CALIFORNIA ENERGY COMMISSION

ENERGY RESEARCH AND DEVELOPMENT DIVISION

FINAL PROJECT REPORT

Scale-up of Magnetocaloric Materials for High Efficiency Refrigeration

June 2024 | CEC-500-2024-057

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ACKNOWLEDGEMENTS

The authors thank Dr. Aashish Rohatgi and Dr. Mert Efe from Pacific Northwest National Laboratory for their assistance with this work, which was supported by an award from the U.S. Department of Energy Contract No. DE-AC05-76RL01830 CRADA 446. Additionally, many thanks are due to the technical advisory committee for this project which included Prof. Renkun Chen and Prof. Sungho Jin from the University of California, San Diego. The Southern California Energy Innovation Network has also been a key supporter of General Engineering & Research's goal of developing and commercializing magnetic refrigeration technologies, and their support is greatly appreciated.

PREFACE

The California Energy Commission's (CEC) Energy Research and Development Division supports energy research and development programs to spur innovation in energy efficiency, renewable energy and advanced clean generation, energy-related environmental protection, energy transmission, and distribution and transportation.

In 2012, the Electric Program Investment Charge (EPIC) was established by the California Public Utilities Commission to fund public investments in research to create and advance new energy solutions, foster regional innovation, and bring ideas from the lab to the marketplace. The EPIC Program is funded by California utility customers under the auspices of the California Public Utilities Commission. The CEC and the state's three largest investor-owned utilities—Pacific Gas and Electric Company, San Diego Gas and Electric Company, and Southern California Edison Company—were selected to administer the EPIC funds and advance novel technologies, tools, and strategies that provide benefits to their electric ratepayers.

The CEC is committed to ensuring public participation in its research and development programs that promote greater reliability, lower costs, and increase safety for the California electric ratepayer and include:

- Providing societal benefits.
- Reducing greenhouse gas emission in the electricity sector at the lowest possible cost.
- Supporting California's loading order to meet energy needs first with energy efficiency and demand response, next with renewable energy (distributed generation and utility scale), and finally with clean, conventional electricity supply.
- Supporting low-emission vehicles and transportation.
- Providing economic development.
- Using ratepayer funds efficiently.

For more information about the Energy Research and Development Division, please visit the CEC's research website (www.energy.ca.gov/research/) or contact the Energy Research and Development Division at ERDD@energy.ca.gov.

ABSTRACT

Magnetic refrigeration is a promising technology to replace compression-based refrigeration systems, offering a significant improvement in efficiency and eliminating hydrofluorocarbons. For magnetic refrigeration to move into production, economical and functioning commercially available magnetocaloric materials are needed. During this project, a furnace was installed to scale up production of General Engineering & Research's patented magnetocaloric material compositions. This optimized material processing provided a greater than 20 percent increase in material performance and achieved the project target low-rate initial production of one kilogram per day. Magnetic refrigeration developers have most commonly used magnetocaloric material in their systems as either thin plates or sub-millimeter sized particles/spheres. General Engineering & Research successfully installed the equipment and developed the processes to produce these materials for commercial use.

Keywords: magnetic refrigeration, magnetocaloric, compression-based refrigeration systems

Please use the following citation for this report:

Ihnfeldt, Robin. 2024. *Scale-up of Magnetocaloric Materials for High Efficiency Refrigeration*. California Energy Commission. Publication Number: CEC-500-2024-057.

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Background

Refrigeration and air conditioning systems are a major contributor to climate change and consume a significant portion of California's electricity. Conventional refrigeration systems use a vapor compression cycle with a hydrofluorocarbon refrigerant (such as R410A or R134). These refrigerants are a substantial contributor to global warming and hydrofluorocarbon emissions are the fastest growing source of greenhouse gases in California. Conventional refrigeration systems also consume a great deal of power and have no room for improvement because they are nearing their thermodynamic limits with regard to efficiency, cost, and performance.

Additionally, regulatory requirements are pushing conventional refrigeration manufacturers to move from high global warming potential hydrofluorocarbon refrigerants to even less efficient, low global warming potential refrigerants (such as carbon dioxide, ammonia, hydrofluoro-olefins, and hydrocarbons), which will increase energy consumption by as much as 20 percent and introduce additional safety issues such as operation under very high pressure (carbon dioxide), toxicity (ammonia), and flammability (hydrofluoroolefins and hydrocarbons).

Magnetic refrigeration is a promising technology to replace compression-based refrigeration systems. It offers a significant improvement in efficiency and eliminates hydrofluorocarbons. The technology uses the magnetocaloric effect, which is the temperature variation of a special magnetic material (known as a magnetocaloric material) when exposed to a changing magnetic field. Essentially, these special magnetocaloric materials can change temperature when exposed to a changing magnetic field, and this change in temperature can be used for refrigeration and cooling. The magnetocaloric effect was first used in refrigeration systems in the 1930s as a method to reach near absolute zero (–459 degrees Fahrenheit [–273 degrees Celsius]), but its use in higher temperature refrigeration applications has been inhibited by the lack of functioning magnetocaloric materials at higher temperatures.

For magnetic refrigeration to become commercially viable, economically available magnetocaloric materials that function in the required temperature ranges are needed, and refrigeration prototypes demonstrating the technology functionality must be developed.

With this project, General Engineering & Research developed and scaled-up the production of magnetocaloric materials that operate in the necessary temperature ranges to provide an economically viable source of the material, which will act as a catalyst for further development of magnetic refrigeration technology.

General Engineering & Research, in collaboration with the University of California, San Diego, has discovered and developed a novel line of high-performance, low-cost magnetocaloric materials. General Engineering & Research magnetocaloric materials are the only known compositions that will meet the cost and performance requirements necessary to be viable in the mass production of magnetic refrigeration systems for residential and commercial refrigeration, air conditioning applications, and cryogenic applications (gas liquefaction). The team's primary project goal was to scale-up the production of magnetocaloric materials to achieve one kilogram per day in the form of sub-millimeter-sized particles and thin plates at economical prices. This low-rate initial production will enable high efficiency magnetic refrigeration systems to move from prototype to production.

Project Purpose and Approach

The team explored scale up of in-house manufacturing capabilities to accommodate one kilogram per day low-rate initial production of magnetocaloric materials in useful forms (sub-millimeter sized particles and thin plates) for economical prices. This was accomplished by implementing the following objectives:

- Installed casting equipment and developed procedures to accommodate one kilogram per day production.
- Worked with Pacific Northwest National Laboratory to develop and characterize heat-treated materials to reduce processing time and cost and to improve performance.
- Developed processes to form magnetocaloric materials into useful forms of sub-millimeter sized particles and thin plates.
- Optimized processing to meet cost and performance requirements.

Key Results

During this project, General Engineering & Research installed new equipment essential to scale-up production of magnetocaloric material compositions. Optimization of material processing provided a 20 percent increase in material performance and achieved the project target low-rate initial production rate of one kilogram per day.

Magnetic refrigeration developers have most commonly used magnetocaloric material in their prototype refrigeration systems in the form of either thin plates or sub-millimeter-sized particles/spheres. General Engineering & Research successfully identified, installed, and developed the processing to provide the materials in these forms.

Further, theoretical models of magnetic refrigeration have shown this technology to be up to 50 percent or more energy efficient compared to vapor compression cycle technologies, without using environmentally hazardous materials (i.e., no hydrofluorocarbons). The technological advancements achieved with this Electric Program Investment Charge (EPIC) project have eliminated a significant barrier for developers to build high efficiency magnetic refrigeration systems and enabled these systems to move from prototype to production. Assuming 10 percent per year deployment of magnetic refrigeration technology, Californians would see an annual energy savings of about 2,000 GWh, which equates to about $300 million in electricity costs. Additionally, given the role hydrofluorocarbons play in California’s greenhouse gas emissions, a 10 percent conversion/growth rate of magnetic refrigeration systems would eliminate about 5 million metric tons of carbon dioxide equivalent annually in California.

Knowledge Transfer and Next Steps

The magnetocaloric materials developed during this effort are currently available for purchase through General Engineering & Research's webstore. The webstore will be updated with performance metrics specific to each of the magnetocaloric material compositions so that end users can determine the best material for their system. As customers develop their prototypes and move into production, General Engineering & Research will scale accordingly and add space and equipment to meet these needs.

A journal publication entitled, "Optimization of a Packed Particle Magnetocaloric Refrigerator: A Combined Experimental and Theoretical Study" has been submitted for publication to the International Journal of Refrigeration. This paper discusses General Engineering & Research's magnetocaloric materials and validates the excellent functionality of these materials.

Additionally, a manuscript is currently being prepared by General Engineering & Research detailing the discovery and development of these magnetocaloric materials and submission for publication is expected by mid-2024.

In collaboration with the University of California, San Diego, a theoretical magnetic refrigeration model has been built that can be used to predict performance of a magnetic refrigeration system with various input parameters. This model is highly useful for magnetic refrigeration system designers. It will be put into a software package that can be easily used and will be made available to the public, for free, from the General Engineering & Research website. It is expected that this software tool will facilitate design of magnetic refrigeration systems and help customers determine the quantities and properties of the magnetocaloric materials needed in their system.

To continue commercialization and increase sales of the magnetocaloric materials, General Engineering & Research will attend the following industry conferences to showcase these products and demonstrate their superior performance:

1. 10th IIR Conference on Caloric Cooling and Applications of Caloric Materials, Baotou, China, August 21 to 24, 2024.
2. International Conference on Magnetism, Bologna, Italy, June 30 to July 5, 2024.
3. 16th Joint MMM-Intermag Conference, New Orleans, Louisiana, January 13 to 17, 2025.
4. 70th Annual Conference on Magnetism and Magnetic Materials, Palm Beach, Florida, October 27 to 31, 2025.

General Engineering & Research has a two-fold commercialization approach for magnetic refrigeration technologies:

1. Sell magnetocaloric materials for all refrigeration applications.
2. Demonstrate small-scale magnetic refrigeration for cryogenic applications and license/sell this technology to strategic partners for deployment.

Under another EPIC award, EPC-19-021, General Engineering & Research is using their magnetocaloric materials to demonstrate a small-scale magnetic refrigeration system that operates in the sub-80 Kelvin (–315 degrees Fahrenheit [°F] or –193 degrees Celsius[°C]) region for cryogenic applications. Specific objectives for this project are as follows:

1. Build an at-scale system and demonstrate sustained magnetocaloric cooling below 80 Kelvin (–315°F [–193°C]).
2. Use the validated theoretical model to identify optimized system configuration to achieve high efficiency and cost reduction compared to comparable vapor compression cycle system.

General Engineering & Research believes that the successful demonstration of a magnetic refrigeration prototype with improved efficiency and capital cost over vapor compression systems will lower the risk for industrial financing and licensing to move magnetic refrigeration into the cryocooler market, as well as to stimulate industrial efforts for the use of magnetic refrigeration in other refrigeration applications (which will in turn lead to growth in magnetocaloric material sales).

CHAPTER 1: Introduction

Magnetic refrigeration is a promising technology to replace vapor compression cycle systems (VCC) systems that offers a significant improvement in efficiency and the elimination of hydrofluorocarbons (HFCs). The technology uses the magnetocaloric effect, which is the temperature variation of a special magnetic material when exposed to a changing magnetic field. Magnetic refrigeration prototypes have been developed for household refrigerators (General Electric), kitchen appliances (Camfridge), and building air conditioning (CoolTec Applications), just to name a few, but these technologies have not been able to move into production due to the lack of economical, properly functioning, and commercially available magnetocaloric materials.

General Engineering & Research (GE&R), in collaboration with the University of California, San Diego (UCSD), have discovered and patented a novel line of high-performance, low-cost magnetocaloric materials. GE&R magnetocaloric materials are the only known compositions that will meet cost and performance requirements to be viable in mass production of magnetic refrigeration systems for residential and commercial refrigeration and air conditioning applications, as well as cryogenic applications (gas liquefaction). The primary goal with this Electric Program Investment Charge (EPIC) project was to scale up the production systems to achieve one kilogram per day (kg/day) production in useful forms for economical prices. This low-rate initial production (LRIP) will enable magnetic refrigeration systems to move from prototype to production. It is large enough to facilitate current magnetic refrigeration prototype development and will remove the barrier to entry for other developers to build high efficiency systems. As these magnetic refrigeration prototypes move to production, GE&R will scale the magnetocaloric materials production line accordingly.

The EPIC 2018 to 2020 Triennial Investment Plan (EPIC, 2017) states, "Heating, ventilation, and air conditioning (HVAC) and refrigeration systems are among the largest consumers of electricity. In California, the energy required to heat and cool buildings uses roughly 40 percent of total electricity consumed. Furthermore, this demand will likely increase as California's climate warms. … As a result of AB 32, SB 350, and Senate Bill 32 (Pavley, Chapter 249, Statutes of 2016), there is strong impetus to focus on HVAC and refrigeration systems that have low greenhouse gas (GHG) emissions, and use refrigerants with low global warming potential (GWP) while being highly efficient."

While evolutionary improvements continue to be obtained, the ability for traditional VCC technologies to meet the efficiency, cost, and performance requirements of future applications is limited, and in many cases, not possible. For VCC systems, the movement to low GWP or natural refrigerant options comes with an energy consumption penalty as high as 20 percent. This would mean an increase in energy demand of 8,700 gigawatt hours (GWh) annually in California (Kelsey, 2018). VCC systems with low GWP refrigerants also introduce additional issues such as operation under very high pressure (carbon dioxide [CO_2]), toxicity (ammonia), and flammability (hydrofluoroolefins and hydrocarbons), which will require implementation of significant safety precautions (Gallagher, 2018).

Magnetic refrigeration has been shown to be up to 50 percent or more energy efficient compared to VCC technologies, without using environmentally hazardous materials (no HFCs) (Teschler, 2014; Cooltech Applications, 2017). Further, the European Commission Technology Roadmap for eco-design requirements for household and commercial refrigeration applications identify magnetic refrigeration technologies as the best not-yet-available alternative to replace current VCC technologies (VHK et al., 2016).

There have been several issues with the magnetic refrigeration market:

1. There is a "chicken or egg problem" – to build these refrigerators it is necessary to have functioning magnetocaloric materials, but because there are very few entities building refrigerators and a market is not yet established, there is no commercial incentive to invest in developing magnetocaloric materials.
2. There had not been a viable material set yet discovered that met the cost and performance requirements for large production refrigeration and cooling applications, until now.

GE&R magnetocaloric materials are the only known compositions that have the ability to meet both pricing and performance constraints to be viable in large scale magnetic refrigeration system production. The goal of this project was to scale up in-house manufacturing capabilities to accommodate one kg/day LRIP of magnetocaloric materials in useful forms for economical prices, and this goal was achieved. The manufacture of magnetocaloric materials required a large upfront capital expenditure in specialty equipment to synthesize and characterize these materials, as well as significant engineering expertise. GE&R's expertise in this field, and the on-site specialty equipment (vibrating sample magnetometer, furnaces, etc.) were key to the success of this project.

CHAPTER 2: Project Approach

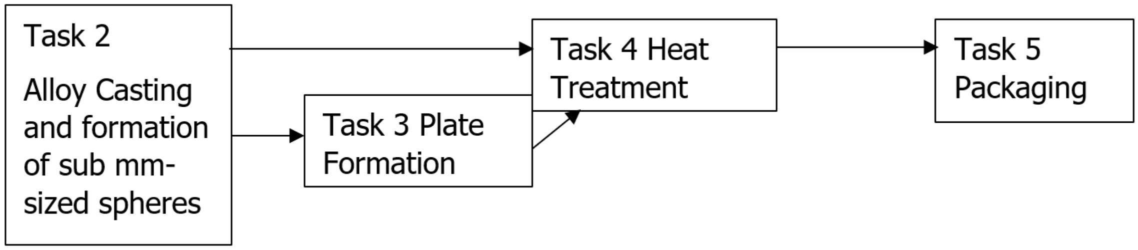
Magnetic refrigeration uses the magnetocaloric effect, which is the temperature variation of a magnetic material after exposure to a magnetic field. The magnetocaloric effect (MCE) is an intrinsic property of a magnetic solid. The thermal response of the magnetocaloric material to the application or removal of a magnetic field is typically maximized when the material is near its magnetic ordering temperature, also known as the Curie temperature. The useful portion of the MCE usually spans about 25 degrees on either side of the material's Curie temperature (Chuke et al., 2014). Therefore, to span a wide temperature range, a refrigerator must contain several different magnetocaloric materials arranged according to their Curie temperatures. General Electric recently announced that their magnetic refrigeration prototype uses 50 stages to produce an 80°F (27°C) temperature span (Teschler, 2014).

A major issue that must be solved before the technology of magnetic refrigeration can move forward from prototypes to mass production is the lack of commercially available low cost magnetocaloric materials that will actually function, for a long period of time, in a magnetic refrigeration environment such as the active magnetic regenerator (AMR) which is in development by several entities (Bjork et al., 2010; Adapa et al., 2024; Brueck, 2015; Teschler, 2014). Synthesizing magnetocaloric materials is not easy, and the known materials are expensive and rare-earth based and/or have poor performance.

There is currently only one other magnetocaloric material supplier (Vacuumschmelze GmbH) that can provide materials in large enough quantity to build a refrigeration system, however, their materials have significant stability issues that make them unviable for large production refrigeration and cooling applications (Kim et al., 2017; Svitlyk et al., 2010). The team's compositions are the only known magnetocaloric materials that will meet cost and performance requirements to be viable in mass production of magnetic refrigeration systems. They are the highest performance magnetocaloric materials available on the market, but before this EPIC award, GE&R's production capacity was limited to small quantities (about five grams [g]), and in the form of three to five millimeter (mm) pieces only.

For this project, GE&R's approach was to bring in new equipment to increase production capacity and develop the processing procedures to manufacture the magnetocaloric materials in forms needed for magnetic refrigeration systems (spheres and thin plates). Figure 1 shows the originally proposed processing steps to manufacture magnetocaloric materials into these forms.

Figure 1: Proposed Processing Steps to Manufacture GE&R Magnetocaloric Materials into Spheres or Thin Plate Form



Source: General Engineering & Research

For high efficiency magnetic refrigeration systems to be a viable solution, the magnetocaloric materials used in these systems must achieve the following two metrics:

1. Cost less than (<) $1,000/kg (includes materials and processing); and
2. Performance - change in entropy greater than three Joules per kilogram × Kelvin[1] (J/kgK) in a three-Tesla (3T) magnetic field.

GE&R magnetocaloric compositions comprise metals with bulk purchase prices <$200/kg and with scale-up, the processing costs were expected to be <$200/kg, which will meet and/or exceed the cost metric when manufactured at large scale. Performance characterization (ΔS) of magnetocaloric materials is done using specialty equipment, namely a vibrating sample magnetometer. GE&R has a vibrating sample magnetometer in-house, and results obtained prior to this award demonstrated the materials were very close to meeting the performance requirements for all temperature applications. It should also be noted, during this project GE&R expected to achieve even higher performance of the materials with the installation of new equipment with better processing capabilities (higher temperatures for faster anneals and less susceptibility to oxidation).

Table 1 provides an outline of the proposed technical tasks along with expected timelines. It should be noted, the tasks are described in the order in which the magnetocaloric materials are processed but were not necessarily developed in this order. Task 4, Heat Treatment, was expected to be the most time consuming, as each anneal can take about one week or more, and systematic testing of different temperatures for each magnetocaloric composition was needed. Under a previous grant award from the U.S. Department of Energy (DOE) (Phase II ended August 2019), testing of heat treatments was performed on the magnetocaloric materials using the furnaces that were in-house at the time (three furnaces with 2012°F (1100°C) capability, one furnace with 2552°F (1400°C) capability, and an induction furnace with 3632°F (2000°C) capability but that was only capable of running for a maximum of about six hours at a time). Results from the Phase II DOE effort provided a great baseline for developing anneals with new higher temperature furnaces, and with the materials in different forms (spheres or thin plates or both).

[1] The amount of heat required to raise a unit mass of a material by 1 Kelvin (or degree Celsius).

Table 1: Technical Tasks and Timeline

Task	Description	Period of Performance	
2	Alloy Casting	25.5 months	07/12/2019 – 09/30/2021
3	Plate Formation	14 months	08/01/2021 – 09/30/2022
4	Heat Treatment	GE&R Effort – 54 months Pacific Northwest National Laboratory Effort – 36 months	07/12/2019 – 01/30/2024 01/01/2020 – 12/31/2022
5	Packaging	14 months	08/01/2021 – 09/30/2022

Source: General Engineering & Research

A detailed description of the proposed approach for the technical tasks follows. With successful performance of these tasks, the magnetocaloric materials products were expected to achieve a manufacturing readiness level of 8 by the end of the EPIC project.

Task 2 ALLOY CASTING

During a previous grant award from the DOE, several casting techniques were tested, and it was found that the arc melt atomizer was the fastest, most economical method to simultaneously melt the pure metals into the desired alloy composition and then form them into sub-millimeter-sized spheres. The proposed approach for this task was to purchase an arc melt atomization furnace from Arcast Inc. and install this equipment in the facility. Suppliers were identified to provide the pure metals in quantities and purities needed for the magnetocaloric materials. These starting metals oxidize slowly in air, so preparation and storage procedures also needed to be developed.

The goal of this task was to install the casting equipment capable of one kilogram (kg) per day production and, if possible, during casting, develop processing to achieve sub-millimeter-sized sized spherical particles. The magnetocaloric materials vary in composition depending on the desired temperature range of functionality. Specifically, a material that functions in the temperature range near 300 Kelvin (K) (80°F [27°C], or room temperature) has a different composition than a material which functions at 10K (–442°F [–263°C]). To classify the compositions, they are identified by the temperature where the peak ΔS is achieved. The final objective with this alloy casting task was to determine composition and processing needed to have a magnetocaloric material available with functionality at every 10-K interval within the 10k to 330K temperature range (for a total of 33 compositions): Peak ΔS = 10K, 20K, 30K, 40K, 50K, 60K, 70K, 80K, 90K, 100K, 110K, 120K, 130K, 140K, 150K, 160K, 170K, 180K, 190K, 200K, 210K, 220K, 230K, 240K, 250K, 260K, 270K, 280K, 290K, 300K, 310K, 320K, 330K. Custom compositions with change in entropy peaks in between these temperature ranges can also be made if requested.

Because the composition for each magnetocaloric material is slightly different, it was expected that processing to synthesize these would also likely vary, thus procedures to form each composition needed to be developed. It was expected that procedures would be similar for groups of compositions (10K to 70K, 80K to 200K, 200K to 330K) and once optimal processing had been determined for one composition within each group, the rest of the compositions would use similar optimal processing.

It was also expected that parameters could be adjusted on the furnace to obtain the desired diameter of the spheres formed (about 30µm up to 1mm). For magnetic refrigeration applications, in general, the smaller the diameter the better the performance in a magnetic refrigeration system because heat transfer to/from the material is faster. However, magnetocaloric materials are also susceptible to surface oxidation (especially at high temperature), and these materials must be able to survive the heat treatment (Task 4) that is needed to homogenize the material and form the crystal structure that induces the magnetocaloric properties. Optimization of sphere size must be performed in conjunction with Task 4 to ensure the diameter is large enough to survive the heat treatment, and small enough to perform as needed in a magnetic refrigerator. It should be noted, during the Phase II DOE effort, a dopant was discovered for the compositions that helps to slow oxidation (patents issued and pending), so GE&R magnetocaloric materials are more stable in air than other magnetocaloric materials, making them easier for end users to implement into magnetic refrigeration products.

Task 3 PLATE FORMATION

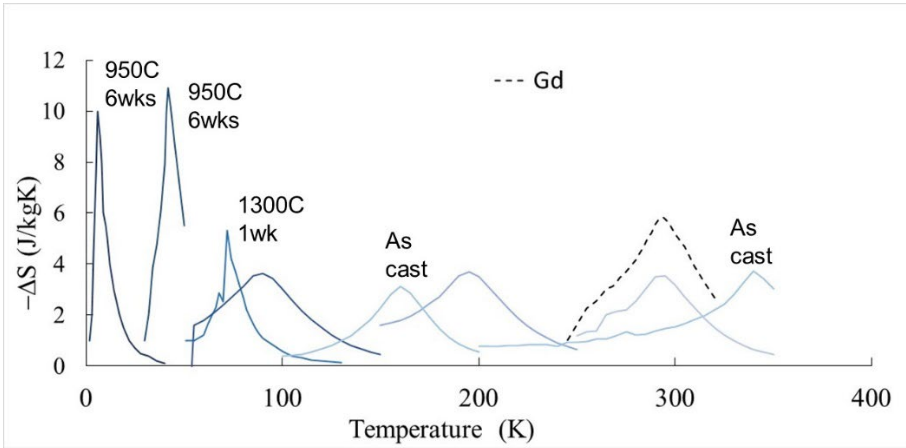
During the prior Phase II DOE effort, several techniques to form plates were tested. GE&R magnetocaloric materials were found to be too brittle to machine so slicing the materials into plates was not an option. By starting with the sub-millimeter-sized spheres, it was expected that this powder could be hot or cold pressed into a pellet or plate structure.

GE&R proposed to purchase a hydraulic pressing system from MTI Corp. and install this equipment in the facility. Hot press dies were proposed to form the materials into various thickness plates, and robust procedures were developed for each magnetocaloric composition. A major advantage of forming the magnetocaloric materials into plates is that they are then less susceptible to oxidation during the heat treatment process.

Task 4 HEAT TREATMENT

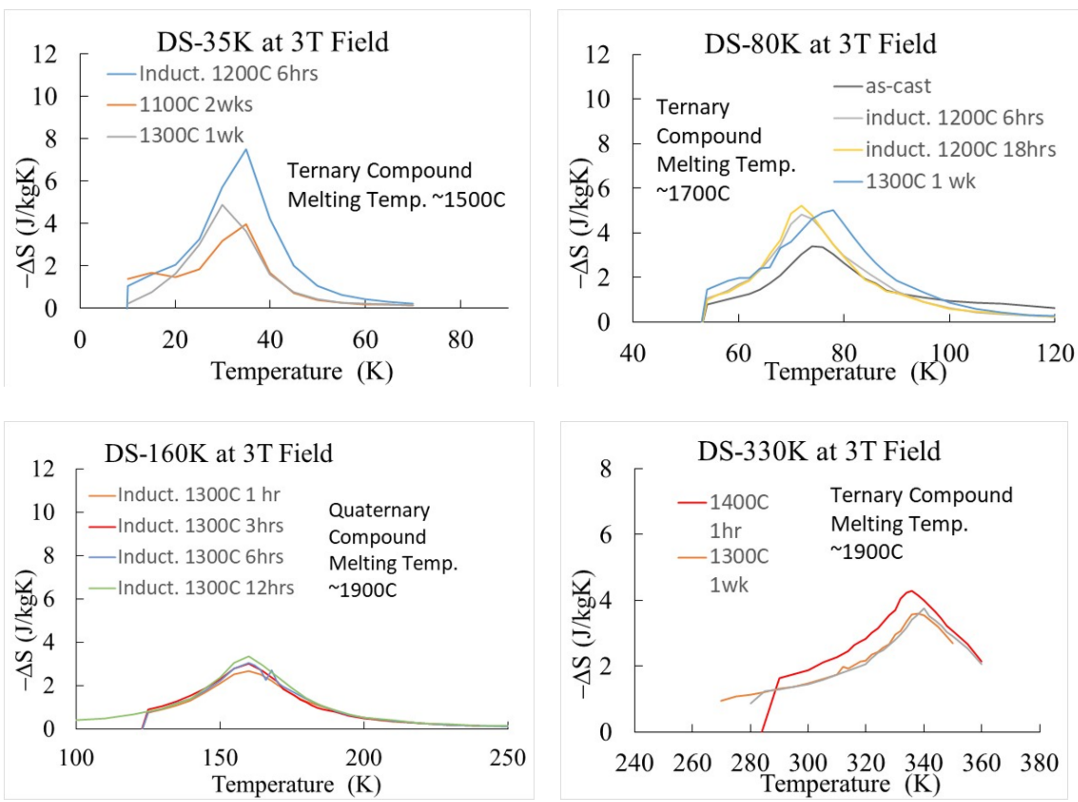
Heat treatments are needed to homogenize the material and induce magnetocaloric properties. The temperature and time of the heat treatment needs to be optimized for each composition. Figure 2 shows the performance (ΔS) versus temperature of the materials, with various heat treatments or with no heat treatments (as-cast), prior to starting the EPIC award. In general, materials with higher melting temperatures require higher temperature anneals, and materials with more complexity (quaternary versus ternary compounds) take longer (Figure 3).

Figure 2: Performance (ΔS) Versus Temperature for GE&R Magnetocaloric Materials with Various Heat Treatments Before EPIC Award



Source: General Engineering & Research

Figure 3: Heat Treatment Test Performed on Various GE&R Magnetocaloric Compositions



Showing higher temperatures reducing anneal time, higher melting point requiring longer anneal time, and higher complexity compounds (ternary versus quaternary) requiring longer anneal time.

Source: General Engineering & Research

Some of the initial heat treatments performed on the magnetocaloric materials took up to six weeks at 1742°F (950°C). The issue with long anneals is not actually energy cost (these furnaces run very efficiently once they reach the set temperature, and energy to hold furnace at 2552°F (1400°C) for long durations is less than HVAC costs for the facility), it is the capital cost of the furnaces. If a six week anneal is required to achieve high magnetocaloric properties, then to have an LRIP of one kg/day the purchase of 6 x 7 = 42 furnaces with one kg/day capacity or one furnace with 42 kg capacity would be needed, and either option is expensive. Thus, the goal was to develop heat treatment processes that achieve the required magnetocaloric properties in one week or less. To do this, two anneal treatments were tested, and the most economical process was implemented for the LRIP line.

Anneal Test 1

GE&R purchased a high temperature vacuum furnace capable of sustaining 3092°F (1700°C) from MTI Corp. and installed this equipment in the facility. Optimal heat treatment times and temperature needed to achieve maximum magnetocaloric performance for each material composition was then determined. This effort was expected to take about three years or longer and was performed for the entire duration of the EPIC award.

Anneal Test 2

GE&R partnered with Pacific Northwest National Laboratory (PNNL), which had developed a proprietary heat treatment technique that significantly lowered time and energy costs of heat treatments needed for alloys in other industries. Based on the heat treatment mechanism, it was believed this may be a useful technique to significantly lower processing time and cost of GE&R magnetocaloric alloys. Based on PNNL's previous work, they were able to reduce anneal time by >80 percent, and this technique can be implemented with additional equipment for about $10,000 to $15,000 as a stand-alone process, or in conjunction with a standard electric furnace. GE&R subcontracted with PNNL to test their heat treatment technique on the magnetocaloric materials. GE&R provided various compositions of magnetocaloric materials initially casted in cylindrical form. PNNL performed their special heat treatment on their equipment, and then the magnetocaloric materials performance was characterized on GE&R's vibrating sample magnetometer. This data was provided to PNNL as feedback so adjustments could be made and the process optimized. This testing was expected to take about one to two years.

Once both anneal tests were complete, a cost/benefit analysis of each technique was performed to determine the optimal process to implement for LRIP. If standard heat treatment equipment was optimal, GE&R planned to purchase additional furnaces to meet the one kg/day LRIP (using cash-in-hand match funds). If PNNL heat treatment was optimal, GE&R planned to license their technology and purchase equipment necessary to perform this treatment at one kg/day LRIP (using cash-in-hand match funds).

It should also be noted, throughout this task, the heat treatment optimization needed to be done in conjunction with Task 2 and Task 3 to ensure compatibility.

Task 5 PACKAGING

GE&R purchased additional packaging equipment which included a vacuum sealer and vacuum storage containers to package magnetocaloric materials for effective long-term shelf-life storage.

Critical Risk Factors

The following are several critical risk factors identified prior to the EPIC award, and descriptions of plans to mitigate these risks.

Heat treatment times - Successful scale-up of the magnetocaloric materials require the development of heat treatments that are one week or less to meet cost requirements. It was shown with low-melting-temperature magnetocaloric compositions that higher temperature anneals significantly lower heat treatment times; thus, it was expected that the installation of a 3092°F (1700°C) higher temperature furnace should meet anneal requirements of less than one week for all the magnetocaloric compositions. In addition, the PNNL proprietary technique that can be used in conjunction with standard heat treatments could potentially reduce the anneal times even further (less than one day), in which case, the processing time and capital equipment needs would be significantly reduced.

Oxidation of spheres during heat treatment - The oxidation of the sub-millimeter-sized spheres during heat treatment was also a concern. The smaller the sphere diameter, the more susceptible it is to oxidation. The plan to mitigate this risk was to use a variety of techniques (vacuum, argon atmosphere, flowing argon) to prevent oxidation of the spheres so that these materials can be supplied in this form. In addition to spheres, the magnetocaloric materials were also formed into thin plates, which should be much less susceptible to oxidation during heat treatment, and end users have indicated this is an acceptable form to use in these systems. Additionally, once the materials are formed into spheres, they can then be pressed into other custom forms if requested, such as ingots or rods, then heat treated and supplied to the customer.

Deliverables for this project included reports detailing the results of each of Tasks 2 through 5. The quantifiable success metric for each task is detailed in Table 2.

Table 2: Quantifiable Success Metric for the Project Technical Tasks

Market	Size
Task 2 – Alloy Casting	Demonstrate formation of sub-millimeter-sized spheres.
Task 3 - Plate Formation	Demonstrate formation of thin plates.
Task 4 - Heat Treatment	Demonstrate heat treatments of <1 week for each ΔS composition with performance of at least 3 J/kgK at a 3T field.
Task 5 - Packaging	Demonstrate 6-month shelf-life packaging with zero degradation in performance.

Source: General Engineering & Research

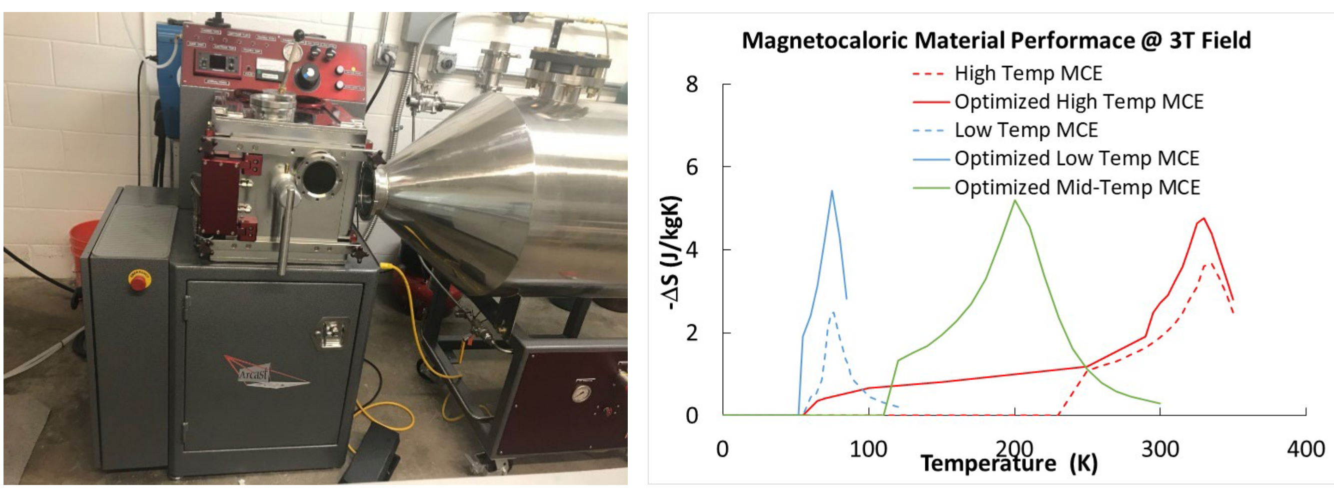
CHAPTER 3: Results

The goal of this project was to scale up in-house manufacturing capabilities to accommodate one kg/day LRIP of magnetocaloric materials in useful forms for economical prices. This goal was accomplished by implementing the following objectives:

- Installed casting equipment and developed procedures to accommodate one kg/day production.
- Worked with PNNL to develop and characterize heat treated materials to reduce processing time/cost and improve performance.
- Developed processes to form magnetocaloric materials into useful forms of sub-millimeter-sized particles and thin plates.
- Optimized processing to meet cost and performance requirements.

During this project, GE&R installed an arc melt casting furnace essential to scale up production of the magnetocaloric material compositions. Optimization of the starting compositions provided a 20 percent increase in material performance and the project target low-rate initial production of one kg/day was achieved. Figure 4 shows the installed arc melt furnace in the GE&R facility along with the magnetocaloric performance before and after composition optimization for some example alloys.

Figure 4: Installed Arc Melt Furnace (left) and Magnetocaloric Performance Before and After Composition Optimization (right)



Source: General Engineering & Research

Further, magnetic refrigeration developers have most commonly used magnetocaloric material in their prototype refrigeration systems in the form of either thin plates or sub-millimeter-sized particles/spheres. GE&R successfully identified, installed, and developed the processing to provide magnetocaloric materials in these forms. Figure 5 shows the GE&R magnetocaloric materials that are now commercially available for purchase from the GE&R webstore. Purchases of up to 200g quantities can be made directly from the webstore. The forms that are available are bulk ingots, various sized plates, and various sized powders. Also offered are larger bulk purchases and bulk pricing. At these current quantities, an order of greater than 10 kg can be synthesized within about two to four weeks, which is acceptable turnaround time for customers.

Figure 5: GE&R Magnetocaloric Materials Commercially Available for Purchase

From the www.geandr.com webstore in quantities up to 200g and in the form of (left) bulk ingots, (center) various sized plates, (right) various sized powder.

Source: General Engineering & Research

Table 3 shows the magnetocaloric material metrics achieved during this project. With the technological advancements obtained, the current pricing for purchase of about one kg of magnetocaloric material is <$10,000 at the current scale, which is almost entirely labor and facility costs. As customer orders increase in size and frequency, so that the facility is running near the one kg/day LRIP, the pricing of these products is expected to significantly decrease to meet (or fall below) the $1,000/kg cost target. Further, all GE&R magnetocaloric materials meet or exceed the 3 J/kgK performance metric (and in some cases, like the sub-50K materials, significantly exceed this metric with ΔS>9 J/kgK).

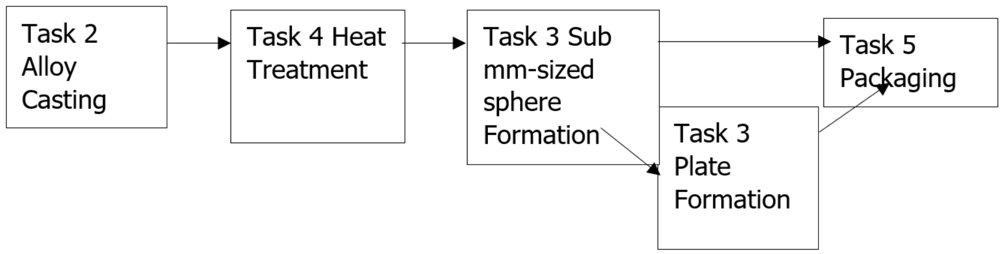
Table 3: Magnetocaloric Material Metrics

Performance Metric	Unit	Beginning	Goal	Final
Quantity	kg/day	0.01	1 or greater	2 kg/day
Material Performance	-ΔS J/kgK at 3T Field	1.5 to 3.5	>3 for all materials	3 to 13
Price	$/kg	>$30,000/kg	$1,000/kg at 1kg/day LRIP	$1,000/kg at 1kg/day LRIP

Source: General Engineering & Research

Figure 6 shows the finalized processing steps needed to manufacture MCE materials into the useful forms developed during this project.

Figure 6: Finalized Processing Steps to Manufacture GE&R Magnetocaloric Materials into Spheres or Thin Plate Form



Source: General Engineering & Research

A detailed description of the results achieved for each of the technical tasks is provided.

Task 2 ALLOY CASTING RESULTS

The Arcast furnace was purchased and installed in the GE&R facility (Figure 7).

Figure 7: Photograph of the New Arcast Furnace

In the GE&R facility with atomizer on the right, water circulator in back and new Argon gas cylinders in place.

Source: General Engineering & Research

The Alloy Casting process development included the following efforts:

- Developing material preparation procedures.
- Testing Argon-grade gas needed during casting process.
- Testing within batch uniformity versus number of sample melts.
- Developing a technique to reduce the number of melts to increase throughput while maintaining batch uniformity.
- Optimizing starting material composition to maximize magnetocaloric performance.
- Demonstrating large batch casting (about 200g).
- Demonstrating formation of magnetocaloric material into a rod using tilt and pour into a mold.

- Demonstrating atomization process to form sub-millimeter-sized spheres.
- Developing post casting materials handling procedures.

A summary of the key results of these efforts is described, and additional details for the Alloy Casting process development are provided, in Appendix A.

The Arcast furnace was successfully installed, and procedures developed to cast GE&R magnetocaloric materials with excellent uniformity and high performance. The production capacity of the casting furnace exceeds the target capacity of one kg/day.

The atomization process available on the Arcast furnace was also tested to try and produce sub-millimeter-sized spheres. This option requires attaching the large cylindrical container to the furnace chamber. To perform the atomization, the molten alloy is poured into a high-pressure Argon gas stream that blasts the material into the cylindrical chamber and forms the sub-millimeter-sized spheres. Appendix A provides scanning electron microscope images of the powders obtained by atomization on our furnace over two different runs, along with the measured particle sizes. The particle sizes range from 20μm up to 500μm, which covers the desired size range (200 to 300μm).

There are a several major issues with this process. One, it is very difficult to get the timing correct during the tilt/pour into the gas stream, and most of the material does not get into the gas stream and ends up wasted. This leads to a very low yield of material. The best yield per run on the atomizer that was obtained is less than five grams of atomized material. This is too low of a yield to be practical for producing these materials at the scale needed to build magnetic refrigeration systems. Another significant issue is the atomized material is more easily oxidized during the process due to the difficulty of fully removing the oxygen from the much larger chamber prior to atomization and also due to the high-pressure gas stream breaking the chamber seals during atomization and allowing air to enter while the sample is still hot. Further, the atomized materials are not compatible with the subsequent high temperature anneal step. These sub-millimeter-sized spheres have such a high surface area that they are more prone to oxidation during anneal, thus magnetocaloric performance after anneal is reduced instead of being improved.

The atomization process issues were anticipated, and a backup plan to form sub-millimeter-sized pieces of magnetocaloric materials was developed where the magnetocaloric materials are casted into large ingot forms using the developed processing techniques on the Arcast furnace, then the large ingots are annealed to improve performance with minimal oxidation issues due to the reduced surface area, then a grinding/milling technique is used to break the materials into sub-millimeter-sized pieces. This process is described more thoroughly in the next section.

Task 3 PLATE FORMATION RESULTS

A hydraulic pressing system was purchased and installed in the GE&R facility with a 30-ton pressing capability (Figure 8).

Figure 8: New Electric Hydraulic Press With 30-Ton Pressing Capability

Source: General Engineering & Research

The Plate Formation process development included the following efforts:

- Developing methods to form magnetocaloric materials into sub-millimeter-sized particles.
- Developing pressing recipes to form robust plates of various sizes.
- Verifying magnetocaloric properties of the plates.

Additional details for the Plate Formation process development are provided in Appendix B. A summary of the key results is described here.

Following the anneal process, the magnetocaloric materials are in the form of 10 to 200g pieces. The material is too brittle to cut, so to form plates the material needs to be crushed into powder and then pressed into a plate form. To form the powder, a pulverizer was used (Figure 9a) that can be filled with an inert gas to prevent sparking of the material during pulverization. The pulverizer is capable of breaking down the magnetocaloric materials into powder within a few seconds. Once the powder is formed, sieving equipment (Figure 9b) is used to separate the particles by size.

Figure 9: The Pulverizer (a) and Sieving Equipment (b)

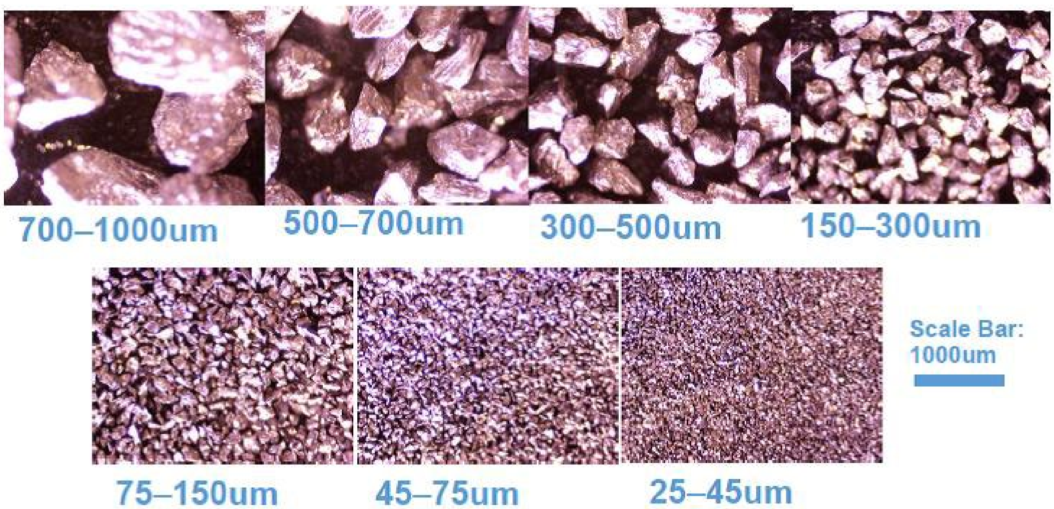
a) 

b) 

Source: General Engineering & Research

Below are scanning electron micrographs (Figure 10) of the magnetocaloric materials formed into sub-millimeter-sized particles using the new pulverizer, and then separated into various sizes using the new sieving equipment. Appendix B provides data showing the performance of the magnetocaloric material after the pulverizing and sieving where the particles were left exposed to air for two weeks and no oxidation was shown. This is good news for GE&R compositions that show these materials are very stable in air even when they are in the form of small particles, as this is not the case for other known magnetocaloric compositions. This makes material handling much easier for customers and provides improved device lifetimes.

Figure 10: Scanning Electron Microscope Images of the Sub-millimeter-sized Particles



Source: General Engineering & Research

The formation of the magnetocaloric plates was challenging. Several different die sizes were purchased to use in the hydraulic press, including circle dies with 0.5-inch, 1-inch, 1.5-inch, 2-inch, and 3-inch diameters, as well as a 1-inch square die. Appendix B details the processing needed to form the plates, with the various plates formed using the optimized processing methods. These plates do not shed material and are strong enough to hold together without falling apart when handled using a reasonable amount of care, which should suffice for customers to use in magnetic refrigeration systems.

Task 4 HEAT TREATMENT RESULTS

Anneal Test 1

The GSL-1700X anneal furnace was purchased and installed in the GE&R facility in 2019 (Figure 11).

Figure 11: New GSL-1700X Anneal Furnace with Heat Treatment Capability

Treatment capacity is up to 2912°F (1600°C) continuously.

Source: General Engineering & Research

Additional details for the Heat Treatment process development are provided in Appendix C. A summary of the key results is described here.

The Anneal Test 1 Heat Treatment process development included the following efforts:

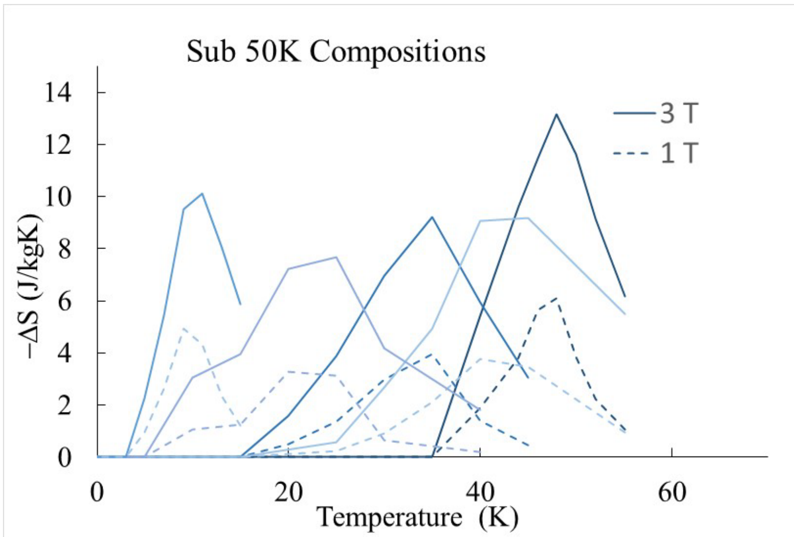
- Developing Argon gas purging process.
- Determining best sample containment materials.
- Testing and optimizing the time and temperature treatments for various alloys.
- Testing within temperature uniformity within the furnace.

Testing and optimizing the time and temperature treatments that achieve high performance magnetocaloric response was a time-consuming and arduous effort. The wide-range of GE&R's magnetocaloric alloys, all of which have slightly different melting temperatures and require different heat treatments to achieve the crystal structure needed, made this task the bulk of this EPIC effort. Ideally, heat treatments that are on the order of one week or less are preferred, as well as those that are lower in temperature because high temperature furnaces are both expensive to purchase and maintain, as well as requiring more energy to run. Further, the longer the anneal, the more likely degradation of the material may occur due to oxidation if small leaks into the furnace chamber occur, as well as having samples ruined due to power outages (power outages can also cause the furnace tube to crack due to the thermal shock of rapid cooling). GE&R magnetocaloric materials can be divided into two main categories:

1. Magnetocaloric material with peak functionality below 50K (–370°F [–223°C]).
2. Magnetocaloric material with peak functionality above 50K (–370°F [–223°C]).

It should be noted, optimizing the anneal time and temperature was also done simultaneously with optimization of the compositions because small changes in one of these variables can affect the other. Figure 12 shows a summary of ΔS versus temperature for GE&R's magnetocaloric compositions with peak functionality below 50K (–370°F [–223°C]) where the materials received the optimized heat treatment of 2012°F (1100°C) for three to six days depending on the composition. This annealing time and temperature provide the shortest anneal time possible to limit oxidation issues, while providing the highest consistent magnetocaloric performance with good uniformity within the batch. For these sub-50K materials, the target performance can easily exceed, and in some cases double, the target performance by annealing at 2012°F (1100°C) for three to six days.

Figure 12: Summary of ∆S Versus Temperature for GE&R Magnetocaloric Compositions with Peak Functionality Below 50K



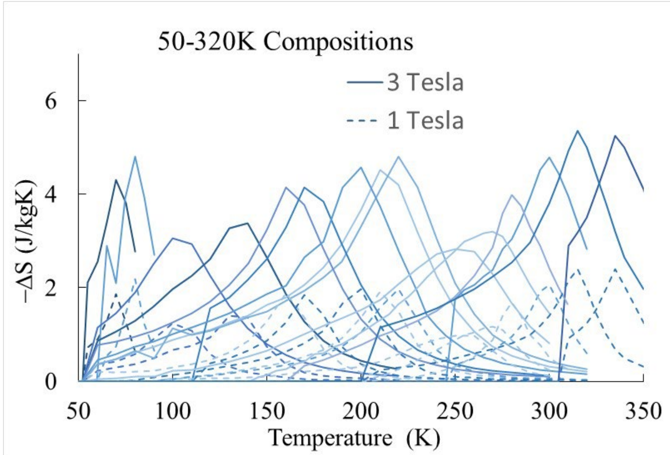
The materials received the optimized heat treatment of 1100°C for three to six days.

Source: General Engineering & Research

For the category 2 magnetocaloric materials with peak functionality above 50K, the heat treatments are a bit more complicated as these are quaternary compositions (the sub-50K materials are ternary compositions), which also contain gadolinium (Gd) and chromium (Cr), both of which significantly increase the melting temperature compared to the category 1 compositions. Similar to the category 1 compositions, the heat treatment optimization for the category 2 compositions must be optimized simultaneously with the composition. In general, the optimal anneal temperature (the point where the highest ∆S occurs) seems to increase with increasing Gd concentration, which makes sense as an increase in Gd concentration likely increases the melting temperature of the material, thus a higher temperature would be needed for diffusion to occur and to homogenize the material while in solid state.

It should be noted, even with no anneals, the materials exhibit good magnetocaloric functionality and can be synthesized to function at any temperature below 320K. These materials are currently commercially available and can be purchased from GE&R's webstore at www.geandr.com. Figure 13 shows the summary of ∆S versus temperature for GE&R magnetocaloric compositions with peak functionality above 50K where the materials received various heat treatments, which are currently available for purchase. As improved compositional and heat treatment processing optimization is achieved, the commercial product line will be updated accordingly.

Figure 13: Summary of ∆S Versus Temperature for GE&R Magnetocaloric Compositions with Peak Functionality Above 50K



The materials received various heat treatments.

Source: General Engineering & Research

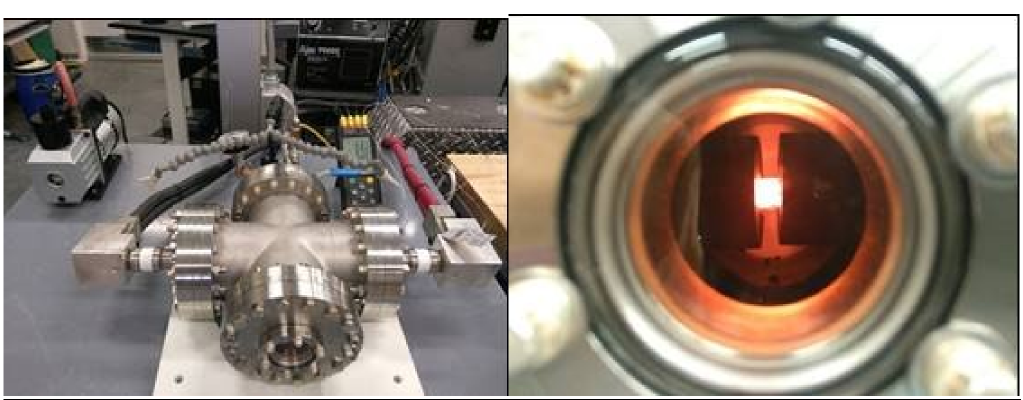
Anneal Test 2

The Anneal Test 2 Heat Treatment process is a proprietary Joule-heating technique developed by PNNL using match funding with the goal of developing a faster annealing process. This development included the following efforts:

- Modifying existing setup to enable higher temperature operation and with inert gas.
- Compare peak ∆S performance of selected magnetocaloric materials after traditional furnace anneal and Joule-heating treatments.

PNNL's existing setup was initially only capable of up to about 500°C annealing and was open-to-atmosphere. This setup had to be significantly modified to achieve much higher temperatures (about 1832°F [1000°C]) as well as to allow inert atmosphere processing. A new processing chamber was built by PNNL (Figure 14) and 1832°F (1000°C) temperatures under inert gas were successfully achieved.

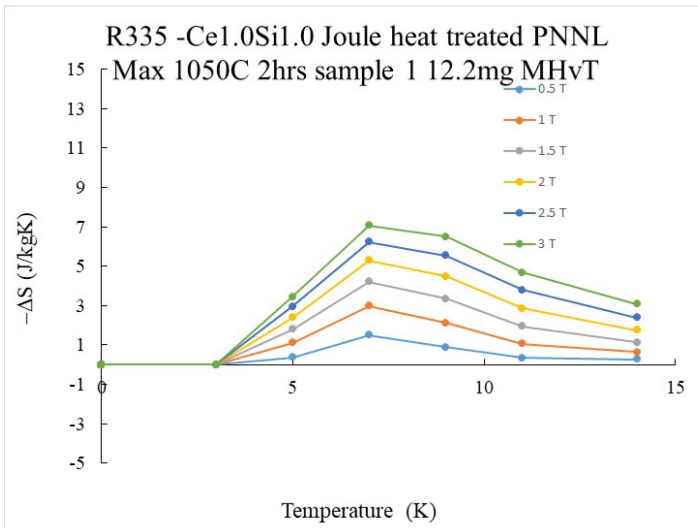
Figure 14: New Chamber Built by PNNL for Heat Treatment System and GE&R Sample Heated in the PNNL System



Source: General Engineering & Research

Figure 15 shows the ∆S versus temperature results for the magnetocaloric alloy with peak performance near 10K after PNNL Joule-heat treatment for two hours at 1922°F (1050°C). The peak performance meets our target for this material and is similar performance to that achieved with our standard furnace anneal of 2012°F (1100°C) for 12 days. While this was a promising result, it should be noted, the alloy that was tested on the PNNL system was the simplest magnetocaloric composition (binary). Further, this technique is currently only able to process about 30g samples which have to be in a cylinder shape. The cylinder shape is not easy to synthesize as these materials are very brittle, and the processing size will likely need to be at least around 100g per batch to justify the cost of implementing this technique in the GE&R facility. Thus, implementing this technique is not feasible at this time.

Figure 15: ∆S Versus Temperature for GE&R Magnetocaloric Alloy with Peak Performance



Near 10K after PNNL Joule-heat treatment for two hours at 1050°C.

Source: General Engineering & Research

Task 5 PACKAGING RESULTS

An industrial vacuum sealer was purchased and installed in the GE&R facility (Figure 16).

Figure 16: New Industrial Vacuum Sealer in Facility

Source: General Engineering & Research

The Packaging process development included the following efforts:

- Developing storage methods for starting materials.
- Developing vacuum sealing methods for materials in between processing steps, and post processing.
- Verifying effective long-term storage in vacuum-sealed packaging.

A summary of the key results is provided below.

The starting materials for the magnetocaloric compositions are purchased in pure form (99.9 percent purity) from various suppliers. The materials are supplied in 5g to 10g pieces and shipped in vacuum packaging to prevent oxidation. Once the starting materials arrive at the GE&R facility they are kept in their vacuum packaging and also placed into vacuum desiccators.

The oxidation of the alloys in air is very slow compared to the oxidation of the pure elements prior to casting. The alloys have a small amount of chromium which probably acts to protect the material from oxidation. To prevent any degradation of the surface over time, the materials are vacuum sealed after casting, which is a cheap and quick process. A similar procedure is also used following the annealing process, the milling/grinding process, and the plate formation process, and vacuum sealed packaging is also used for the final product shipping to customers (Figure 17).

Figure 17: GE&R Final Material in Packaging for Shipping

Source: General Engineering & Research

CHAPTER 4: Conclusion

The Arcast furnace has been successfully installed and procedures developed to cast GE&R magnetocaloric materials with excellent uniformity and high performance. The production capacity of the casting furnace exceeds the target capacity of one kg/day.

Procedures for pulverizing the magnetocaloric materials into sub-millimeter-sized powder, sieving the powder into various particle sizes, and then using the powder to form the material into robust one inch and smaller diameter plates have been successfully developed. To form plates that are larger than one inch in diameter, it was found that a hydraulic press with higher pressure capabilities is needed. If customers request larger diameter plates, GE&R will consider purchasing another hydraulic press with this higher-pressure capability.

A new anneal furnace was successfully installed and procedures developed to heat and treat GE&R magnetocaloric materials to improve performance. Anneal treatments of magnetocaloric materials with peak performance below 50K (–370°F [–223°C]) were successfully optimized and performance targets were exceeded. For magnetocaloric materials with peak performance above 50K (–370°F [–223°C]), the anneal treatments have achieved performance near, or above, the targets for all of the compositions. The production capacity of the anneal furnaces is currently lower than the target capacity of one kg/day; however, ramp-up of this production capacity can be done quickly when needed by purchasing a larger anneal furnace. GE&R plans to purchase this larger anneal furnace once magnetocaloric materials sales justify this cost.

Vacuum storage procedures for the starting materials to prevent oxidation have been successfully implemented. Vacuum sealing procedures for magnetocaloric alloys during processing and as final packaging for customers have also been verified as effective long-term storage for preventing oxidation.

GE&R's magnetocaloric materials are now commercially available for purchase from our webstore. Purchases of up to 200g quantities can be made directly from the webstore. The forms that are available are bulk ingots, various sized plates, and various sized powders. Larger bulk purchases and bulk pricing are also available for purchase by directly contacting GE&R for a quote. At these current quantities, orders of greater than 10 kg can be synthesized within two weeks, which is an acceptable turnaround time for customers.

GE&R currently has a 1600-square foot industrial space with all the necessary equipment to manufacture and characterize magnetocaloric material orders of up to one kg/day. This one kg/day capacity is more than sufficient to accommodate current customer orders. However, as customers develop their prototypes and move into production, GE&R will need to scale accordingly and add space and equipment to meet the production needs.

Once customer orders begin to exceed the one kg/day capacity, the plan to increase manufacturing capacity to a five kg/day capacity includes the following:

1. Add two more larger annealing furnaces with heating up to 3092°F (1700°C) and internal capacity three times the size of the current annealing furnaces.
2. Add a continuous melt adaptor to the Arcast furnace to increase per batch melt capacity.

As customers build magnetic refrigeration prototypes and look to move their products into production, the magnetocaloric materials used in these systems must achieve the following two metrics to be viable in large production magnetic refrigeration systems:

1. Cost <$1,000/kg (includes materials and processing); and
2. Performance - change in entropy (ΔS) greater than 3J/kgK in 3T magnetic field.

The current pricing for purchase of about one kg of magnetocaloric material is <$10,000 at the current scale, which is almost entirely labor and facility costs. As customer orders increase in size and frequency, it is expected that the pricing will significantly decrease to meet or fall below the $1,000/kg cost target. Further, all GE&R magnetocaloric materials meet or exceed the 3J/kgK performance metric (and in some cases, like the sub 50K (–370°F [–223°C]) materials, significantly exceed this metric with $\Delta S>9$ J/kgK).

GE&R has a two-fold commercialization approach:

1. MCM Sales - Sell magnetocaloric materials for all refrigeration applications.
2. Small Scale Cryogenic Refrigeration – Demonstrate small scale magnetic refrigeration for cryogenic applications and license/sell this technology to strategic partner for deployment.

Under another EPIC award EPC-19-021, GE&R is using their magnetocaloric materials to demonstrate a small-scale magnetic refrigeration system that operates in the sub 80K(–316°F [–193°C]) region for cryogenic applications. Specific objectives for this project are:

1. Build an at-scale system and demonstrate sustained magnetocaloric cooling below 80K.
2. Use validated theoretical model to identify optimized system configuration to achieve high efficiency and cost reduction compared to a comparable VCC system.

The GE&R team believes that the successful demonstration of a magnetic refrigeration prototype with improved efficiency and reduced capital cost compared to VCC will lower the risk for industrial financing/licensing to move magnetic refrigeration into the cryocooler market, as well as to stimulate industrial efforts for the use of magnetic refrigeration in other refrigeration applications (which will in turn lead to growth in GE&R magnetocaloric material sales).

Further, theoretical models of magnetic refrigeration have shown this technology to be up to 50 percent or more energy efficient compared to VCC technologies, without using environmentally hazardous materials (no HFCs). The technological advancements achieved with this EPIC project have eliminated a significant barrier for developers to build high-efficiency magnetic refrigeration systems and enabled these systems to move from prototype to production. Assuming 10 percent per year deployment of magnetic refrigeration technology, Californians would see an annual energy savings of about 2,000 GWh, which equates to about $300 million in electricity costs. Additionally, with HFC emissions being the fastest growing source of greenhouse gases both in California and globally, a 10 percent conversion/growth rate of magnetic refrigeration systems would eliminate about 5 million $MTCO_2e$ annually in California.

GLOSSARY AND LIST OF ACRONYMS

Term	Definition
< >	less than, greater than
3T	three-Tesla magnetic field
Al_2O_3	alumina oxide
AMR	active magnetic regenerator
BN	boron nitride
°C	degree Celsius, a temperature unit
CEC	California Energy Commission
CO_2	carbon dioxide
cryogenic	temperatures below about –184°F (–120°C) (153 K)
DOE	U.S. Department of Energy
EPIC	Electric Program Investment Charge
°F	degree Fahrenheit
g	gram
GdSiCr	gadolinium, silicon, and chromium
GE&R	General Engineering & Research
GHG	greenhouse gas
GWh	gigawatt hour
GWP	global warming potential
HFC	hydrofluorocarbon
HVAC	heating, ventilation, and air conditioning
J/kgK	Joules per kilogram × Kelvin (The amount of heat required to raise a unit mass of a material by 1 Kelvin [or degree Celsius]).
K	Kelvin, a temperature unit
LRIP	low-rate initial production
kg	kilogram
MCE	magnetocaloric effect
MCM	magnetocaloric material
MPa	megapascal pressure unit
$MTCO_2e$	a metric tonne of CO_2 equivalent
µm	micrometer
PNNL	Pacific Northwest National Laboratory

Term	Definition
ΔS	performance, change in entropy
Ta	tantalum
UCSD	University of California, San Diego
VCC	vapor compression cycle

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Project Deliverables

The Project Deliverables include the following list of products produced:

- Task 2 Alloy Casting Report
- Task 3 Plate Formation Report
- Task 4 Heat Treatment Report
- Task 5 Packaging Report

The above project deliverables are available upon request by submitting an email to pubs@energy.ca.gov.

ENERGY RESEARCH AND DEVELOPMENT DIVISION

Appendix A: Details from Alloy Casting Report

June 2024 | CEC-500-2024-057

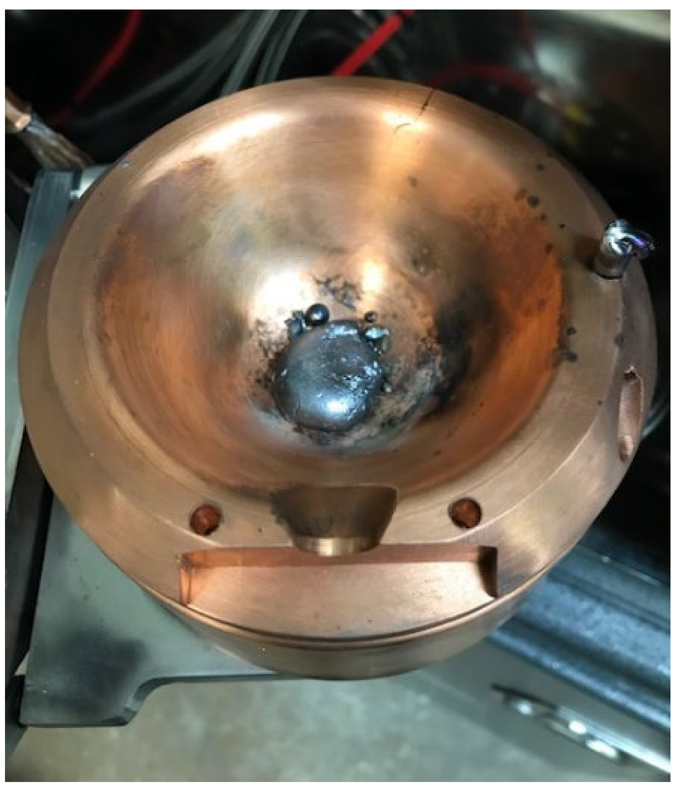
APPENDIX A:
Details from Alloy Casting Report

Developing materials preparation procedures

The starting materials for the alloy casting are purchased in pure form (99.9 percent purity) from various suppliers. The materials are supplied in 5g to 10g pieces and shipped in vacuum packaging to prevent oxidation. Once the starting materials arrive at the GE&R facility they are kept in their vacuum packaging and also placed into vacuum desiccators to ensure no oxide-tion of the materials occur prior to their use in the alloy casting process. It was found that the oxidation of these materials is slow enough that exposure to air for a few minutes does not cause much oxidation, thus, the compositions do not need to be measured out in an Argon glove box. This saves on cost and time, and all materials are stored in vacuum desiccators pre- and post-measurement.

To form the alloys, the compositions are weight measured in standard environment using a lab-grade scale with accuracy to 0.0005g, and then placed under vacuum until the casting process is performed. To perform the casting process, the materials are placed into the copper crucible of the Arcast furnace, and the chamber of the furnace is vacuumed to less than 10 millitorr and then re-filled with Argon gas prior to casting. Figure A-1 shows a photograph of the first alloy melt in the copper crucible of the Arcast furnace.

Figure A-1: First Alloy Melt Obtained on the New Arcast Furnace

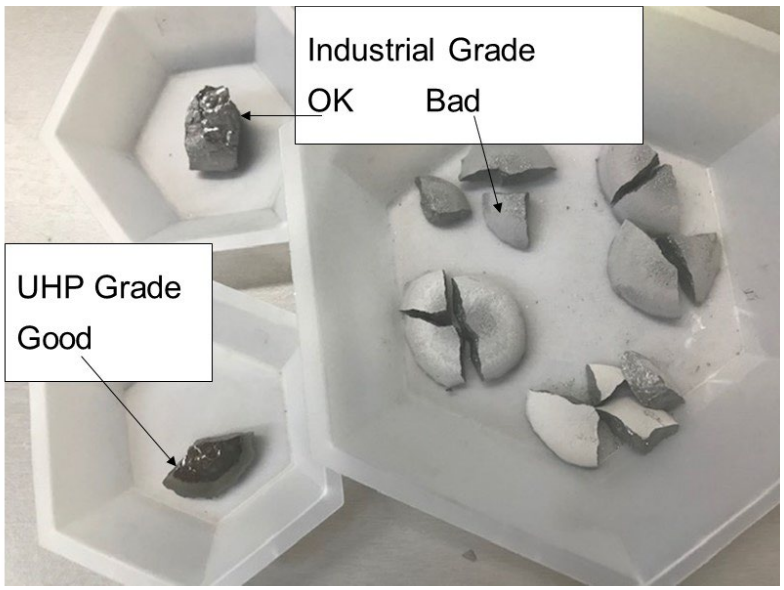


Source: General Engineering & Research

Testing Argon grade gas needed during casting process

The typical Argon grade gas used in the GE&R facility has been the Industrial grade. Unfortunately, oxidation issues with this grade supply were noticed during the casting process. Figure A-2 shows the results of casting using different Argon Industrial-grade bottles where some of the batches were very oxidized and only one of the Industrial grade was not oxidized. The more expensive Ultra High Purity grade of Argon provided good results (no oxidation), thus all casting in the Arcast furnace must be done with this more expensive Ultra High Purity grade of Argon.

Figure A-2: Different Argon Bottles Used to Cast Each Batch



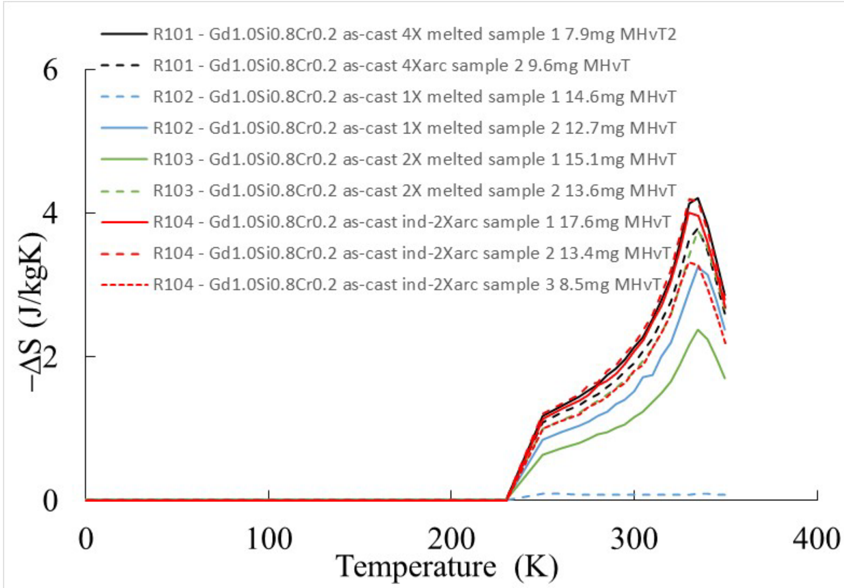
Some of the Argon bottles used yielded very oxidized product and only one of the Industrial grade was not oxidized. Casting with Ultra High Purity grade Argon produced the best results (no oxidation) with a very shiny sample.

Source: General Engineering & Research

Testing within batch uniformity versus number of sample melts

Magnetocaloric material homogeneity is required so that performance is consistent and maximized throughout the material. The copper crucible in the Arcast furnace is water cooled during processing which keeps the crucible from melting. This also makes it difficult to fully melt the casted material because any material touching the copper will also remain solid. To fully homogenize the material, it must be melted several times and flipped in-between each melt. Figure A-3 shows the within batch magnetocaloric performance variation of casted samples that were melted various times. With only a single melting, the batch variation was wide, while increasing the number of melts reduced this variation. The initial processing determined the optimal number of melts needed to homogenize the material was seven times. It should be noted this number of melts was obtained without using the electromagnetic stirrer, and the chamber was opened between each melt. This high number of melts and having to open the chamber in-between melts is not ideal as production yield per day is low (about 400g). Improvements to this technique are described in the next section.

Figure A-3: Within Batch Magnetocaloric Performance of gadolinium, silicon, and chromium (GdSiCr) Composition with Various Number of Melts

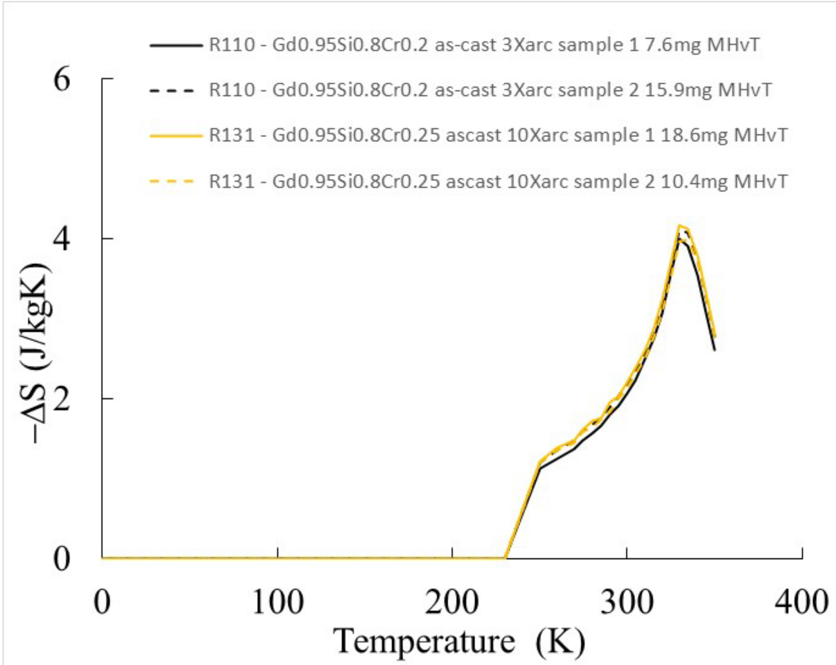


Source: General Engineering & Research

Developing technique to reduce number of melts to increase throughput while maintaining batch uniformity

A technique to flip the alloy inside the chamber in-between each melt was developed that significantly reduced the processing time because the chamber did not need to be opened and re-pumped to vacuum after each melt. Further, the use of the electromagnetic stirrer during the casting process allowed much more of the material to fully melt and homogenize during each melt. By implementing these two techniques the time to process one batch on the Arcast furnace is about one hour, which allows a production of more than two kg per day on this equipment – this EXCEEDS the production target for this project. Figure A-4 shows the within batch magnetocaloric performance of GdSiCr composition where 3 melts provides similar within batch homogeneity compared to 10 melts when electromagnetic stirring and in-chamber flipping techniques are used.

Figure A-4: Within Batch Magnetocaloric Performance of GdSiCr Composition with Various Number of Melts Using Electromagnetic Stirring



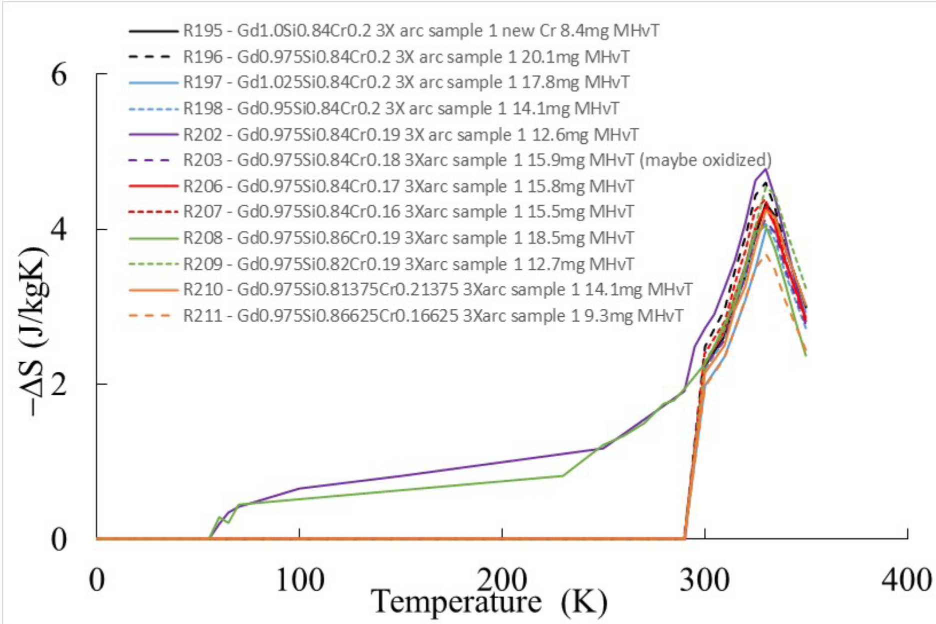
Various number of melts where electromagnetic stirring and in-chamber flipping techniques were implemented.

Source: General Engineering & Research

Optimizing starting material composition to maximize magnetocaloric performance

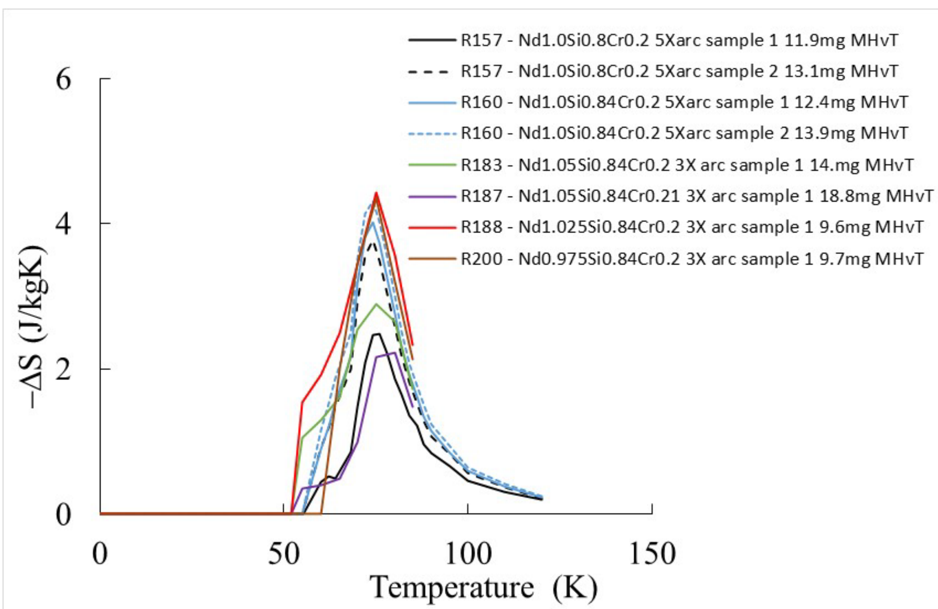
The Arcast furnace melts the sample material using a torch that can exceed 5432°F (3000°C). This provides rapid casting but can also lead to some sample evaporation if the starting materials evaporation temperature is below 5432°F (3000°C), which is the case for all of our starting materials. This evaporated material ends up deposited on the chamber walls and is cleaned and disposed of once the chamber is cooled and opened. This means that there is likely some evaporation of all of the starting materials, but some of the pure elements evaporate more than others, thus optimization of the starting compositions can be done to account for this issue so that post casting performance is optimized. Figure A-5 shows the magnetocaloric material performance for the GdSiCr composition where systematic adjustment of the composition was performed to optimize and achieve maximum performance. It was found that using 2.5 percent less gadolinium, 5 percent more silicon, and 5 percent less chromium, in each composition was optimal. Similarly, this technique was also used to determine 2.5 percent excess neodymium and 2.5 percent less cerium was optimal for the compositions that have lower temperature magnetocaloric performance (Figures A-6 and A-7).

Figure A-5: Magnetocaloric Material Performance for Various Compositions of GdSiCr



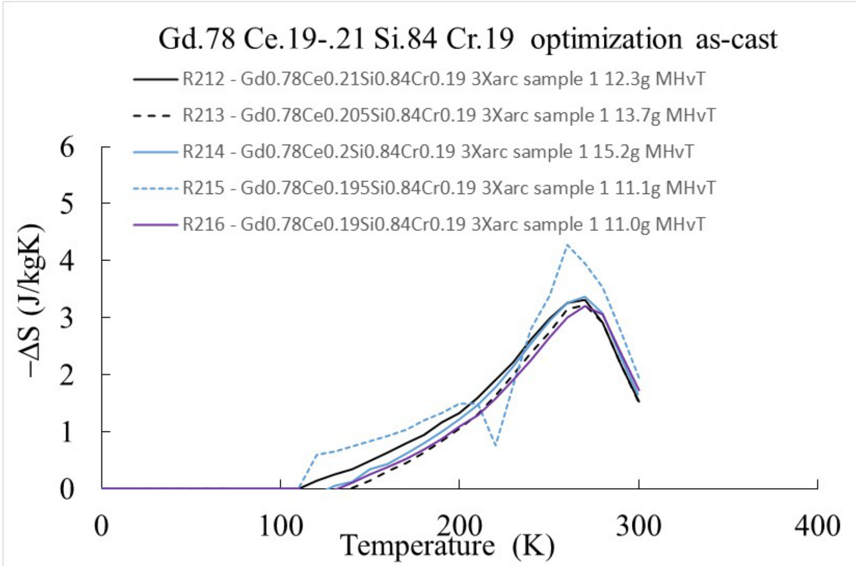
Source: General Engineering & Research

Figure A-6: Magnetocaloric Material Performance for Various Compositions of NdSiCr



Source: General Engineering & Research

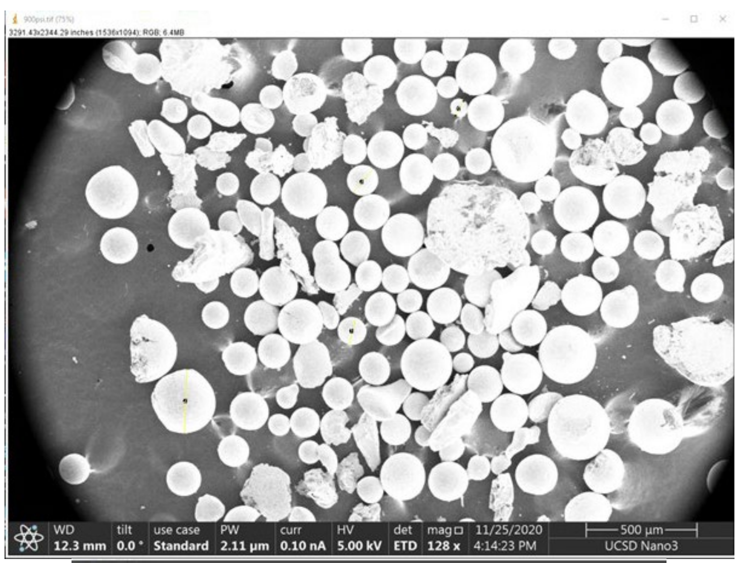
Figure A-7: Magnetocaloric Material Performance for Various Compositions of GdCeSiCr



Source: General Engineering & Research

Figures A-8 and A-9 show scanning electron microscope images of the powders obtained by atomization on the furnace over two runs, along with the measured particle sizes. The particle sizes range from 20µm up to 500µm, which covers the desired size range (200 to 300µm).

Figure A-8: Scanning Electron Microscope Image and Particle Size Measurement of Atomization Run 1 at a 900 pounds per square inch (psi) Argon Gas Stream



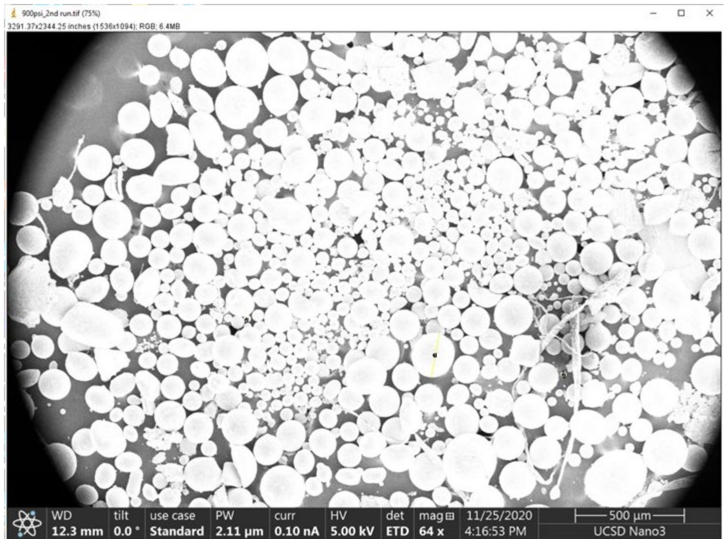
Results

File Edit Font Results

	Label	Area	Mean	StdDev	Min	Max	Angle	Slice	Length
1	900psi.tif	257	242	7	225	255	76	1	118
2	900psi.tif	615	235	14	209	255	88	1	286
3	900psi.tif	285	243	8	226	255	50	1	130
4	900psi.tif	165	243	10	199	255	60	1	75

Source: General Engineering & Research

Figure A-9: Scanning Electron Microscope Image and Particle Size Measurement of Atomization Run 2 at a 900psi Argon Gas Stream



Results

File Edit Font Results

	Label	Area	Mean	StdDev	Min	Max	Angle	Slice	Length
1	900psi_2nd run.tif	436	251	4	238	255	80	1	201
2	900psi_2nd run.tif	55	246	3	240	251	79	1	23
3	900psi_2nd run.tif	60	208	24	141	239	99	1	26

Source: General Engineering & Research

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Appendix B: Details from Plate Formation Report

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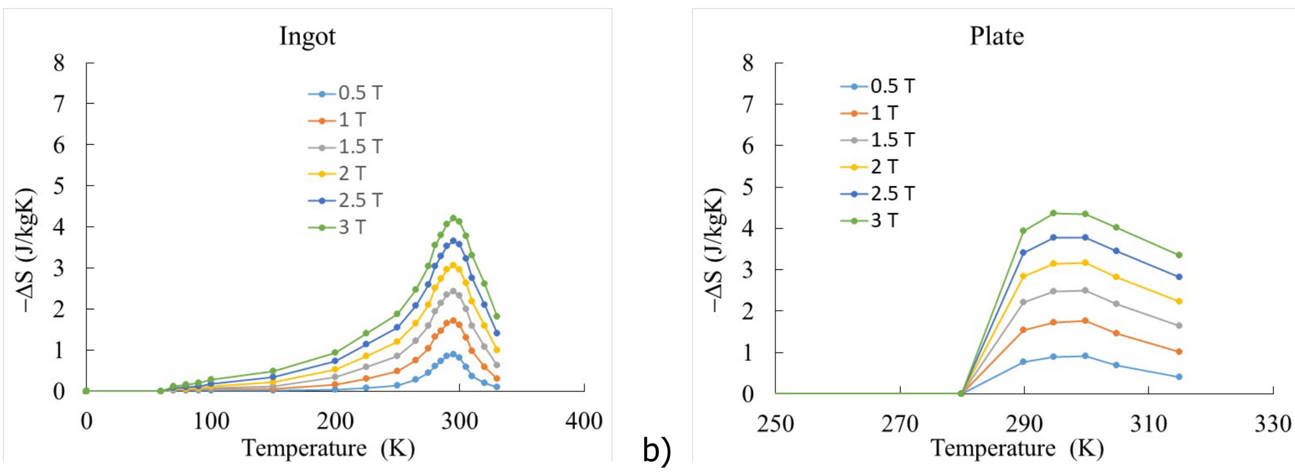
APPENDIX B:
Details from Plate Formation Report

Verifying magnetocaloric properties of the plates

Figure B-1 shows the magnetocaloric material performance of the room temperature MCE composition before and after being pulverized into powder and then pressed into a plate with the Loctite additive. The addition of the Loctite additive reduces the magnetocaloric performance by about 3 percent. This is an acceptable performance reduction to allow robust plate formation.

Figure B-1: Magnetocaloric Material Performance of GE&R Room Temperature Composition Before and After



Composition a) before and b) after being pulverized into powder and then pressed into a plate with the Loctite additive.

Source: General Engineering & Research

ENERGY RESEARCH AND DEVELOPMENT DIVISION

Appendix C: Details from Heat Treatment Report

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APPENDIX C: Details from Heat Treatment Report

Developing Argon gas purging process

Our anneal furnaces are alumina tube furnaces with metal sealing flanges on each end of the furnace that can be used to create a vacuum or inert atmosphere within the tube space. The magnetocaloric alloys are highly susceptible to oxidation at elevated temperatures and can also react with certain materials. Therefore, it is important to remove all oxygen from the tube prior to anneal, as well as ensure the metal sealing flanges on each end are well sealed prior to starting the heat treatment.

The procedure that was developed to properly purge the alumina tube prior to initiating the heat treatment includes first pulling a vacuum inside the tube furnace using a vacuum pump connected to a plastic tubing line. Then, filling the furnace back up to atmospheric pressure with pure argon, or a mixture of 98 percent Argon and 2 percent hydrogen gas (this mixture is preferred as it helps to reduce the oxidation reaction). This vacuum pump and argon fill process is repeated 10 times to ensure all oxygen is purged from the alumina furnace tube. Once the purging is complete the tube is vacuum pumped to a pressure of -0.07MPa[2] for all heat treatments that are below 2732°F (1500°C), and -0.06MPa for heat treatments above 2732°F (1500°C). The pressures in these furnaces are important as the alumina tube cannot be pressurized (if pressure inside the tube is higher than the pressure outside the tube, the tube will crack). Further, at temperatures above 2732°F (1500°C) the alumina tube will collapse if the pressure inside the tube is lower than the pressure outside the tube. Testing at different temperatures and then heating the furnace and monitoring the gas expansion and pressure increase was done to determine optimal starting pressures for the chamber.

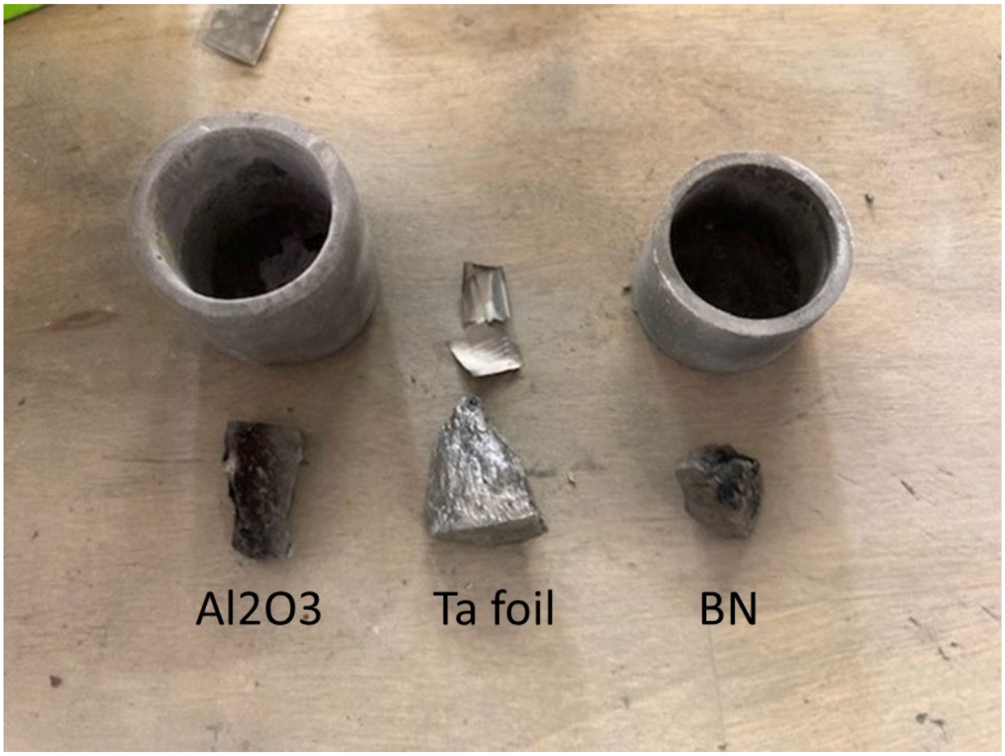
Determining best sample containment materials

The magnetocaloric compositions can be easily oxidized as well as reactive at elevated temperatures. The magnetocaloric materials need to be placed into crucibles within the alumina furnace tube so that the samples have no exposure to the furnace tube (this is to protect the furnace tube and the magnetocaloric samples). The most common crucible materials are aluminum oxides. There are also boron nitride and yttrium oxide crucibles. Unfortunately, all of the crucible materials will react with the rare earth elements that are in our magnetocaloric materials at elevated temperatures. The magnetocaloric material does not need to melt for this reaction to happen. Solid state diffusion of the rare earth is seen from the magnetocaloric material in contact with these crucible materials at temperatures above 1472°F (800°C). Because of this, tantalum foil wrapping is used around the samples during the anneal. This tantalum foil seems to provide very good protection from reaction with the crucible. Shown in Figure C-1 is a photograph of GE&R's room temperature magnetocaloric material after annealing at 2732°F (1500°C) for 12 days where pieces of the material were in either an alumina oxide (Al_2O_3) crucible, wrapped in tantalum foil (Ta), or in a boron nitride (BN)

[2] Mpa = Megapascal pressure unit

crucible. The Al_2O_3 and the BN showed significant surface degradation (not shiny metallic), indicating these crucibles are likely reacting with the magnetocaloric material at the high anneal temperatures. The Ta foil seemed to provide no degradation and will be used for all future anneals.

Figure C-1: GE&R's Room Temperature MCE Material After Annealing at 1500°C for 12 Days



Annealing where pieces of the MCE material were in either an alumina oxide (Al_2O_3) crucible, wrapped in Tantalum (Ta) foil, or in a boron nitride (BN) crucible.

Source: General Engineering & Research