

Theoretically, one would expect ordering to occur simultaneously throughout the material at the critical temperature, creating a high, narrow heat capacity

spike. In actuality, the heat capacity peak is broadened over a range of temperatures due to impurities in the lattice which impede the realignment of spins during ordering.¹⁶ Because of the low temperature heat capacity peak found in lanthanide metals and compounds, researchers have turned to these materials as alternatives to lead in low temperature cryogenic coolers.

Lanthanide metals, such as Nd, and lanthanide intermetallic compounds such as $(\text{Gd}_x\text{Er}_{1-x})\text{Rh}$, ErNi_2 , $(\text{Er}_x\text{Dy}_{1-x})\text{Ni}_2$, Nd_3Ni , and $\text{Er}(\text{Ni}_{1-x}\text{Co}_x)_2$, have all come under scrutiny as potential heat exchanger matrix materials.^{1, 6, 13-19} Some, such as Er_3Ni , have been tested and used widely while others have been found to be unsatisfactory.

2.3.2 Matrix shape

Researchers have determined that low temperature heat transfer in heat exchangers is most efficient using fine wires (in a stacked screen assembly) or particulate (in a loosely packed bed) due to their high surface to volume ratios. Particulate forms, i.e., lead "shot" pellets, have been preferred for lead because they are easier to fabricate than wires. Likewise, the brittleness of lanthanide intermetallic compounds dictates the use of these materials in particulate rather than wire form. It is desired that the brittle lanthanide intermetallic particulate be as spherical as possible since angular particulate packs less efficiently than spherical particulate, allowing more shifting of the packed bed during operation and leading to greater disintegration and erosion. Dust from bed erosion can congest the heat exchanger and destroy the gas seals and, thus, cause equipment failure.^{1, 6, 17, 20}

Now that we have determined that the matrix should be composed of spherical particles, the following question arises: What size (diameter) should the particles be? On one hand, smaller diameter spheres provide the opportunity for higher surface area per unit volume and, therefore, faster cycle times and quicker cooling. On the other hand, as the spheres become smaller, the pressure drop across the heat exchanger increases, decreasing the refrigeration performance.¹⁰ There is, therefore, a compromise to be made in the diameter of the matrix material. Hashimoto et al.¹⁵ show how heat transfer equations may be used to determine the penetration depth of heat for a single

cycle and, hence, the maximum diameter which is useful. However, these calculations involve the thermal conductivity of the matrix material and the cycle time for the refrigerator; therefore, there is no one optimal sphere diameter for all matrix materials or refrigeration systems. Trial and error determinations of optimal particle size have consistently resulted in heat exchanger designs specifying powders with diameters ranging from 100 to 500 μm .^{1, 6, 10, 15, 17-21} Some of these specifications, however, appear to be determined not by heat exchanger testing, but by the capability of the particle production technique.

2.4 Heat Exchanger Particulate Production Techniques

In the following two quotations from his 1992 paper (Ref. 1), Ackermann sums up the primary considerations involved with using lanthanide alloys in cryocooler heat exchangers:

"The test results also provided clear evidence that the single most important parameter affecting both performance and endurance was material manufacturability."

"Manufacturability of the materials and the ability to produce high-quality spherical particles economically is the major challenge to their commercial use. It appears that both the performance and erosion of material from the regenerator is a function of this parameter."

Lanthanide intermetallic compounds and the reactivity of lanthanide elements, as well as the limitations inherent to certain processing techniques, provide restrictions to the commercial production of lanthanide intermetallic materials.^{1, 6, 17} For example, gas atomization produces exceptional fine powders (<100 μm) at high production rates (5 Kg/minute), but larger powders often have prominent internal porosity.^{17, 21} Low velocity jet atomization also produces high quality particles, but the mean particle size is larger than desired (about 400 μm) and production rates are low.²⁰ The rotating electrode process is capable of producing solid Nd particles in the desired size range; however,

the fabrication of a starting billet of a lanthanide intermetallic compound would be difficult due to the brittle nature of the material.¹⁷ Also, inhomogeneous particles can result if the compound melts incongruently. Spark erosion, mechanical attrition, and molten salt processing have all been shown to have more serious drawbacks such as the formation of thick oxide layers and angular particles.^{1, 17, 20} Toshiba has shown, however, that centrifugal atomization with a rotating disk, can be used to produce high-quality, spherical particles of lanthanide intermetallic materials.^{22, 23}

2.5 Centrifugal Atomization

In general terms, centrifugal atomization is the disintegration of a molten material by the centrifugal force associated with a rotating disk, cup, or wheel. Examples of various centrifugal atomization techniques may be found in German's book, Powder Metallurgy Science,²⁴ or various reviews by Lawley.²⁵⁻²⁷ We will briefly discuss rotating disk atomization which forms the basis for this study.

As the name implies, a rotating disk atomizer employs a spinning disk upon which molten metal is atomized. In "two-step" atomization (Figure 2.4), the charge material is melted prior to being poured onto the atomization disk. The

Figure 2.4. Rotating disk centrifugal atomization such as was used for this study

molten metal flows outward across the disk to the disk periphery where it forms a liquid torus. Instabilities within the liquid cause the formation of small protuberances from which liquid droplets are flung. At higher liquid supply rates, the protuberances may form arms which disintegrate into droplets or, at

Figure 2.5. Atomization mechanisms observed for rotating disk atomization (after Ref. 28)

even higher supply rates, the arms will merge into a liquid film (Figure 2.5). In a study on rotating electrode atomization, Champagne and Anger developed an empirical equation for the mass mean particle diameter of centrifugally atomized particles:²⁹

$$d_{50} = 3.65 (1/\omega) (\gamma/\rho)^{0.46} (1/D)^{0.58} Q^{0.06} \quad \text{Eqn. 2.4}$$

where: d_{50} = mean particle diameter by mass (m)
 ω = disk rotational speed (radians/sec)
 γ = liquid surface energy (N/m)
 ρ = liquid density (kg/m^3)
 D = disk diameter (m)
 Q = liquid supply rate (m^3/s)

In the simplest case, the droplets solidify during flight with heat transfer out of the particles, primarily, by convection to a static atmosphere. Some systems, such as Pratt & Whitney's Rapid Solidification Rate (RSR) unit, use high velocity gas jets to enhance convective cooling³⁰⁻³² while others, such as the Ames Laboratory's Centrifugal Atomizer with Rotating Quench Bath (CA/RQB), employ a liquid quenchant for even higher cooling and solidification rates.³³ Liquid quenching also allows the Ames Laboratory's atomizer to be more compact than other centrifugal atomization systems.³⁴

The Ames Laboratory's (CA/RQB) was developed in 1990 by K. S. Funke and I. E. Anderson as a process for producing large, spherical metal powders. Funke and Anderson came up with a system which used a ceramic atomization disk with a concentric, spinning bath filled with liquid quenchant. A disk made from a thermally insulating ceramic allows rapid heating of the disk surface. This creates a "hot disk" which prevents extensive solid metal buildup and, therefore, maintains optimal atomization conditions. Section 3.2 discusses other desirable characteristics for atomization disks.

Funke and Anderson's research showed that the CA/RQB was capable of producing very spherical powders of Ag in the size range of 400-500 μm as well as all smaller size ranges. The particle size distributions for these particles were very narrow with geometrical standard deviations down to 1.4. For Ag-15Cu (Ag with 15 wt. % Cu), however, large particles were not spherical due to the formation of a surface oxide layer which prevented spherodization. Chapter 3 describes the adaptation of Funke and Anderson's equipment for use in an inert environment in order to overcome the problems associated with an oxygen-containing atmosphere - not only nonsphericity of the particles, but also excessive chemical contamination.

CHAPTER 3. DEVELOPMENT

The Ames Laboratory's Centrifugal Atomizer with Rotating Quench Bath (CA/RQB) was developed in 1990 by Dr. Iver Anderson and Kelly Funke, a graduate student of Dr. Anderson's. Funke's research involved the design and construction of an apparatus for the production of large, spherical particles to be used on fountain pen nibs. A series of experiments over a two year period led to an ambient atmosphere, spinning disk atomizer which employed a flat, three inch diameter atomization disk and a concentrically rotating liquid bath. Funke demonstrated that his machine was capable of producing large, spherical silver particles with narrow size distributions.³³ Funke's machine, however, could not produce large, spherical particles of materials which oxidize easily (i.e., most metals, including the pen tip alloys) due to the rigidity of the oxide shells which formed during atomization in the air atmosphere. Under this research program, the CA/RQB has been adapted to operate within a controlled atmosphere (i.e., low oxygen) and, thereby, to produce spherical particles of oxide forming metals, especially lanthanide alloys. These adaptations, as well as other significant improvements, are described below.

3.1 Inert Atmosphere Chamber

The CA/RQB is contained in a vacuum-capable chamber, allowing atomization within an inert atmosphere (Figure 3.1). Since the chamber was not designed for the CA/RQB system originally, some adaptations were necessary. In order to minimize equipment cost, it was determined to place both of the motors (one for the disk and one for the bath) inside the chamber rather than use expensive rotational feedthroughs. The vacuum pump and speed controllers are attached to the chamber base allowing mobility of the entire system. Viewing ports in the top of the chamber allow for observation of the crucible and charge during operation. Likewise, a window in the front of the chamber and a mirror mounted within the chamber allow the operator to view atomization as it occurs.

Figure 3.1. The CA/RQB containment chamber

3.2 Atomization Disk

The most important part of a spinning disk atomizer is the atomization disk. Improper disk design can lead to wide size distributions, larger than desired particle diameters, excessive chemical contamination, and poor particle shape. The ideal characteristics for an atomization disk and the effects of such characteristics are given in Table 3.1.

Table 3.1. The ideal disk characteristics and their effects

Characteristics		Effects
perfect wetting by the liquid metal	—→	atomization at the disk edge
resistance to chemical attack	—→	minimal impurity addition
low heat capacity	—→	rapid heating of the disk surface - thin skull
low thermal conductivity	—→	rapid heating of the disk surface - thin skull
moderately rough surface finish	—→	physical bonding of the skull
smooth profile that redirects liquid motion from vertical to horizontal	—→	consistent skull thickness

Funke's final disk design consisted of a flat, machinable alumina disk, 75 mm in diameter (Figure 3.2a). In his research, Funke noticed that the molten metal sometimes only wet the inner 50mm diameter of the disk before building up a frozen metal "skull." Atomization then occurred not at the disk periphery, but at the edge of the skull, resulting in an effective disk diameter of about 50mm. At the onset of this project, it was decided that complete wetting of the disk surface might be encouraged by decreasing the disk diameter to about 50mm and using a thin metal disk surface (Figure 3.2b). A locking pin with a conical head was used to hold the composite disk together and attach it to the drive shaft. The conical shape of the locking pin head was intended to reduce liquid metal splashing.

Due to skull formation problems experienced in the early experiments (e.g., incomplete wetting, uneven skull thickness, skull "shedding"), it was decided to angle the disk surface upward toward its outer edge so that centrifugal force would physically "push" the liquid against the disk surface (Figure 3.2c). Disk wetting was found to be better, but uneven skull thicknesses still indicated splashing of the liquid metal.

At this point, a new disk design was considered and tests were conducted using brass disks of both the old disk design and the new configuration (Figure 3.2d) to atomize water. The new disk shape retained the conical-headed locking pin in the center of the disk and also the upward sloping outer rim. However, a continuous curve was added which connected the edge of the

Figure 3.2. CA/RQB atomization disk designs explored during this study

locking pin and the beginning of the upward slope. This curve was intended to smoothly redirect the molten metal stream from vertical to horizontal flow. Videotapes of the water testing were viewed at slow speed in order to determine where splashing occurs on the disks and how it might be prevented. Digitized photos showing splashing on disk design 'c' and the absence of splashing on disk design 'd' are given in Figures 3.3 and 3.4.

Figure 3.3. Digitized videotape images of disk design 'c' showing: a) initial liquid contact and b) liquid splashing

The present disks were constructed from an alumina board made of Zircar (Zircar Products Inc., Florida, New York), 30% dense AL-30AA board (97% Al_2O_3 - 3% SiO_2). The board was machined using standard high speed machine tools and ethyl alcohol to minimize dust evolution. The disks were then baked out in air at 800°C for 8 hours to remove volatile contaminants. With the stainless steel center pins in place, a Ta coating, 0.08-0.13 mm thick, was plasma sprayed on the concave surface (plasma spraying done by Plasma Coatings Corporation, Gardena, CA - see Figure 3.5). The low density alumina board has very low thermal conductivity which allows the disk surface to heat quickly, thus minimizing solid metal buildup which may encourage

a)

c)

b)

Figure 3.4. Digitized videotape images of disk design 'd' showing: a) initial liquid contact, b) liquid redirection, and c) complete disk wetting

Figure 3.5. Low conductivity, composite disk design used in this study

nonoptimal atomization. The thin tantalum layer provides an inert, wettable surface for molten metal contact.

3.3 Quench Bath

In Funke's experiments, the rotating quench bath was filled with quenchant as it was rotating in order to prevent the liquid from flowing into and through the rotational bearings in the center of the bath. On shutdown, a cylinder was placed around an o-ring just beyond these bearings, and so provided a dam for the quenchant. Since it was desired for this project to operate the system in an inert atmosphere, it was necessary to develop a more complex system for quenchant introduction and removal. In the first experiments, a permanent dam was added at the point where Funke's temporary dam was used and the quenchant was added to the bath prior to sealing the vacuum chamber (Figure 3.6). However, this prevented the disk from being lowered sufficiently within the bath and caused secondary problems such as droplet impingement on the

Figure 3.6. The initial quench bath design

bath lid and particles being thrown from the bath. In order to overcome these problems (and as a step towards scale-up), the current system was constructed (Figure 3.7). The bath is brought to the desired rotational speed after chamber evacuation and refill. A container of quenchant outside the system is then pressurized, forcing quenchant through simple plumbing and into the bath. As

Figure 3.7. The current quench bath design

the bath is slowed after an atomization run, the quenchant moves towards the center of the bath and runs through holes bored through the bottom of the bath. A stationary pan beneath the bath catches the quenchant and funnels it into a large bin beneath the atomizer. This adaptation has increased the quenchant volume from 1.5 L to 2.5 L and so provided a larger heat sink for the system and a longer path for particle solidification.

In the original configuration, a single motor was used to drive both the atomization disk and the quench bath. A large sheave on the motor and a small sheave on the disk shaft allowed the disk to be spun at a high speed (~ 3000 rpm). At the same time, a small sheave on the motor and a large one on the bath shaft allowed the bath to be spun at a much lower speed (~ 700 rpm). For the current project, it was desired to produce finer particles which dictates an increase in the disk speed (see Equation 2.4). With the single motor design, however, increasing the disk speed also increases the bath speed leading to vibration of the atomizer. A smaller, secondary motor was therefore added to the system in order to spin the bath independently at any desired speed. This small motor is voltage controlled and capable of spinning the bath at 100-1000 rpm.

3.4 Equipment Testing and Material Selection

Preliminary equipment testing was conducted using Cu and Ag-15 wt.% Cu to determine if the atomization atmosphere was sufficiently low in oxygen to prevent heavy surface oxidation. (Thick oxide surface layers will prevent spherodization of the particles.) Micrographs of the resulting particles are shown in Figure 3.8. The Cu particles are mainly spherical with small dimples resulting from shrinkage of the droplet upon solidification. The Ag-15%Cu particles are very spherical and appear to have rather smooth surfaces. Further testing was performed using Ni_3Al to investigate high-temperature atomization (poured at 1465°C). The particles in this case appear to have spherodized and then flattened upon impact with the quenchant (Figure 3.9) and a dark surface coating on one side of the particles indicates that there may have been a chemical reaction with the quenchant. The experiment did, however, show that the CA/RQB was capable of atomizing a high melting point material. This is

Figure 3.8. SEM micrographs of a) Cu powder, -300+250 μ m and b) Ag-15%Cu powder; -500+425 μ m showing spherical particle shapes

Figure 3.9. SEM micrograph of Ni₃Al powder; -300+250 μ m

the state of development of the atomizer which allowed us to begin our study into the atomization of lanthanide alloys.

In choosing which lanthanide materials to use in this study, it was natural to begin with Er_3Ni since it has been widely used as a replacement for Pb in cryocooler applications. Nd metal was another obvious choice because of increasing interest in it as a more reliable matrix material than Er_3Ni (i.e., more reliable $\equiv$ less brittle). Pr_3Ni and Nd_3Ni were also examined as it was believed that their heat capacities might be similar in magnitude to Er_3Ni and that they might have better physical strength. Pr_3Ni was reported to order at 2K and Nd_3Ni at 15K,³⁵ so it was decided to also investigate a blended lanthanide material, $(\text{Pr}_{0.62}\text{Nd}_{0.38})_3\text{Ni}$, which was expected to have an intermediate ordering temperature (about 7K). Subsequent heat capacity measurements on trial cast samples showed that the Pr_3Ni material ordered at about 11K and the $(\text{Pr}_{0.62}\text{Nd}_{0.38})_3\text{Ni}$ ordered at about 12K (Figure 3.10). The heat capacity magnitudes for both Pr_3Ni and $(\text{Pr}_{0.62}\text{Nd}_{0.38})_3\text{Ni}$ were rather low and research into these two materials was discontinued. The magnitude of the Nd_3Ni heat capacity, however, was sufficient to warrant further study in this project.

A second blended material, $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$, was also investigated to discover how mixing different lanthanide elements in the R_3Ni structure would affect heat capacity. Would the blended material have an intermediate ordering temperature and similar heat capacity peak breadth such as observed in $\text{Er}_{1-x}\text{Dy}_x\text{Ni}_2$?¹³ Or would the material order continuously between the Néel temperatures of Er_3Ni and Nd_3Ni creating a broad, plateau-like heat capacity such as observed in $\text{Er}(\text{Ni}_{1-x}\text{Co}_x)_2$?¹³ Figure 3.10 shows the heat capacity of a cast sample of $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$. There is a slight hump in the curve at about 11K with a peak magnitude of about 0.3 J/cm³K. While the "peak" in the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ curve is rather unimposing compared to the peaks found in the other materials, the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ heat capacity above ~8K is greater than that of the other materials, prompting us to include this material in our study.

Figure 3.10. Heat capacities of Er_3Ni , Nd , Nd_3Ni , Pr_3Ni , $(\text{Pr}_{0.62}\text{Nd}_{0.38})_3\text{Ni}$, $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$, and Pb at low temperatures

CHAPTER 4. EXPERIMENTAL METHODS

The Ames Laboratory centrifugal atomizer with rotating quench bath (CA/RQB) employs a spinning disk with a concentrically rotating liquid quench bath.³³ All atomization experiments occurred within an ultra-high purity argon atmosphere to suppress interstitial impurity atom (i.e., C, N, O) contamination. The atomization equipment, materials, and assembly and operation are described below followed by the powder characterization methods. Parameters for each atomization experiment are given in Table 4.1.

4.1 Equipment

4.1.1 Chamber

The Ames Laboratory centrifugal atomizer is operated within an inert atmosphere chamber (see Section 3.1, Figure 3.1) in order to minimize contamination of the material being processed by interstitial impurity atoms such as oxygen, nitrogen, and carbon. This is especially important in the case of lanthanide cryocooler alloys due to the rare earth elements' affinity for interstitial elements and the adverse effect that interstitial elements have on heat capacity (see Section 2.3). The chamber was mechanically evacuated to a total pressure of 20-70 millitorr and then backfilled with ultra-high purity (99.998%) argon to slightly over atmospheric pressure. For pure neodymium, the chamber was evacuated to at least 30 millitorr total pressure, backfilled, and the sequence repeated four times in order to remove as much gaseous contaminant as possible. The atomization disk, quench bath, driving motors, and melting system are all contained within the chamber.

4.1.2 Atomizer

The CA/RQB is a compact, rotating disk atomizer. The atomization disk is driven by a frequency controlled, 230 volt induction motor using a drive belt, drive shaft, and rotational bearings. This primary motor is mounted inside the controlled atmosphere chamber and the speed controller is mounted externally. The rotating quench bath is driven using a second motor, speed controller, etc., which allow the quench bath's speed and direction to be independent of

Table 4.1. Operational parameters for the atomization experiments

	CA-035	CA-039	CA-053	CA-057
alloy	Er ₃ Ni	Er ₃ Ni	Nd	Nd
liquidus (°C)	875	875	1021	1021
disk speed (rpm)	3510	3000	3250	4000
bath speed (rpm)	844	704	700	290
charge mass (g)	254	251	273	261
quenchant ^a	2 L of 100 cS	2 L of 100 cS	2 L of 100 cS	2 L of 100 cS
vacuum (millitorr)	45	250	28	100
disk type ^b	c	d	d	d
superheat (°C)	50	100	60	100
(fraction of liquidus temperature)	(0.044)	(0.087)	(0.046)	(0.077)

^a The quenchant in each case was Dow Corning 200 silicone fluid (polydimethyl siloxane). The volume of quenchant used and the quenchant viscosity are given (cS = centistokes).

^b Disk type c is the angled composite design and d is the low density composite design (see Section 3.2).

Table 4.1. (continued)

	CA-061	CA-065	CA-069
alloy	Nd ₃ Ni	Nd ₃ Ni	(Er _{0.5} Nd _{0.5}) ₃ Ni
liquidus (°C)	590	590	~725
disk speed (rpm)	6000	4500	4515
bath speed (rpm)	300	300	300
charge mass (g)	242	261	209
quenchant	2 L of 100 cS	2 L of 100 cS	2 L of 10cS
vacuum (millitorr)	110	30	20
disk type	d	d	d
superheat (°C)	75	150	200
(fraction of liquidus temperature)	(0.087)	(0.174)	(0.208)

the rotating disk. Both the disk's and the bath's rotational speeds are checked using a reflected light, digital tachometer prior to each atomization run. The current disk design uses a low density, alumina backing disk with a plasma sprayed tantalum surface (see Section 3.2). The liquid quench bath is a hollow aluminum cylinder, 29.25 cm i.d. and 5.1 cm inside height. An aluminum lid with a 14 cm center opening for introduction of the molten charge is attached to the top of the cylinder.

4.1.3 Melting system

The CA/RQB uses a 3 kHz, 50 kW power supply and an induction furnace for melting the charge materials. Electrical current from the power supply travels through a water-cooled coil of copper tubing, creating an induction

field within and about the coil. The induction field transfers energy to either a Ta susceptor (for the lanthanide intermetallic experiments) or a Ta crucible (for the Nd experiments) which, in turn, radiates this energy to the alumina crucible (for the lanthanide intermetallic experiments) or the charge material (for the Nd experiments). The charge temperature is monitored using a type 'R' thermocouple (Pt, Pt-13Rh) connected to a digital thermometer. The thermocouple is housed within the hollow stopper rod.

Due to the high chemical reactivity of lanthanide containing materials, it is important to choose the containment materials carefully to prevent excessive contamination of the charge. Previous gas atomization work with Er_3Ni had shown that there is little reaction between the liquid metal and high purity, high density Al_2O_3 , evidently due to the low melting temperature of Er_3Ni and the liquid's short residence time in the crucible.²¹ For this reason, high purity, high density Al_2O_3 crucibles (Coors AD998, 99.8% alumina) were used to contain the Er_3Ni , Nd_3Ni , and $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ charges (Figure 4.1a). The crucibles were cylindrical with a hemispherical bottom, 10 cm tall, 4.45 cm o.d., and 3.8 cm i.d. A 0.3 cm hole for charge pouring was bored through the

Figure 4.1. Schematics of the melting systems used for the a) lanthanide intermetallic compounds and b) Nd

bottom of each crucible using a diamond core drill with water as a lubricant. A high purity, high density alumina, one-end-closed tube (Alfa Degussit AL23, 99.8% alumina or Omega Omegatite 450, 99.8% alumina) was used to "stopper" the pour hole (for the lanthanide intermetallic runs) until the moment of pouring when a pneumatic actuator lifted the rod. The stopper rods were 7 mm o.d., 4 mm i.d., and had a hemispherical bottom that was hand ground to a point in order to insure a tight seal between the stopper rod and the crucible. Prior to each atomization experiment, the crucibles and stopper rods were baked in air at 800°C for 12 hours in order to remove moisture and volatile contaminants from the ceramic.

A tantalum melting system (crucible and stopper rod) was used for containment of the liquid Nd, consistent with accepted practice for high purity melting and casting of the lanthanide metals.³⁶ A cylindrical crucible (5 cm o.d., 10 cm tall) with a conical bottom was made from 0.75 mm thick tantalum sheet (Figure 4.1b). The stopper rod was made from 7 mm o.d. tantalum tubing with a conical insert of solid tantalum welded in one end for the seating surface. Prior to each atomization experiment, the tantalum pieces were baked out in vacuum at 1300°C for 12 hours to remove water and other volatile contaminants.

4.2 Materials

4.2.1 Lanthanide intermetallic compounds

The starting materials used for these experiments were obtained from the Ames Laboratory's Materials Preparation Center (MPC). The charge components for each experiment were alloyed as four separate buttons, each with the desired stoichiometry, by arc melting on a water-cooled copper hearth. Excess lanthanide was not added as earlier research (Reference 21) had shown no detectable loss of Er in the high purity alumina crucible. The buttons were broken into small pieces for easy charging and samples were taken for chemical analysis and differential thermal analysis. The actual charge masses were typically 200 to 250 grams per run. Chemical analyses of the starting materials are given in Table 4.2.

Table 4.2. Chemical analyses of the starting alloys

	CA-035	CA-039	CA-053	CA-057
alloy	Er ₃ Ni	Er ₃ Ni	Nd	Nd
Er ^a	75 (89.53)	75 (89.53)	--- ^b	---
Nd	---	---	balance	balance
Ni	25 (10.47)	25 (10.47)	---	---
O ^c	226 (26)	226 (26)	496 (55)	496 (55)
N	11 (1.1)	11 (1.1)	155 (15)	155 (15)
C	229 (20)	229 (20)	144 (12)	144 (12)
Si	ND ^d	ND	ND	ND
Al	19 (6)	19 (6)	---	---
Ta	---	---	ND	ND

^a units for Er, Nd, and Ni are atomic percent (weight percent)

^b --- entries were not investigated

^c units for O, N, C, Si, Al, and Ta are ppm atomic (ppm weight)

^d not detected using ICP-AES

Table 4.1. (continued)

	CA-061	CA-065	CA-069
alloy	Nd ₃ Ni	Nd ₃ Ni	(Er _{0.5} Nd _{0.5}) ₃ Ni
Er	---	---	37.58 (47.8)
Nd	75 (88.06)	75 (88.06)	37.74 (41.4)
Ni	25 (11.94)	25 (11.94)	22.85 (10.2)
O	3240 (422)	3240 (422)	1224 (149)
N	1264 (144)	1264 (144)	38 (4)
C	389 (38)	389 (38)	329 (30)
Si	ND	ND	ND
Al	ND	ND	ND
Ta	---	---	ND

4.2.2 Neodymium

The neodymium used in this study was produced from high-purity oxide by the Ames Laboratory's Materials Preparation Center. The purified metal was DC (direct current) arc-cast on a water-cooled copper hearth into 1 cm

diameter rods for easy loading into the crucible. Chemical analyses of the starting charge materials are given in Table 4.2.

4.3 Assembly and Operation

The assembly and operation of the CA/RQB are described in this section. Operational parameters for each atomization experiment are given in Table 4.1. All of the atomizer parts were cleaned and assembled immediately prior to each atomization experiment in order to insure the highest degree of system cleanliness. The parts were cleaned with a water based degreasing agent to remove residual quenchant and then wiped with a cloth dampened with ethyl alcohol.

After cleaning, the system was assembled in the following order:

- The quenchant drain pan was placed atop the atomizer frame and the quench bath was attached to its rotational bearing and locked to the bath drive shaft.
- An atomization disk was attached to the atomization drive shaft and secured with a set screw. The shaft and disk were threaded through the upper rotational bearing (built into the bath), through the driving sheave and finally through the lower rotational bearing. The shaft was secured with a set screw in the lower bearing and the driving sheave was secured to the shaft with a set screw.
- The bath lid was attached to the bath and sealed with silicone sealant and the quenchant fill tube was positioned.
- At this point, the disk and bath were spun and their speeds measured using a reflecting light tachometer to determine the controller settings required for the desired rotational speeds.
- For the intermetallic experiments: two layers of 0.25 cm ZrO_2 insulating felt were wrapped around the Ta susceptor which was then placed in the induction coil. A prepared crucible was placed within the
- For the Nd experiments: two layers of 0.25 cm ZrO_2 insulating felt were wrapped around the Ta crucible which was then placed in the induction coil.

susceptor with strips of ZrO_2 felt between the two to prevent contact.

- Next, the stopper rod was attached to the stopper control actuator and the chamber was closed. The stopper was seated, blocking the pour hole and some pressure was applied on the stopper by the pneumatic actuator to prevent movement of the stopper while loading the crucible. The charge was then loaded into the crucible and a low density Al_2O_3 lid was placed over the crucible to minimize heat loss.

After assembly of the system, the chamber was sealed, evacuated and backfilled with UHP Ar. The steps for a typical atomization experiment were as follows:

- The bath was started rotating and the quenchant introduced by overpressuring a storage container outside of the atomizer. The charge was heated using the power supply and induction coil setup described above.
- When the charge temperature was 100°C below the first liquid formation temperature, the disk was started spinning. Heating continued and the completely molten charge was held at the desired pour temperature for one or two minutes to allow complete homogenization of the melt.
- The stopper rod was lifted, allowing the molten charge to pour out of the crucible and onto the atomization disk. After all of the charge had poured (usually about 10-15 seconds), the induction power was shut off. The disk and bath were allowed to continue spinning for about 5 minutes to enhance quenchant cooling.
- After the system cooled to room temperature, the chamber was opened and the atomizer was disassembled.

The quenchant and powder were removed from the bath and filtered through a coarse cloth. The powder was then soaked for 5 minutes in heptane to dissolve the remaining oil, filtered, and rinsed repeatedly with clean heptane. Ethyl alcohol was used as a final rinse to remove heptane residue. The powders' attributes were then characterized using the methods described in Section 4.4.

4.4 Characterization

After cleaning, the powders were characterized according to the techniques given in Table 4.3, in order to determine the corresponding powder attributes. A description of each technique follows.

Table 4.3. Characterization techniques and the corresponding material attributes

Technique		Attribute
mechanical sieving	→	particle size distribution
scanning electron microscopy	→	shape and surface morphology
chemical analysis	→	contamination/stoichiometry
optical microscopy	→	solidification morphology
x-ray diffractometry	→	solidification phases
differential thermal analysis	→	solidification phases
low temperature calorimetry	→	heat capacity

4.4.1 Size analysis

Normally, a representative sample of powder is used for size analysis; however, due to the small batch sizes produced for this project, it was possible to perform an analysis on the entire yield and, therefore, achieve higher accuracy. The powders were dry-sieved by hand through a series of woven wire mesh screens, starting with the largest and ending with the smallest mesh sizes. The powder trapped on top of each screen was weighed and reported as being smaller than one mesh size and larger than the next; i.e., powder which passed the screen with 250 μ m openings was reported as -250 μ m while that which did not pass through the 212 μ m screen was reported as +212 μ m. Using this convention, material which was trapped between the two screens was reported as being in the -250+212 μ m size range. The powder within each range was stored in its own stoppered glass vial for further study.

4.4.2 Scanning electron microscopy (SEM)

In order to study particle shapes and surface morphologies, loose powder from each run was observed in the scanning electron microscope (SEM). The powder was mounted in a single particle layer on a piece of conductive double-faced tape. Back-scattered electron imaging (BSE) and secondary electron imaging (SE) were both used to observe the particles. Micrographs of the powders were taken for continued study and to aid in determining the effects of atomization parameters on particle shapes and morphologies.

4.4.3 Chemical analysis

The starting material (see Table 4.2) and powder from each of the atomization experiments were chemically analyzed to determine the amount of impurity pickup and any deviation from the desired stoichiometry. Oxygen and nitrogen concentrations were measured using a Leco TC-436 inert gas fusion analyzer. Metal concentrations were measured by dissolving the samples in 5% HNO_3 and analyzing the solution using an ARL Minitorch ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy) analyzer. Carbon concentrations were measured by combustion using a Horiba EMIA-520 analyzer. All measurements were performed by the Ames Laboratory's Material Preparation Center Analytical Services section.

4.4.4 Optical microscopy

It is important for each particle in a heat exchanger packed bed to be composed solely of the desired phase since different microstructural phases contribute differently to the specific heat (i.e., each phase has a different ordering temperature). In order to determine which phases were present, powders from each atomization run were mounted and cross-sectioned for microscopic observation. The powders were mounted in epoxy and ground and polished in the following manner:

- grind almost halfway through the first particle layer on 600 grit paper
- polish with 6 μm diamond paste to remove 600 grit scratches
- polish with 0.3 μm alumina/methanol slurry to remove final scratches.

lanthanide intermetallic compounds are very difficult to polish due to their brittle nature and powders are especially troublesome because of the propensity of particles to pull out of the epoxy and drag across the sample face, scratching other particles. Best results were achieved using light polishing pressure and short polishing times.

Chemical etching is necessary to provide topological contrast needed for the viewing of microstructural detail. Generally, acids which preferentially attack one phase of the matrix are used. Unfortunately, limited research has been done on etchants appropriate for the materials studied here and some experimentation was necessary. Roman's etch (20 ml lactic acid, 5 ml phosphoric acid, 10 ml acetic acid, 15 ml nitric acid, and 1 ml sulfuric acid) was first tried on the Er_3Ni . The etch revealed the microstructure well, but appeared to be slightly too strong. It was found that glycerin-40% nitric acid was a good etchant for the Er_3Ni materials but appeared to be too strong for the Nd_3Ni and $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ samples. Lesser nitric concentrations had no effect. Some detail was resolved in the Nd_3Ni samples when they were polished with an alumina/water slurry, however. The Nd samples were "automatically" etched during final polishing in the alumina/methanol slurry.

Optical micrographs of each sample were taken in the as-polished state and micrographs of etched samples were taken of those samples for which microstructural detail was resolvable.

4.4.5 X-ray diffractometry

X-ray diffractometry was used as another means to identify the solidification reaction product phases. Analysis was performed with the assistance of Mr. Kevin Dennis on powder from one Er_3Ni experiment, one Nd_3Ni experiment, and the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ experiment. No analysis was performed on the Nd powders since any second phases would be interstitial compounds which, according to chemical analyses, would be of such small volumes as to be undetectable (detectable limit by x-ray diffractometry is about 10 vol.%). The powders were crushed immediately prior to scanning in order to eliminate any preferred orientation and mounted on a glass slide using a

small amount of vacuum grease. $\text{CuK}\alpha$ radiation ($\lambda_{\text{mean}} = 1.5418\text{\AA}$) and step scanning of 3 seconds and 0.05° per step were used.

4.4.6 Differential thermal analysis

As a final check on microstructural phases, differential thermal analysis was performed on both starting materials and powders for one Er_3Ni run, one Nd_3Ni run, and the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$. Endothermic events during heating indicate phase change in the sample and, when correlated with the appropriate phase diagram, can indicate what the secondary (or ternary, quaternary, etc.) phase may be. The samples were analyzed with the assistance of Mr. Kevin Dennis using a Perkin-Elmer 1700 DTA with 50cc/minute flowing UHP Ar and a heating rate of 5°C per minute.

4.4.7 Low temperature calorimetry

A zero magnetic field, adiabatic heat-pulse-type calorimeter was used for measuring low temperature heat capacities.³⁷ Accuracies for the measurements are estimated to be $\pm 1\%$ below 20K.³⁸ Because of the configuration of the calorimeter, bulk samples with parallel faces were required. A small, boron nitride hot press die was used to consolidate Er_3Ni powder into a compact about 0.5 cm in diameter by 0.75 cm tall. The powder was pressed in a vacuum furnace at 700°C [$973\text{K} \cong (0.84)T_{\text{liquidus}}$ for Er_3Ni] for 88 hours with a pressure of 0.15 MPa. Similar consolidation of the Nd was done at 800°C [$1073\text{K} \cong (0.83)T_{\text{melting}}$ for Nd] for 20 hours. Consolidation of Nd_3Ni in this manner was unsuccessful. In order to decrease consolidation time, (and so minimize grain growth, impurity diffusion, etc.) the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powder was hot isostatically pressed (HIPed) at 600°C for 4 hours at 275MPa in a tantalum can. The resultant "slug" appeared to be highly densified and had good physical strength. Parallel faces were formed on each of the three pressed samples by light grinding on 600 grit SiC paper.

Additional measurements were performed by Mr. Mike Hundley of the Los Alamos National Laboratory on one Er_3Ni powder, one Nd_3Ni powder, and the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powder using a thermal relaxation-type microcalorimeter capable of measuring the heat capacity of loose particles.³⁹ Because the heat

exchanger matrix is generally formed of loose powder, heat capacity measurements on unconsolidated material should be more representative of how the material will behave in actual use.³⁹

CHAPTER 5. RESULTS

In this section, the results from each characterization step and overall observations of the atomization process will be presented with limited discussion. Detailed explanations including causal relationships will be presented in Chapter 6. Experimental observations for each atomization experiment are presented in Table 5.1. The reader may wish to refer to Table 4.1 for the atomization parameters. Characterization was performed on particles in the $-250+212\mu\text{m}$ size range as this range is currently believed to contain the ideal particle size for cryocooler heat exchangers.

5.1 Skulls

One of the most important parameters affecting the quality of centrifugal atomization is the atomization disk. A poor disk design may result in wide particle size distributions and may skew the mean particle size (see Section 3.2). Insight into the quality of the disk design may be gained by studying the "skulls" or solid metal remaining on the disks after atomization (Figures 5.1-5.7). An ideal skull should be consistently thin across the surface of the disk and should extend to the edge of the disk. A consistently thick skull indicates either too low superheat of the melt or a disk which failed to heat quickly. It is not apparent how Pratt & Whitney can achieve high-quality atomization using a water-cooled disk which should, in theory, form a thick, irregular skull. A skull of inconsistent thickness will cause the liquid droplets to leave the disk before reaching the disk periphery and will result in a larger than desired mean particle size and a wide particle size distribution.

5.2 Particle Size Distributions

Size analysis data are reported in three configurations in Figures 5.8-5.14. The top curve in each figure shows the cumulative amount of powder passing a given sieve size as a percentage of the total mass of powder recovered, not including powder larger than the largest sieve size (i.e., the "oversize" fraction). The second and third curves show the amount of powder passing a sieve size as a percentage of recovered powder mass (again excepting the

Table 5.1. Characteristics of the atomized powders

	CA-035	CA-039	CA-053	CA-057
alloy	Er ₃ Ni	Er ₃ Ni	Nd	Nd
disk speed (rpm)	3510	3000	3250	4000
particle shape ^a	spherical	flattened spheres	blocky	semi- spherical
skull	thick- irregular	thin - some ligaments	thick-long ligaments	thin-some ligaments
d ₁₆ ^b	270	285	285	240
d ₅₀ ^c	370	430	430	335
d ₈₄ ^d	525	575	570	470
σ_g ^e	1.39	1.42	1.41	1.40
% oversize ^f	40.4	18.3	19.8	18.2

^a Average particle shape in the -250+212 μ m range.

^b The screen hole diameter through which 16% of the particles pass; one standard deviation.

^c The screen hole diameter through which 50% of the particles pass; the median particle size.

^d The screen hole diameter through which 84% of the particles pass; one standard deviation.

^e The geometrical standard deviation. Defined as $\sigma_g = (d_{84}/d_{16})^{1/2}$

^f The amount of particulate larger than the largest sieve size (includes some skull fragments) as a percentage of the total powder mass.

Table 5.1. (continued)

	CA-035	CA-039	CA-053
alloy	Nd ₃ Ni	Nd ₃ Ni	(Er _{0.5} Nd _{0.5}) ₃ Ni
disk speed (rpm)	6000	4500	4515
particle shape	flakes	flattened spheres	irregular - flattened
skull	thick - many ligaments	very thin - no ligaments	very thin - no ligaments
d ₁₆	160	180	180
d ₅₀	270	280	285
d ₈₄	420	410	405
σ _g	1.62	1.51	1.50
% oversize	13.0	5.4	5.4

Figure 5.1. Atomization skull from CA-035 (Er_3Ni)

Figure 5.2. Atomization disk from CA-039 (Er_3Ni)

Figure 5.3. Atomization disk from CA-053 (Nd)

Figure 5.4. Atomization disk from CA-057 (Nd)

Figure 5.5. Atomization disk from CA-061 (Nd_3Ni)

Figure 5.6. Atomization disk from CA-065 (Nd_3Ni)

Figure 5.7. Atomization disk from CA-069 ($[\text{Er}_{0.5}\text{Nd}_{0.5}]_3\text{Ni}$)

"oversize" fraction) and charge mass, respectively. The second curve suggests the breakup efficiency of the atomizer while the third curve indicates how efficient the atomizer is on a production basis.

5.3 Particle Shapes

Shape analysis of the powders is qualitative and determined solely by SEM observation of the loose powders. Figures 5.15-5.21 show SEM images of the powders from each of the seven atomization experiments. Figure 5.22 shows powders from the first Nd_3Ni experiment which provide evidence that powder shape becomes more spherical as the powder diameter decreases due to the higher surface to volume ratio.

5.4 Powder Chemistries

Results of the chemical analyses on the atomized powders and the starting materials are given in Table 5.2. Each material was analyzed for its component elements in order to detect deviations from stoichiometry. Analyses were also performed for oxygen, nitrogen, and carbon as they may directly affect heat

Figure 5.8. Size analysis of CA-035 (Er_3Ni)

Figure 5.9. Size analysis of CA-039 (Er_3Ni)

Figure 5.10. Size analysis of CA-053 (Nd)

Figure 5.11. Size analysis of CA-057 (Nd)

Figure 5.12. Size analysis of CA-061 (Nd_3Ni)

Figure 5.13. Size analysis of CA-065 (Nd_3Ni)

Figure 5.14. Size analysis of CA-069 ($[\text{Er}_{0.5}\text{Nd}_{0.5}]_3\text{Ni}$)

Figure 5.15. SEM micrograph of CA-035 (Er₃Ni) powder; -212+180μm

Figure 5.16. SEM micrograph of CA-039 (Er₃Ni) powder; -250+212μm

Figure 5.17. SEM micrograph of CA-053 (Nd) powder; -250+212 μ m

Figure 5.18. SEM micrograph of CA-057 (Nd) powder; -250+212 μ m

Figure 5.19. SEM micrograph of CA-061 (Nd₃Ni) powder; -250+212 μ m

Figure 5.20. SEM micrograph of CA-065 (Nd₃Ni) powder; -250+212 μ m

Figure 5.21. SEM micrograph of CA-069 ($[\text{Er}_{0.5}\text{Nd}_{0.5}]_3\text{Ni}$) powder; -250+212 μm

capacity and the shape of the magnetic ordering peak. The powders were analyzed for silicon to see if there was appreciable pick-up from the quenchant and for tantalum, in the Nd cases, or aluminum, in the lanthanide intermetallic cases, to investigate contamination from the crucibles.

5.5 Solidification Product Phases

Since it is desirable for the heat exchanger material to order at a given temperature, it is necessary for the particulate composing the exchanger to be all of the desired phase. In order to determine if this was so, the solidification reaction phases were examined by observation of the microstructure, x-ray diffractometry, and differential thermal analysis.

5.5.1 Microstructures

In order to study solidification phases and porosity, the powders were cross-sectioned, polished, and etched as described in Section 4.4.4. As-polished

-250+212 μ m

-180+150 μ m

-125+106 μ m

-106+90 μ m

Figure 5.22. SEM micrographs of CA-061 (Nd_3Ni) powder showing increasing roundness with decreasing particle size

Table 5.2. Comparative chemical analyses of the starting materials and atomized powders

	CA-035		CA-039		CA-053		CA-057	
	Er ₃ Ni		Er ₃ Ni		Nd		Nd	
	<u>starting</u>	<u>atomized</u>	<u>starting</u>	<u>atomized</u>	<u>starting</u>	<u>atomized</u>	<u>starting</u>	<u>atomized</u>
Er ^a	75	76.04	75	75.04	--- ^b	---	---	---
Nd	---	---	---	---	balance	balance	balance	balance
Ni	25	23.96	25	24.96	---	---	---	---
O ^c	226	4326	226	5867	496	7735	496	7482
N	11	160	11	280	155	556	155	804
C	229	479	229	560	144	3125	144	1659
Si	ND ^d	ND	ND	ND	ND	ND	ND	ND
Al	ND	ND	ND	ND	---	---	---	---
Ta	---	---	---	---	ND	ND	ND	ND

^a units for Er, Nd, and Ni are atomic percent

^b --- not analyzed

^c units for O, N, C, Si, Al, and Ta are ppm atomic

^d not detected using ICP-AES

Table 5.2. (continued)

	CA-061		CA-065		CA-069	
	Nd ₃ Ni		Nd ₃ Ni		(Er _{0.5} Nd _{0.5}) ₃ Ni	
	<u>starting</u>	<u>atomized</u>	<u>starting</u>	<u>atomized</u>	<u>starting</u>	<u>atomized</u>
Er	---	---	---	---	37.5	37.45
Nd	75	74.80	75	75.20	37.5	37.84
Ni	25	25.20	25	24.80	25	24.71
O	3240	5790	3240	5329	1224	5615
N	1264	1009	1264	693	38	564
C	389	1003	389	614	329	899
Si	ND	ND	ND	ND	ND	ND
Al	ND	ND	ND	ND	---	---
Ta	---	---	---	---	ND	ND

optical micrographs for each material are given in Figures 5.23-5.29. Optical micrographs of etched cross-sections are shown in Figures 5.30-5.32.

5.5.2 X-ray diffraction data

X-ray diffractometry was used as another determination of solidification reaction phases. XRD traces for one Er_3Ni , one Nd_3Ni , and the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powder are shown in Figures 5.33-5.35. XRD was not performed on the Nd powders since any second phases would be interstitial compounds which, according to chemical analyses, would be of such small volumes as to be undetectable by x-ray diffractometry (i.e., < 10 vol. %).

5.5.3 Differential thermal analysis data

Differential thermal analyses (DTA) were performed on the atomized powders as well as the starting materials (except in the case of Nd) as a third indicator of microstructural phases present in the atomized particles. Figures 5.36-5.38 are heating traces of normalized differential temperature versus

Figure 5.23. Optical micrograph of CA-035 (Er_3Ni) powder cross-section as-polished; $-250+212\mu\text{m}$

Figure 5.24. Optical micrograph of CA-039 (Er₃Ni) powder cross-section as-polished; -250+212μm

Figure 5.25. Optical micrograph of CA-053 (Nd) powder cross-section as-polished; -250+212μm

Figure 5.26. Optical micrograph of CA-057 (Nd) powder cross-section as-polished; -250+212μm

Figure 5.27. Optical micrograph of CA-061 (Nd₃Ni) powder cross-section as-polished; -250+212μm

Figure 5.28. Optical micrograph of CA-065 (Nd₃Ni) powder cross-section as-polished; -250+212μm

Figure 5.29. Optical micrograph of CA-069 ([Er_{0.5}Nd_{0.5}]₃Ni) powder cross-section as-polished; -250+212μm

Figure 5.30. Optical micrograph of CA-035 (Er_3Ni) powder cross-section etched with 40% HNO_3 in glycerin; -250+212 μm

Figure 5.31. Optical micrograph of CA-053 (Nd) powder cross-section etched with alumina/methanol slurry; -250+212 μm

Figure 5.32. Optical micrograph of CA-061 (Nd₃Ni) powder cross-section etched with alumina/water slurry; -250+212µm

Figure 5.33. X-ray diffraction pattern of CA-039 (Er_3Ni) powder; calculated Er_3Ni data points and JCPDS Er_3Ni_2 data points included for reference

Figure 5.34. X-ray diffraction pattern of CA-065 (Nd₃Ni) powder; calculated data points included for reference

Figure 5.35. X-ray diffraction pattern of CA-069 ($\text{Er}_{0.5}\text{Nd}_{0.5}\text{I}_3\text{Ni}$) powder

Figure 5.36. DTA traces for CA-039 (Er_3Ni) arc-cast starting material and as-atomized powder; equilibrium reactions from the Er-Ni phase diagram are shown for reference

Figure 5.37. DTA traces for CA-065 (Nd_3Ni) arc-cast starting material and as-atomized powder; equilibrium reactions from the Nd-Ni phase diagram are shown for reference

Figure 5.38. DTA traces for CA-069 ($[\text{Er}_{0.5}\text{Nd}_{0.5}]_3\text{Ni}$) arc-cast starting material and as-atomized powder; four endothermic reactions are noted for the powder

temperature for Er_3Ni , Nd_3Ni , and $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powders ($-250+212\mu\text{m}$) plotted with traces for the starting materials. Vertical lines indicating the equilibrium phase transformation temperatures are superimposed on Figures 5.36 and 5.37. Table 5.3 summarizes the DTA results.

5.6 Low Temperature Heat Capacities

Heat capacity measurements were made on at least one run of each material using either an adiabatic-heat-pulse type calorimeter or a thermal relaxation microcalorimeter. Adiabatic heat pulse calorimetry was performed at the Ames Laboratory by Mr. Mark Gailloux and thermal relaxation microcalorimetry was performed at Los Alamos National Laboratory by Mr. Mike Hundley. In both cases, there was no magnetic field applied. Heat capacity versus temperature curves are shown in Figures 5.39-5.42 with data for Pb included as a reference. A summary of peak temperatures and peak heat capacities are given in Table 5.4.

Table 5.3. Summary of the differential thermal analysis results on the atomized powders

	Er_3Ni	Nd_3Ni	$(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$
apparent liquidus	870°C	605°C	770?°C
phase diagram liquidus	875°C	590°C	??
apparent eutectic/peritectic	765°C eut.	(570°C) ^a	690°C, 695°C, 760°C
phase diagram	765°C eut.	565°C eut.#1	??
eutectic/peritectic	845°C per.	570°C eut.#2	

^a Apparent eutectic melting seen in the starting material.

Figure 5.39. Volumetric heat capacity of CA-035 (Er_3Ni) arc-cast starting material and hot-pressed powder; the Pb heat capacity is shown for reference

Figure 5.40. Volumetric heat capacity of CA-057 (Nd) arc-cast starting material and hot-pressed powder; the Pb heat capacity is shown for reference

Figure 5.41. Volumetric heat capacity of CA-065 (Nd₃Ni) arc-cast starting material and hot-pressed powder; the Pb heat capacity is shown for reference

Figure 5.42. Volumetric heat capacity of CA-069 ($[\text{Er}_{0.5}\text{Nd}_{0.5}]_3\text{Ni}$) arc-cast starting material and HIPed powder; the Pb heat capacity is shown for reference

Table 5.4. Temperatures and magnitudes of volumetric heat capacity peaks

	CA-039	CA-053	CA-065	CA-069
Material	Er ₃ Ni	Nd	Nd ₃ Ni	(Er _{0.5} Nd _{0.5}) ₃ Ni
Temperature (K)				
charge ^a	7.3	8.2	11.1	10.5 ^d
compact ^b	6.6	7.7	6.4	10.5 ^d
powder ^c	7.6	--	--	--
Magnitude (J/cm ³ K)				
charge	0.83	0.35	1.34	0.37 ^d
compact	0.41	0.35	0.61	0.33 ^d
powder	0.43	--	--	--

^a Measurements on the charge material.

^b Measurements on hot pressed or HIPed compacts.

^c Measurements on loose powder.

^d No peak - data measured at break in the heat capacity curve.

CHAPTER 6. DISCUSSION

6.1 Operation

The intent of this research project was to develop a practical method for the production of lanthanide intermetallic compound and lanthanide metal powders for use as heat exchanger matrix materials in cryocoolers. The first indicator of the success of the project was the reproducible operation of the equipment during experimentation. There were no serious complications concerning the atomization chamber, power supply, motors, or any other piece of hardware. There were minor vacuum leaks which had to be corrected as with any piece of vacuum equipment and also design complications arising from the limited space within the chamber. These setbacks were minor and had no lasting effect on the operation of the equipment.

As with any process development project, it is important to consider how the system can be scaled up for commercial use. Efficiency is paramount for commercial production, especially when considering the high cost of the lanthanide metals. In order to study the efficiency of the technique (efficiency $\equiv$ powder yield within the desired size range) and how the efficiency may be controlled, we examined the atomization skulls and the effects of superheat on yield within selected particle size ranges.

6.1.1 Skulls

In Figures 5.1-5.7, the atomization disks from the seven atomization experiments are shown. The first experiment, CA-035 (Er_3Ni), used the angled, composite disk made of machinable alumina with a thin Ta sheet surface (0.15 mm). The skull from this experiment was rather thick with a central depression where the molten charge impacted. Correlating Figure 5.1 with Figure 3.3, it appears that the liquid metal splashed upon initial contact with the disk and built a concentric ridge halfway to the edge of the disk. We can tell by the frozen metal ligaments extending from this ridge that atomization did not occur exclusively at the edge of the disk, as desired, but also from the ridge. Equation 2.4 suggests that atomization from this ridge skewed the particle size distribution to higher sizes since the disk diameter, D ,

was effectively the diameter of the raised ridge. From the evidence provided by this skull, it was decided to design a new disk shape and construction technique to utilize a lower density, lower thermal conductivity disk material to reduce excessive skull buildup and a smooth atomization surface profile to prevent splashing of the liquid charge material.

The new disk design was used for the second and subsequent atomization experiments. In Figure 5.2, we see the atomization disk from the second experiment, CA-039 (Er_3Ni). The skull was much thinner and of a more consistent thickness than the skull for the first experiment. A few ligaments extend just past the disk edge indicating atomization at or near the disk periphery, their diminutive size suggests that the atomization mode was near direct drop formation (see Section 2.5).

The skull from the third atomization experiment, CA-053 (Nd#1), was somewhat thick and extended past the edge of the disk. This excessive amount of build-up is attributed to the low superheat (60°C or $0.26T_m$ for Nd) used for this experiment. Ligaments are present at the edge of the disk and are rather thick at their base indicating that they may have been quite long during atomization and that the atomization mode was ligament disintegration bordering on film disintegration (see Section 2.5).

For the fourth atomization experiment, CA-057 (Nd#2), the superheat was increased to 100°C or $0.29T_m$ for Nd. Increasing the superheat appeared to result in a much thinner skull and, thus, to shift the atomization mode from ligament or film disintegration and closer to direct drop formation. This is evidenced by the narrower, near-normal particle size distribution for CA-057 (Nd) compared to the wider, skewed distribution seen for the CA-053 (Nd).

The fifth experiment, CA-061 (Nd_3Ni #1), resulted in a skull which was thick and irregular and which exhibited ligament disintegration from a large area of the disk surface. The superheat in this case was 75°C or $0.40T_m$ for Nd_3Ni and was presumed to be high enough to prevent the formation of a heavy skull. The disk speed for this experiment was 6000 rpm, 50% faster than any previous experiment, and the high speed may have resulted in increased cooling of the disk during operation and, so, led to the formation of a heavy skull. For the second Nd_3Ni experiment, CA-065, the superheat was

raised to 150°C ($0.49T_m$) and the disk speed lowered to 4500 rpm. The skull in this case was very thin and even and suggested that the atomization mode was very near direct drop formation.

Due to the success of the sixth experiment, the seventh experiment, CA-069 $[(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}]$, was run with the same superheat and disk speed as the sixth experiment, $0.49T_{\text{liq}}$ and 4500 rpm, respectively. The skull from the seventh experiment was the best to date being very thin and even. There was virtually no erosion of the disk surface and the absence of ligaments suggests that the atomization mode was very near direct drop formation.

From the evidence provided by the atomization skulls, it appears that the current disk design is very near optimal for lanthanide metals and lanthanide intermetallic compounds. All of the skulls indicated good wetting of the Ta disk surface by the molten metal, unlike the apparent nonwetting seen in the case of Ni_3Al atomized with an identical disk (Figure 6.1). The disks exhibited little erosion and there was no evidence of thermal shock. The disks are relatively simple to fabricate due to the machinability of the low density alumina board.

Figure 6.1. Poor disk wetting shown for a Ni_3Al atomization experiment

6.1.2 Powder yield

Efficiency is a prime concern with any processing technique, especially when the material being processed is particularly expensive as are the lanthanide materials used in cryocooler heat exchangers. The key indicator of efficiency for an atomization process is the yield of material in the desired size range. Yields as a function of superheat for each atomization experiment are shown in Figure 6.2 along with the corresponding disk speeds. Figure 6.2 shows the yield from each experiment for four size ranges as a percentage of powder mass (not including the oversize fraction mentioned above). The disk speeds are plotted to show that yield is affected more by the superheat than by the disk speed, especially for the final three experiments.

In the above section, Section 6.1.1, it was inferred that atomization mode plays a direct role in determining the shape of the particle size distribution and that atomization mode can be controlled by the shape of the skull that forms on the atomization disk. Since it was established that the skull shape can be controlled by controlling the superheat, it follows that the atomization mode, and thus the shape of the size distribution, can be controlled by controlling the superheat. If we examine Figure 6.2, we notice that, in general, those experiments with the highest superheat also had the highest yields which indicates that superheat does have an effect on atomization mode and, thus, an effect on powder yield.

As stated previously, it is important that this technique be scalable for commercial usage and also that the yield (efficiency) from the technique be high, especially due to the high cost of lanthanide materials. It should be noted that the yield quality has improved consistently throughout this project and should improve even more for longer atomization times. With typical atomization times during this research of 10-15 seconds, it is not likely that the process performed in a steady-state mode for more than 7-10 seconds. Particles atomized during the first few and last few seconds of each experiment are most likely to fall outside of the steady state size distribution and, thus, skew the overall particle size distribution, creating so-called "end effects." If the atomization experiments were, say, 60 seconds long, the time allotted to the end effects would be approximately the same, and we would have steady-state

Figure 6.2. Powder yield as a function of superheat

atomization for 45-50 seconds. According to the above argument, this longer steady-state atomization time should result in narrower particle size distributions and higher yields.

6.2 Size Distributions

From the particle size distribution graphs, we see that the atomizer's ability to produce finer particles with narrower size distributions has increased steadily since the beginning of the project. This increase in efficiency may be attributed to increases in both superheat and disk speed which promote a more optimum atomization mode and smaller particle size, respectively. Using the same argument presented in Section 6.1.2, longer atomization times (on a production scale) should result in narrower size distributions and, possibly, a smaller median particle size.

Production efficiency has been the principal motive behind this project as expounded upon in the previous two sections discussing powder yield. Another aspect of efficiency lies in the predictability of the process. Chapter 2 explained that the heat exchanger matrix should be composed of particles of a specific size. Naturally, this implies that we would wish to be able to control the average particle diameter by proper control of the atomization parameters. Champagne and Anger have developed empirical equations relating particle diameter to material and processing parameters for the rotating electrode process (REP).²⁸ The similarity between the REP process and the CA/RQB process allowed Funke to produce Ag powders with average diameters very near those predicted by Champagne and Anger's equations.³³ For the research documented in this manuscript, it was also desired to test the predictability of the CA/RQB process. However, Champagne and Anger's equations require knowledge of liquid density and liquid surface tension, neither of which appear to have been measured for Er_3Ni or Nd_3Ni (or any other lanthanide intermetallic compound). Our predictability investigation was, therefore, limited to the two Nd experiments.

For Nd metal, the liquid density, ρ , is about 6688 kg/m^3 and the surface tension, γ , is about 0.689 N/m at 1021°C .⁴⁰ For this research, the disk

diameter, D , was 50 mm (0.05 m) and the liquid supply rate, Q , was about $2.41 \times 10^{-6} \text{ m}^3/\text{s}$. Equation 2.4 then becomes:

$$d_{50} = 3.65 (1/\omega) (0.689/6688)^{0.46} (1/0.05)^{0.58} (2.41 \times 10^{-6})^{0.06} \quad \text{Eqn. 6.1}$$

For the first Nd experiment, CA-053, the disk speed was 3250 rpm or 340 radians/s. Substituting into Equation 6.1, we calculated $d_{50} = 0.000411 \text{ m}$ or $411 \mu\text{m}$. Consulting Table 5.1, we see that this is only $19 \mu\text{m}$ from the experimentally determined mean particle diameter. Even better agreement is found for the second Nd experiment, CA-057 ($\omega = 4000 \text{ rpm}$ or 419 radians/s), where d_{50} was calculated to be $334 \mu\text{m}$ and experimentally determined to be $335 \mu\text{m}$. The fantastic accuracy of this calculation may be fortuitous, however, since the liquid density and surface tension change with temperature and the actual liquid temperature at the point of atomization is not precisely known. Error is also encountered in experimentally determining the median particle diameter since it usually falls in the middle of a sieve size range, e.g., between 250 and $212 \mu\text{m}$ screen sizes, and the size distribution between each size boundary is unknown. These errors are small, however, compared to the magnitude of the particle diameter and median particle size predictions still appear to be accurate to $\pm 2\text{-}3\%$.

6.3 Particle Shapes

The most difficult aspect of this project has been to determine how to control the shape of the atomized particles. The Cu and Ag-15%Cu particles atomized during the development work were rather spherical as were the Ag particles atomized by Funke (Ref. 33). For the Nd and lanthanide intermetallic compounds, however, the shapes ranged from somewhat spherical to flake. The first experiment, CA-035 (Er_3Ni), produced particles which were mainly spherical and most likely usable in a heat exchanger. Particles from the second experiment, CA-039 (Er_3Ni), appear to have spherodized as liquid droplets and then been flattened upon impact with the quenchant.⁴⁰ The droplets then apparently solidified before being able to respherodize. While these particles are not spherical, their physical strength should not be reduced as they exhibit

no sharp angles which would act as crack initiators. Shifting of the packed bed due to alignment of the particles may, however, be a potential problem.

While the Nd particles from the CA-053 and CA-057 experiments are more spherical than the CA-039 (Er_3Ni) particles, they are not as spherical as the Cu and Ag-15%Cu particles. This decrease in sphericity may easily be explained by the difference in surface tensions for each of the metals: $\gamma_{\text{Cu}} = 1.285 \text{ N/m}$, $\gamma_{\text{Ag}} = 0.903 \text{ N/m}$, and $\gamma_{\text{Nd}} = 0.689 \text{ N/m}$.⁴¹ If we are correct in assuming that the particles are distorted upon impact with the quenchant and that post-impact respherodization is driven by surface tension, then it is obvious from the surface tension values that Cu will respherodize slightly more easily than Ag and much more easily than Nd. Since we cannot increase the surface tension of Nd, we must allow Nd particles more time for respherodization prior to solidification, i.e., an increase in superheat (and the subsequent increase in post-impact respherodization time) should result in more spherical particles. This appears to be exactly what occurred in the CA-061 (Nd_3Ni) and CA-065 (Nd_3Ni) experiments described next.

For the fifth experiment, CA-061 (Nd_3Ni), the disk speed was increased to 6000 rpm in order to shift the size distribution curve toward smaller sizes. It is believed that this increase in disk speed (and the subsequent increase in droplet momentum), along with less than optimum superheat was responsible for the flake shape of most of the particles larger than $90\mu\text{m}$ diameter. When the superheat was increased for the CA-065 (Nd_3Ni) experiment (and the disk speed lowered, somewhat) the particles were more spherical. Particles from the seventh experiment, CA-069 ($[\text{Er}_{0.5}\text{Nd}_{0.5}]_3\text{Ni}$), also appeared to have been flattened upon impact with the quenchant and failed to completely respherodize in the time before solidifying. The particles are slightly more flattened than those from CA-039 (Er_3Ni).

Although most of the powders produced during this research may be usable in cryocooler heat exchangers, it is still important to determine how particles of lanthanide materials (and other low surface tension materials) can be produced with a near-spherical shape. We have already mentioned superheat as a possible control parameter, and there are certainly other parameters which may affect particle shape. Another parameter which was considered late in this

research was the viscosity of the liquid quenchant. From a simple mechanical viewpoint, it is apparent that a quenchant with a high viscosity is more resistant to flow and will, thus, cause greater deformation of an impacting liquid droplet and slower respherodization than a quenchant with a lower viscosity. For this reason, the seventh experiment utilized quenchant which was chemically identical to that used for the previous experiments, but which had a viscosity one-tenth that of the previous quenchant (10 centistokes compared to 100 centistokes). This difference in viscosity may account for the greater "roundness" of the CA-069 ($[\text{Er}_{0.5}\text{Nd}_{0.5}]_3\text{Ni}$) powder compared to the CA-065 (Nd_3Ni) powder. In order to formulate a more conclusive statement about the effect of quenchant viscosity, it would be necessary to perform additional atomization experiments where quenchant viscosity is the only control parameter varied. It may be possible that a quenchant of even lower viscosity, say 1 centistoke, may decrease droplet deformation and enhance respherodization such that near-spherical particles are routinely produced.

6.4 Powder Chemistries

Interstitial contamination was less than found in lanthanide compound powders produced using other processes, such as the gas atomization of Er_3Ni , where x-ray detectable Er_2O_3 has been noted and oxygen impurities of 2600 ppm weight (22,700 ppm atomic) have been reported.^{17, 21} In this study, the Nd powders had the highest oxygen and carbon impurities, while the Nd_3Ni powders experienced the most nitrogen contamination.

In Section 2.3.1, it was noted that interstitial impurities can reduce the magnitude of the heat capacity peak by impeding the alignment of the magnetic spins. It, therefore, seemed desirable to minimize the amount of impurity contamination experienced by the lanthanide material during processing. However, some impurities may actually be beneficial since a high, narrow specific heat peak is not as useful as a lower, broader peak for cryocooler applications. The lower, broader peak would allow the heat exchanger to operate somewhat efficiently (efficiency is related to heat capacity) over a wide temperature range whereas the high, narrow peak would allow very efficient operation in the temperature regime of the peak, but lower

efficiency at temperatures away from the peak (see Figure 6.3). Furthermore, the effect of impurities on the heat capacity can not be estimated simply by analyzing the impurity concentration in the material. Referring to Figure 6.4, we see that as-atomized Er_3Ni powder (loose spheres) has a broader heat capacity peak than heat treated Er_3Ni powder (hot-pressed). As stated previously, atomized powders are rapidly solidified and, so, can trap impurities

Figure 6.3. Volumetric heat capacities of Er_3Ni arc-cast starting material and as-atomized powder

Figure 6.4. Volumetric heat capacities of Er_3Ni as-atomized powder and hot-pressed powder

(i.e., interstitial impurities = C, O, N, H) in the crystal lattice where they impede electronic spin realignment and broaden the heat capacity peak. When the powder is heat treated during consolidation, i.e., hot pressing or HIPing, some of the impurities may migrate to grain boundaries or defects within the crystal or form compounds with the matrix atoms (e.g., oxides or carbides). In either case, these impurities should provide less opposition to spin realignment

compared to the as-solidified sample and, thus, the heat capacity peak will become higher and narrower, as demonstrated in Figure 6.4.

ICP-AES chemical analyses of the atomized powders indicated that there was no detectable contamination from the crucibles (Al or Ta) or the quenchant (Si). There is, however, indirect evidence of a chemical reaction between the atomized powders and the quenchant. It was found that Ni_3Al powder quenched in the silicone fluid dissolved very slowly (> 45 minutes required) in a heated 50% nitric acid (HNO_3)/water solution prior to ICP-AES analysis and, after dissolution, small "shells," apparently from the particle surfaces, remained undissolved in the liquid. Conversely, the material from the starting ingot dissolved quickly and completely in the 1:1 HNO_3 solution. The powder did dissolve completely (including "shells"), however, when hydrofluoric acid (HF) was added to the solution, but silicon was still below detection limits, possibly due to loss of the silicon as SiF_4 .⁴² It was also observed that 0.5 g of pure Nd powder (-250+212 μm) left in an open container for 6 weeks experienced no detectable mass change, i.e., less than 0.0001 g, and minor surface discoloration, indicating limited oxidation. Comparatively, even a pure Nd metal *ingot*, when exposed to air, will heavily oxidize within a few days. Further research should be encouraged to study the reaction of particles with the quenchant and how this reaction may be controlled to create passive surface coatings, sintering aid coatings, etc., during processing.

6.5 Solidification Product Phases

The solidification product phases for one Er_3Ni powder, one Nd_3Ni powder, and the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powder were investigated in order to correlate the microstructural phases within the particles to the experimental heat capacity data. It was determined that the Er_3Ni powder contained a small amount of Er_3Ni_2 , the Nd_3Ni was apparently single phase and the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powder contained one major phase and three minor phases. Details of these results will be discussed in the sections that follow.

6.5.1 Microstructures

Microstructural analysis by optical microscopy was not highly informative since little research has been done on the solidification of these materials and it is difficult to identify phases by observation alone. There was also difficulty in locating etchants that were effective for producing microstructural contrast with these materials. Microscopy of the etched cross-sections did provide some information on the solidification morphology within the powders. Figure 5.30 shows that the Er_3Ni particles ($-250+212\mu\text{m}$) solidified with a dendritic morphology in the particle center and a finer, cellular morphology near the particle edge. The fine-scale microstructure in the particle edge is similar to the apparently partitionless "rim" seen in Ag-15%Cu particles atomized during the development portion of this project (see Figure 6.5). Cross-sectioned and

Figure 6.5. Optical micrograph of Ag-15%Cu; $-150+125\mu\text{m}$

etched particles from CA-057 (Nd) also exhibit cellular and dendritic morphologies (see Figure 5.31). Further microscopic analyses of the microstructural phases may be possible using wavelength dispersive spectroscopy (or "microprobe" analysis) and x-ray mapping.

The fine-scale microstructure of rapidly solidified particles, such as are produced in the CA/RQB, also provides a large amount of grain boundary area which inhibits crack propagation and can, therefore, increase the durability of the brittle lanthanide intermetallic materials (see Figure 6.6).

Figure 6.6. Optical micrograph of a -250+212 μ m Er_3Ni particle showing crack termination at a grain boundary

6.5.2 X-ray diffraction data

Two theta (2θ) values for x-ray diffraction reflections from Er_3Ni and Nd_3Ni were calculated by Mr. Chad Miller using the Powder V5 computer program⁴³ and tabulated crystal structure data for the two compounds. The experimentally observed 2θ values for Er_3Ni reflections matched each of the calculated values while the observed 2θ values for the Nd_3Ni were systematically shifted about 0.4° lower than the calculated values (Figures 5.33 and 5.34). The high degree of correlation between the calculated and experimental values and the absence of extraneous peaks indicates that both of these materials were predominantly of the desired phase within detectable limits (i.e., <10 vol.% second phase). The x-ray diffraction trace of the

(Er_{0.5}Nd_{0.5})₃Ni powder shown in Figure 5.35 contains five or six peaks which may correspond to the Er₃Ni phase and one or two which may correspond to the Nd₃Ni phase. The remainder of the reflection peaks are difficult to label as we have no x-ray data for Er-Nd-Ni compounds.

6.5.3 Differential thermal analysis data

DTA analysis is probably the most precise technique of the three used here for detecting phases present in the sample and allows for the most accurate phase determination if an accurate phase diagram is known. Analyses of the Er₃Ni powder and charge both indicate that there is a small amount of melting at about 765°C with the remainder of the samples melting at about 870°C. Upon comparison with the equilibrium phase diagram (Figure 6.7), we see that there is a eutectic reaction, Er₃Ni + Er₃Ni₂ → liquid, at 765°C and that the liquidus temperature for Er₃Ni is about 875°C. From this evidence, we deduce that both the atomized powders and the starting material are predominantly Er₃Ni with a minor fraction of Er₃Ni₂ which was not detected by x-ray diffractometry.

Analysis of the Nd₃Ni powder indicates one melting event at about 605°C, 15°C higher than the published melting temperature of 590°C.⁴⁵ The starting material shows some endothermic phase transformation at 590°C with the remainder of the sample melting at about 605°C. If we assume that a 15°C temperature discrepancy may be applied to the 590°C transformation, the first event seen in the starting material could be melting of the Nd-Nd₃Ni eutectic at 570°C (see Figure 6.8). This noninvariant melting behavior is probably a result of segregation within the arc-cast starting material arising from incomplete liquid homogenization which is known to occur during DC arc melting. It appears that our powder sample was ~100% Nd₃Ni, in agreement with the x-ray diffractometry results.

DTA analysis of the (Er_{0.5}Nd_{0.5})₃Ni powder shows four endothermic events at 690°C, 695°C, 760°C, and 770°C. The 690°C event appears to involve the majority of the sample melting with decreasingly smaller amounts of melting at the three higher temperatures. Since no ternary diagram is available for the Er-Nd-Ni system, it is difficult to postulate which phases are

Figure 6.7. Partial equilibrium phase diagram for Er-Ni (after Ref. 44)

present in the sample. It should be noted, however, that the temperature of the major melting event, 690°C, falls midway between the Er_3Ni liquidus temperature and the Nd_3Ni melting temperature.

6.6 Low Temperature Heat Capacities

The low temperature heat capacity of the loose CA-035 (Er_3Ni) powder exhibits a peak at a slightly higher temperature than that for the consolidated sample and the peak is also broader for the loose powder as seen in Figure 6.5. Assuming little variation due to measurement technique, the change in heat capacity is probably due to changes in the interstitial impurity atom locations

Figure 6.8. Partial equilibrium phase diagram for Nd-Ni (after Ref. 45)

as mentioned in Section 6.4. Compared to gas atomized Er₃Ni, the heat capacity of the CA-035 (Er₃Ni) material is slightly lower from 20-10K, slightly higher from 10-7K, and comparable <7K (see Figure 6.10). Hershberg et al. [39] compare the CA-035 (Er₃Ni) heat capacity to Er₃Ni obtained from other sources. The CA-035 (Er₃Ni) material is shown to have a greater heat capacity than the other materials at temperatures above ~7K and even greater than Pb up to ~16K indicating its suitability as a Pb replacement in cryocooler heat exchangers in this temperature regime.

The heat capacity versus temperature plots for the Nd starting material and hot pressed powder (Figure 5.40) reveal that atomization and consolidation had little effect on the heat capacity of the material. The heat capacity peak in the processed sample was 0.5K lower in temperature (7.7K compared to 8.2K), but had the same magnitude (0.35 J/cm³K) as the starting material. The starting

Figure 6.10. Volumetric heat capacities of Er_3Ni powders - centrifugally atomized and gas atomized

material had a greater heat capacity than the processed sample from ~8-20K and similar heat capacity below 8K.

The Nd_3Ni exhibits what appears to be a remarkable decrease in heat capacity peak temperature due to heat treatment (Figure 5.41). The starting material peak was at 11.1K while the hot-pressed sample peak was at ~6.4K, a difference of almost 5K. This shift may be explained as an effect created by the increase in oxygen and nitrogen during processing with said impurities retarding the alignment of the electronic spins. This retardation then required a greater free energy driving force (driving force $\equiv$ temperature decrease) in order to align the spins. Conversely, we see that the carbon content actually

decreased during atomization (Table 5.2) and it may be possible that the high amount of carbon in the starting material affected the electronic interactions between the matrix atoms and caused the ordering transformation to occur at a higher temperature than would be found in Nd_3Ni with a lower carbon content.⁴⁶ This then implies that the heat capacity peak temperature for the processed material may be nearer the "true" ordering temperature for Nd_3Ni . Further research studying the effects of controlled impurity additions on heat capacity could prove interesting.

The $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ material was studied in order to determine if heat capacity could be controlled by blending lanthanide elements in the R_3Ni structure. In Figure 5.42, we see that the $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ does not have a prominent heat capacity peak such as is seen for the other materials. However, its heat capacity is appreciably greater than the heat capacities of the other materials (see Figure 3.10) above $\sim 10\text{K}$, making it an attractive matrix material for applications involving cooling between 10-20K. We should especially note that the heat capacity of $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ is also as large at 5K as the heat capacity of Pb at 10K. It appears that mixing Nd and Er extended ordering over a broad temperature range between the Er_3Ni and Nd_3Ni ordering temperatures. It may be desirable in future research to increase the Er content of the mixed lanthanide in order to shift the heat capacity to lower temperatures.

CHAPTER 7. CONCLUSIONS

Heat exchangers in low-temperature cryocoolers require high-quality powders of lanthanide metals or lanthanide intermetallic compounds for the most efficient cooling possible. However, the manufacture of these high-quality powders is difficult due to their reactivity and brittleness. This research was, therefore, performed to develop a new and unique production technique for the manufacture of high-quality powders of lanthanide metals and lanthanide intermetallic (lanthanide intermetallic) compounds.

In this document, it has been shown that the Ames Laboratory's Centrifugal Atomizer with Rotating Quench Bath (CA/RQB) is capable of producing near-spherical powders of lanthanide materials with relatively low chemical contamination compared to other methods. Particle size distributions, particle shapes, and skull analyses indicate that superheat is a useful control parameter for manipulating the atomization process and, subsequently, the shape and size uniformity of the atomized particles. Comparison of measured median particle diameters with calculated values indicate that the CA/RQB can be precisely controlled by proper selection of disk rotational speed to produce powders with the desired particle size. The powder yield in the desired size range has increased continuously throughout the project as the equipment and techniques have been refined.

Observation of the atomized powders in corrosive environments has indicated that surface modification has occurred via quenching in the polydimethyl siloxane fluid. Passive coatings are evidently formed on the powders by the reaction of the metal powder with the quenchant and strongly enhance the materials' resistance to acid attack and oxidation. Further study is encouraged using Auger microscopy and similar techniques to determine the form of the surface coating and how coatings with desirable properties can be produced.

Differential thermal analysis (DTA) revealed that the Er_3Ni powder was predominantly single phase with a minor amount of Er_3Ni_2 ; however, the Er_3Ni_2 phase was not detected by x-ray diffractometry (XRD) and must, therefore, comprise less than ~10 vol.% of the sample. Both XRD and DTA

indicated that the Nd_3Ni powder is nearly 100% single phase. The $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ powder contained multiple phases which are difficult to designate as no literature information was found for the Er-Nd-Ni system. Due to the encouraging heat capacity results of this material, it may be beneficial to more closely examine this ternary system.

Optical microscopy performed on polished and etched powder cross-sections show fine solidification morphologies, both dendritic and cellular. Fine cellular structures near the particle surfaces are reminiscent of rapidly solidified, partitionless "rim" seen in Ag-15%Cu particles. The high grain boundary area, arising from the small grain size, within these particles should be beneficial in increasing the physical durability of brittle lanthanide intermetallic compounds by absorbing crack energy.

The low temperature heat capacity results, both by adiabatic-heat-pulse calorimetry and thermal-relaxation calorimetry, are commendatory as they show that the materials produced during this research are among the best ever produced for cryocooler applications. The CA/RQB Er_3Ni powder has been compared to commercially available Er_3Ni powders and Er_3Ni materials from other research facilities and shown to have superior heat capacity.³⁹ The Nd_3Ni powders exhibit a heat capacity peak at low temperatures with a remarkable magnitude. The $(\text{Er}_{0.5}\text{Nd}_{0.5})_3\text{Ni}$ heat capacity results are especially noteworthy, demonstrating that, by blending lanthanide elements in the R_3Ni structure, materials with notable heat capacities over a wide temperature range can be designed and produced.

While the heat capacity results given in this manuscript are encouraging and suggest that the CA/RQB produced powders will operate satisfactorily in a cryocooler heat exchanger, actual cryocooler testing should be conducted to determine if the CA/RQB powders result in more efficient and reliable operation, as was the intent of this research.

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