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# Enhanced Energy Density in Permanent Magnets using Controlled High Magnetic Field during Processing

Orlando Rios

**May 5, 2016**

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Materials Science and Technology Division
Advanced Manufacturing Office

# Enhanced Energy Density in Permanent Magnets using Controlled High Magnetic Field during Processing

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# ABSTRACT

This ORNL Manufacturing Demonstration Facility (MDF) technical collaboration focused on the use of high magnetic field processing (>2Tesla) using energy efficient large bore superconducting magnet technology and high frequency electromagnetics to improve magnet performance and reduce the energy budget associated with Alnico thermal processing. Alnico, alloys containing Al, Ni, Co and Fe, represent a class of functional nanostructured alloys, and show the greatest potential for supplementing or replacing commercial Nd-based rare-earth alloy magnets.

Alnico, alloys show the greatest potential for applications at elevated temperatures, especially above 200°C, but the coercivities are 20 to 30% of theoretical limits adversely limiting performance. The coercivity of alnico depends on the nanostructure developed during spinodal decomposition, which in turn, is strongly affected by processing in an applied magnetic field. Alnico is an established commercial magnet material that is typically processed using energy intensive resistive electromagnets that generate magnetic processing field environments below 0.3 Tesla. The material highest energy product grades of alnico are chill cast to induce crystalline directionality in the form of columnar grains. The casting process is outlined in Figure 1. The final stages in the production of Alnico magnets are 1) solutionizing heat-treatment (1250 °C) followed by 2) an aging heat-treatment near the spinodal decomposition temperature (~820 °C), and 3) a “draw” cycle around 650 °C. The current technical collaboration focused on these heat-treatments.

However, the current practice for Alnico processing may be sub-optimal regarding high magnetic field processing nor has the use of energy efficient superconducting magnet technology been applied to the thermomagnetic processing of Alnico. The previous maximum applied field during before and during spinodal decomposition has been between 0.15 and 0.30 tesla. The superconducting magnet field was applied in the range of 2 and higher tesla. The maximum energy product, $(BH)_{max}$ of Alnico magnets is a strong function of the residual induction (Br), the coercive field strength ($H_{cB}$)and the squareness of the demagnetization loop. Hk, applied on the intrinsic curve, is an indicator of the squarerness of the demagnetization loop. Magnetic fields (2T) were found to have a measurable effect on residual induction (Br) (58% increase) while larger fields (9T) have a significant yet weaker effect on Br (25% increase). Hk however increases by over 300% at 9 Tesla and only 89% at 2 Tesla. The coercivity was increased and as a result the energy product increased by over 700% to a maximum of 6.87 MGOe.

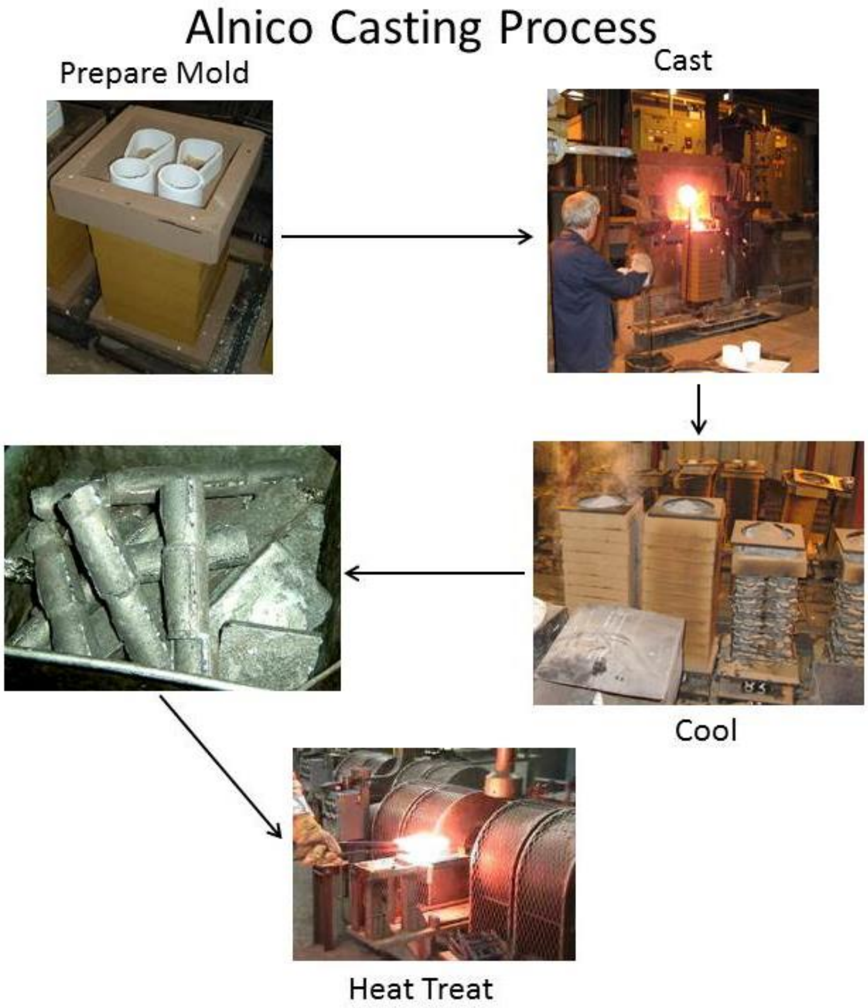

**Figure 1 - Alnico casting process showing casting using sand molds and heat treating under a magnetic field (thermomagnetic processing) using resistive magnets (<0.5T).**

# 1. ENHANCED ENERGY DENSITY IN PERMANENT MAGNETS USING CONTROLLED HIGH MAGNETIC FIELD DURING PROCESSING

This phase 1 technical collaboration project (MDF-TC- 14-05318) was begun on October 31, 2014 and was completed on April 12, 2016. The collaboration partner, Arnold Magnetic Technologies Corporation, is a large business. The results of this technical collaboration indicate that high magnetic field processing has the potential to improve the performance of Alnico magnets and to reduce industrial energy consumption by substituting legacy resistive magnets with high field superconducting magnet technology.

## 1.1 BACKGROUND

Alnico is a commercially produced permanent magnet that is manufactured using thermomagnetic processing. Permanent magnets (PM) with rare earth alloys, such as neodymium, praseodymium and dysprosium, are critical for PM-based motors for hybrid electric vehicles and generators in wind turbines. Recent concern for supply and price of the rare earth alloys has stimulated the search for alternative magnetic materials. Alnico, the first modern PM magnetic alloy, consists of Al, Ni, Co, Cu, Ti, and Fe and has excellent magnetic stability at high temperature. It would be an attractive near- term non-rare earth PM alloy if a modest increase in coercivity can be achieved. Alnico was discovered in 1931 and optimized before 1975, mostly by empirical studies and without the help of today’s advanced characterization and simulation tools. Key to the optimization of magnetic properties is control of the aging process of the Fe-Co ferromagnetic (α 1) phase and a non-magnetic NiAl-based (α 2) phase. The highest energy product alnico alloys are alnico 5-7 and alnico 9, which are both grain aligned and heat-treated with an applied magnetic field using energy intensive resistive electromagnet technology. On the other hand, magnetic field annealed alnico 8 without aligned grains develops the highest coercivity (Hci) after an extended magnetic field heat-treatment. The current investigation focused on commercial Alnico 9 produced by Arnold Magnetic Technologies. To further improve properties of Alnico alloys, understanding and ultimately control of the nanostructure is key, especially the effect of applied magnetic field during heat treatment on phase segregation morphology and magnetic domain structure. Improving performance of permanent magnet alloys is a complex optimization of microstructure through control of chemistry and processing. Alnico represents a class of chemically complex alloys whose functionality as a permanent magnet is dependent on the nano-structuring which develops during thermal heat treatment in an applied magnetic field.

## 1.2 TECHNICAL RESULTS

Current practice includes a solutionizing at 1250 °C to form a single phase structure. This is followed by rapid cooling to below 600 °C to avoid the formation of gamma phase. The optimal structure is formed upon re-heating to ~820 °C by the co-precipitation of two compositionally distinct phases through a spinodal decomposition. Formation of a directional structure during the precipitation step under magnetic fields is is key to enhancing magnetic anisotropy. The onset of the spinodal phase precipitation is quite sharp and rapid. Spinodal phases can occur sub-optimally during initial cooling and without an applied magnetic field. Our examination of samples which have had multiple annealings in the ~820°C range have all exhibited a complex hierarchy of nanostructured spinodal phases. Since the remanance and coercivity of Alnico are so intimately tied to this nanostructuring, non-optimized thermal processing is clearly detrimental. Secondarily, poor processing control in this range can contribute to formation of the fcc phase. This non-spinodal phase is non-magnetic and reduces the energy density at least proportionally to its volume fraction.

Optimal processing should include 1) a magnetic field applied during cooling from the solutionizing temperature (1250°C), 2) cooling of the entire magnet body below the spinodal temperature, and 3) precise hold in magnetic field at the spinodal temperature followed by 4) high rapid cooling to near room temperature. Advanced control of the thermomagnetic processing parameters was demonstrated using a commercial prototype thermomagnetic processing system. This system combines high magnetic fields generated by energy efficient superconducting magnets with intense radiofrequency (RF) electromagnetics (induction heating). The electromagnetics enable rapid heating and precision control of thermal profiles. Gas quench systems were used in this study however liquid quench capabilities under high magnetic fields are available, and will be considered in the future development of thermomagnetic processing parameters.

All thermomagnetically processed samples were sent to Arnold Magnetic Technologies for magnetic property measurements.

Two methods were used to track the energetics of the solutionizing and spinodal decomposition reactions under high magnetic fields. Resistance measurements, as well as a unique high magnetic field calorimeter developed under work sponsored by the DOE Critical Materials Institute (CMI) were applied to the processing of Alnico under high magnetic fields. A key area of research that is distinct from conventional processing of Alnico was the use of high magnetic fields during the solutionizing heat-treatment. In addition this study also investigated the use of fields that are significantly higher than typically available using resistive magnets.

In-situ resistance measurements were used to track the transformation kinetics under high magnetic fields. The Curie temperature was also tracked in-situ by monitoring the electromagnetic coupling efficiency rather than the electrical resistance. Induction heating makes use of an electrical resonator analogous to a simple LRC circuit. The sample (magnet material) is placed within the inductor and is therefore an integral component of the resonant circuit. The electromagnetic coupling efficiency drops sharply at the magnetic phase transition from ferromagnetic to paramagnetic. With proper design of the induction coil and selection of capacitors within the work head it is possible to detect a significant shift in resonance frequency and heating efficiency at the magnetic phase transition. This non-contact analytical method may later be implemented beyond laboratory scale process development and into high throughput commercial process control.

This technical collaboration consisted of the following elements:

1. Differential Scanning Calorimetry under high magnetic fields (HF-DSC)
2. High magnetic field processing experiments in horizontal large bore superconducting magnet
3. Investigation of the Curie temperature and spinodal decomposition kinetics under high magnetic fields
4. Development of electromagnetic processing control parameters
5. Thermomagnetic processing of Alnico
    a. Effect of aging (spinodal decomposition) temperature
    b. Effect of high magnetic fields

### 1.2.1 Differential Scanning Calorimetry under High Magnetic Fields (HF-DSC)

A unique Differential Scanning Calorimetry (DSC) technique was used in order to directly measure the energetics of the phase transformations linked to coercivity enhancement under high magnetic fields. The results were also compared with a commercial calorimeter that is routinely used at Ames National Laboratory. Samples were machined to specifications by Arnold Magnetic and provided to ORNL. These samples heated at 20°C/min under argon atmosphere with either 0 or 9 Tesla uniform magnetic fields to 1200°C and held for 30min. The samples were then cooled at 20°C/min. The results are shown in figure 2. Comparison of the 0T curve and 9T curve reveals that the transformation temperature increases by about 50°C. A similar result is seen at cooling. A discontinuous transformation was seen during the 0T and 9T cooling cycles. This transformation temperature was observed to shift approximately 100°C. This discontinuous shift could possibly be associated with the Curie temperature of the Alnico. The HT-DSC results indicate that significant shift in the transformation temperatures which could guide the future development of high magnetic field heat-treatments enabled by modern energy efficient superconducting magnet technology.

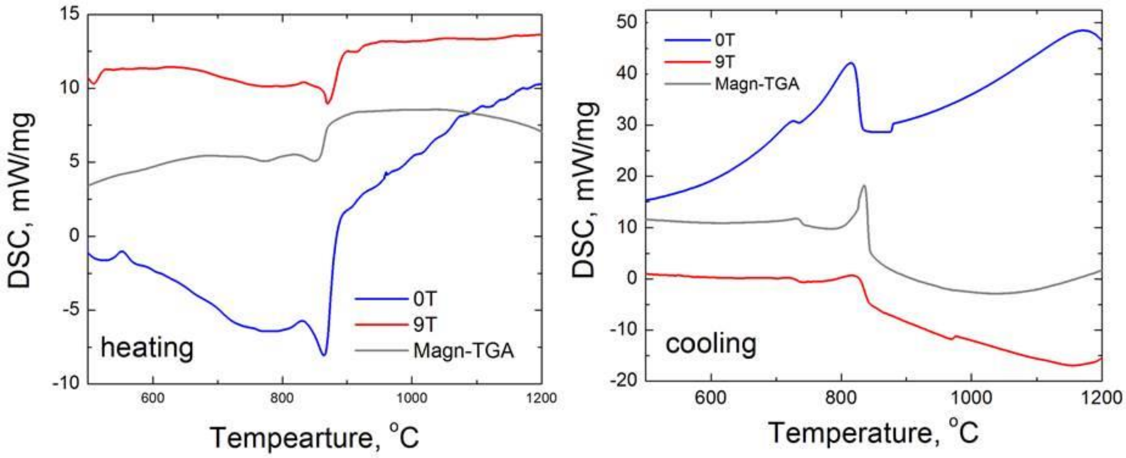

**Figure 2 - DSC results from Alnico samples provided by Arnold Magnetics.**

### 1.2.2 High Magnetic Field Processing Experiments in Horizontal Large Bore Superconducting Magnet

The goal of these experiments was to test the feasibility and effects of thermomagnetic processing at high fields using a superconducting magnetic processing system. The heat-treatment schedules were co-developed by Arnold Magnetics and ORNL during a one week site visit from Arnold Magnetic Technologies. All experiments were run using a high intensity coil in the horizontal magnet under inert gasses in order to better facilitate heating and cooling and to prevent oxidation. Argon was used for the heating and holds, and helium was used for rapid cooling. Changes in the samples were measured by observing changes in the resistivity of the sample. These changes were observed by running a fixed current across the sample and measuring the voltage drop. The temperature of the sample was measured using a thermocouple at the surface. Due to the small sample size, this temperature should be very close to the temperature at the center of the sample and should minimize thermal lag. The samples were heated directly and wrapped in insulation. In addition, part of the rig was loosely wrapped in insulation in order to help center the sample in the coil.

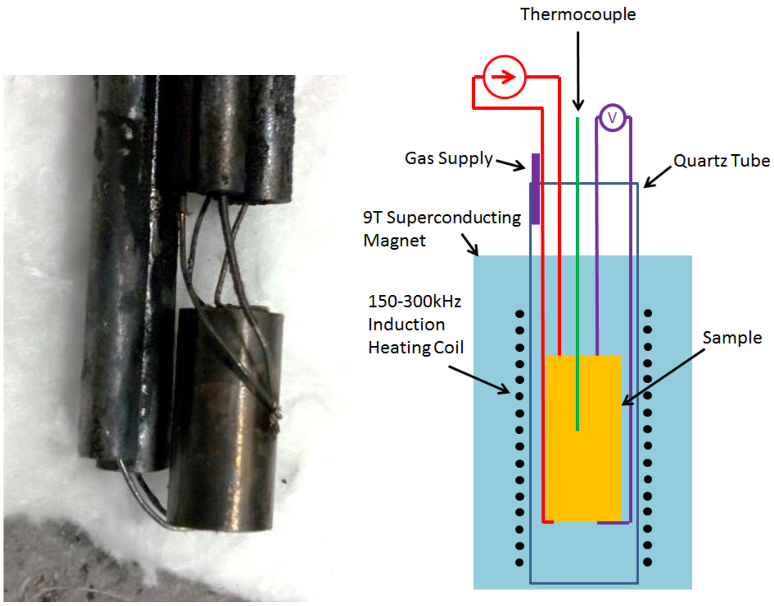

Figure 3 - Alnico sample mounted in resistivity rig and diagram of resistivity rig setup.

### 1.2.3. Investigation of the Curie Temperature and Spinodal Decomposition Kinetics Under High Magnetic Fields

Several tests were run in order to determine the optimum processing times at each temperature. It was discovered that, by reheating a sample back to the solutionizing temperature of 1250°C and holding it there, all previous heat treatment could be reversed allowing for the same sample to be used for multiple thermomagnetic cycles.

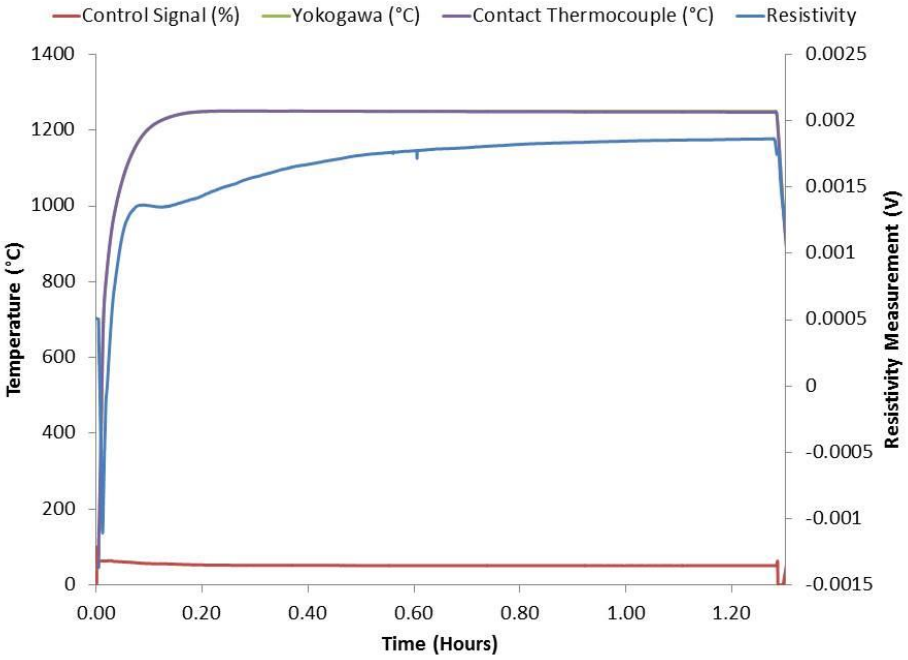

Figure 4 - Solutionizing process showing solutionizing for ≈1 hour.

Based on the discussion and measurements the profile decided upon was a rapid heat to 1250°C (850°C/min) and hold 30 min.

A second experiment was run that consisted of solution-treat at 1250°C for 30 min, gas quench to 600°C to ensure the center of the magnet was below the gamma phase formation temperature, reheated to 815°C and held for 3 hrs. This experiment revealed that the resistivity increased continuously for 60 min before reaching a maximum (Figure 5). The maximum resistivity was interpreted to occur when the spinodal transformation was complete. It was also found that the resistivity then continued to decrease for approximately 2.5 hours. This decrease was interpreted as coarsening of the microstructure. Based on this experiment it was determined that the hold temperature at 815°C should be between 10-30 minutes since the majority of the transformation was complete after that time had elapsed.

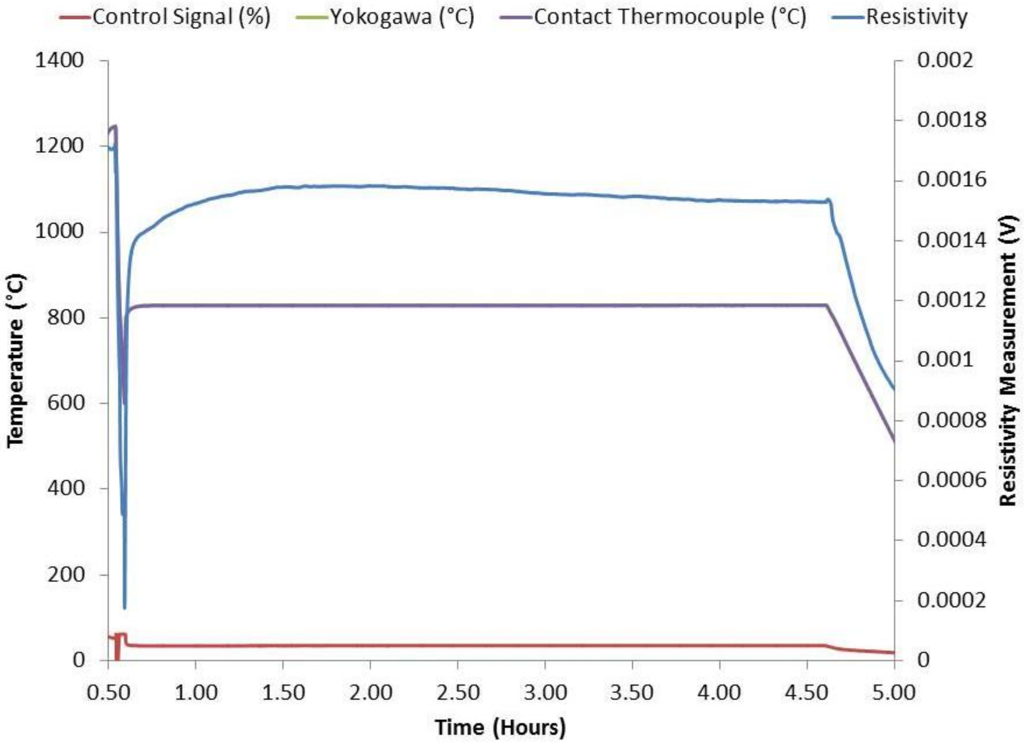

**Figure 5 - Aging process showing aging for >4 hours.**

It was also determined that the transformation temperature can be measured directly by examining the relationship between resistivity and temperature (Figure6). There are two changes in slope within the region circled in blue. In this experiment the Curie temperature was determined to be between 825°C and 850°C.

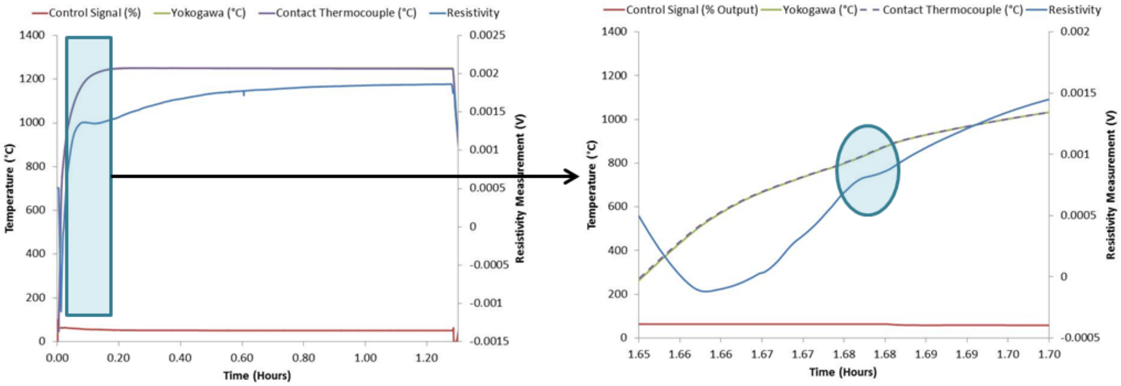

**Figure 6 - Detail view of solutionizing showing curie temperature.**

The process developed in this work is similar to the process currently used at Arnold, but with faster heating and cooling rates. These faster rates were achieved by using induction for the heating and flowing flowing helium for fast cooling. A current of 2A was used to measure the resistivity. This current could be reduced in order to minimize resistive heating at the expense of added signal noise.

### 1.2.4 Development of Electromagnetic Processing Control Parameters

A test sample was processed in a 2T magnetic field. The sample was first rapidly heated to 1250°C under argon and held at temperature for 35 minutes. The sample was then rapidly cooled to 600°C using helium, then rapidly heated back to 800°C under argon and held for approximately 10 minutes. The sample was then rapidly cooled to room temperature using helium. The sample was then rapidly reheated to 1250°C under argon and held for approximately 2 minutes. It was then rapidly cooled to 600°C again using helium and rapidly heated to 800°C under argon. After a 20 minute hold it was rapidly cooled to room temperature using helium before the magnetic field was ramped down (Figure 7).

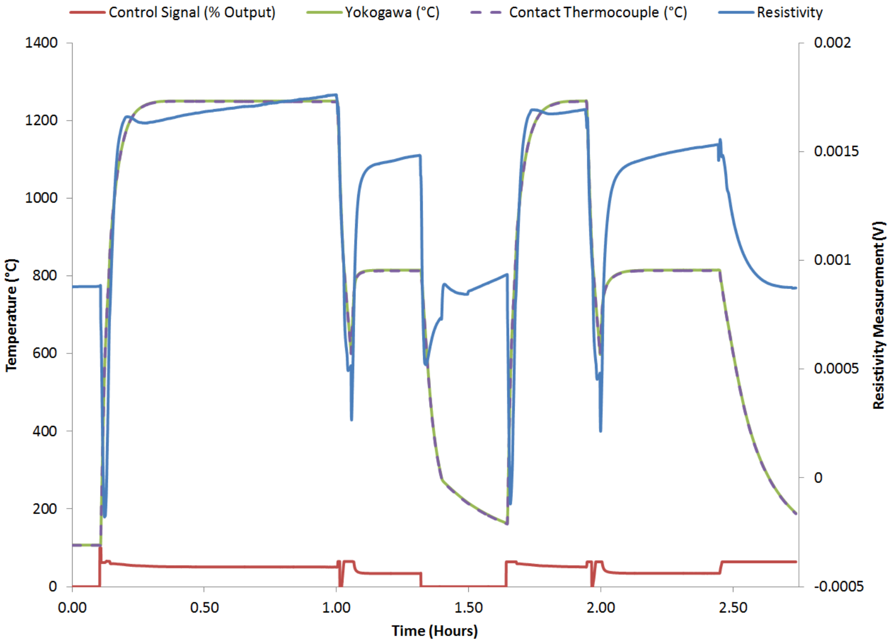

**Figure 7 - Test heat treatment with two back to back treatments.**

A second sample was processed without a magnetic field present. Processing started at around 58°C due to some minor resistive heating. All heating and holding was done under argon and all cooling was done using helium. The sample was first rapidly heated to 100°C and held for 10 minutes. It was then rapidly heated to 200°C and held for 5 minutes. After that it was rapidly heated to 400°C and held for 4 minutes. The sample was then rapidly heated to 600°C and held for 4 minutes then rapidly heated to 800°C and held for 7.5 minutes. Next the sample was slowly heated to 850°C over a period of 20 minutes and held there for 2 minutes. It was then rapidly heated to 1250°C and held for 30 minutes. The sampled was then rapidly cooled to 600°C then rapidly heated to 815°C and held for 13 minutes before being rapidly cooled to room temperature (Figure 8).

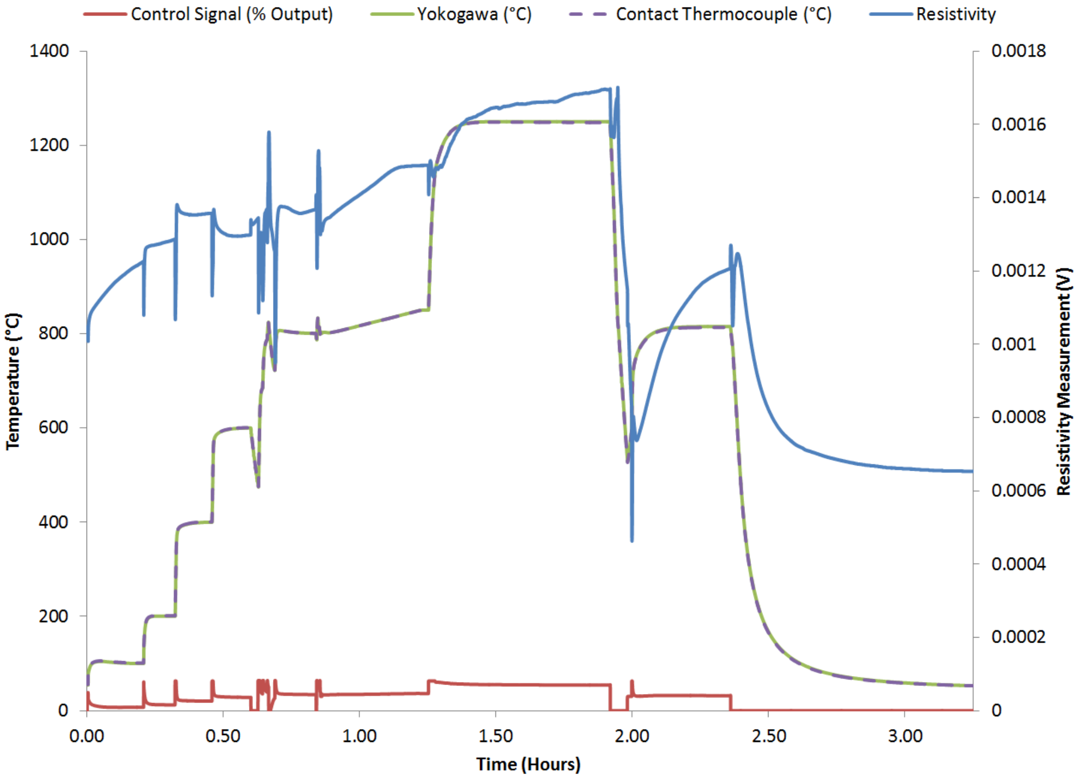

**Figure 8 - Test heat treatment with step up to solutionizing temperature.**

### 1.2.5 Thermomagnetic Processing of Alnico

As-cast Alinco material has very low coercivity and therefore less than 1 MGOe energy product. It is important to note that in all cases Alnico has a saturation magnetization that is on par with the most powerful rare-earth magnets. Unfortunately, these materials are deficient in coercivity and fall short of the minimum required for high energy product.

Thermomagnetic processing is a key step in developing the coercivity in Alnico magnets. In this study we examine the use of combined high magnetic fields generated by energy efficient superconducting magnets with intense radiofrequency (RF) electromagnetic inductively coupled magnet heating. The electromagnetics enable rapid heating and precision control of thermal profiles. Gas and liquid quench capabilities under high magnetic fields are available and will be considered in the future development of thermomagnetic processing parameters. Optimal processing (Figure 9) should include 1) a magnetic field applied during cooling from the solutionizing temperature (1250°C), 2) cooling of the entire magnet body below the spinodal temperature, and 3) precise hold in magnetic field at the spinodal temperature followed by 4) rapid cooling to near room temperature.

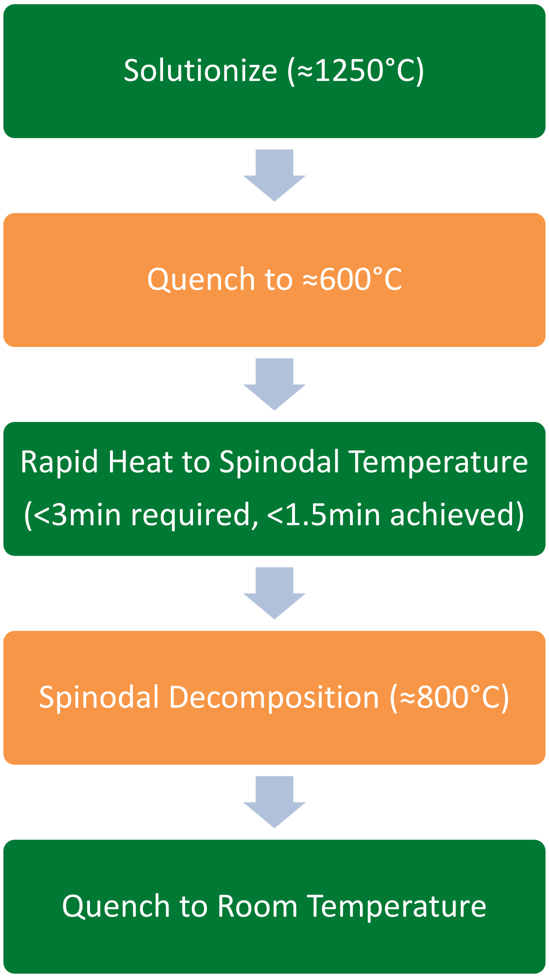

**Figure 9 - Final heat treatment for Alnico.**

Over 40 samples were run through a complete heat-treatment cycle at 0, 2 or 9 T. One sample in each set was run with 2A in order to take a resistivity measurement and the other was run without any current. All samples were set up in exactly the same way (including the wires for the current even on the no current samples) in order to ensure consistency. All samples were heated to 1254°C under argon as quickly as possible, held there for 30 minutes, quenched to 600°C using helium, rapidly heated to 810°C under argon, held there for 15 minutes, then rapidly quenched to room temperature using helium. The samples were then sent to Arnold Magnetic Technologies where their magnetic properties were measured in a closed loop hysteresigraph system to evaluate the magnetization and demagnetization curves to determine the maximum energy product. The resistance measurements during heat treatment were effectively used to determine the transformation kinetics. It was shown that in all cases the Alnico samples were fully solutionized after 30 minutes with and without a high magnetic field. A typical heat-treatment is shown in figure 10 along with an in-situ resistivity measurement.

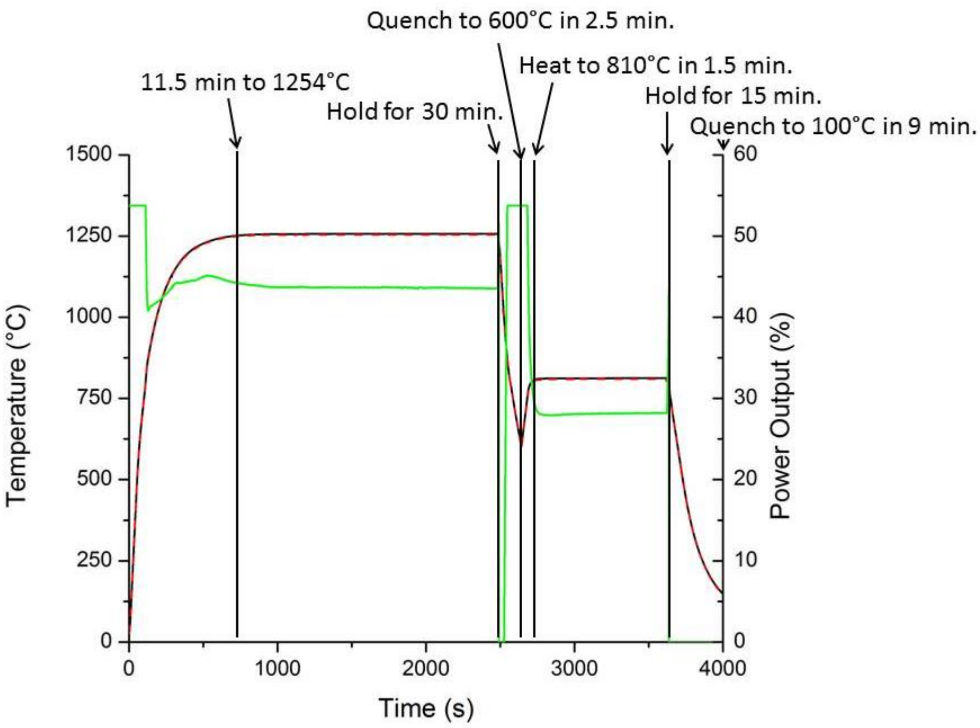

**Figure 10 - Heat treatment detail.**

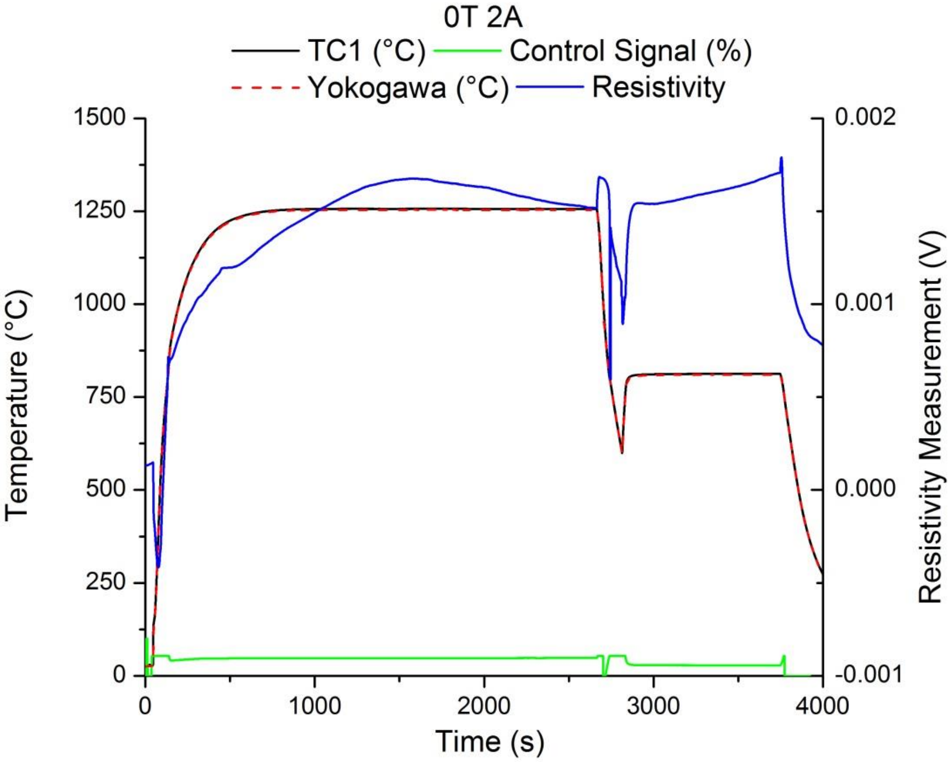

**Figure 11 - Heat treatment at 0T with a 2A signal for measuring resistivity.**

Over 40 high magnetic field processing experiments were conducted. A summary of the processing parameters used on select samples are given in table 1.

**Table 1 - Six samples were evaluated for magnetic properties after heat treatment**

| ID | Field | Process condition |
|---|---|---|
| 1 | 2 T | 1254°C, 30 min.; quench to 550°C; 810°C, 15 min.; quench |
| 2 | 9 T | 1254°C, 30 min.; quench to 550°C; 810°C, 3 min.; quench |
| 3 | 9 T | 1254°C, 30 min.; quench to 550°C; 840°C, 3 min.; quench to room temp |
| 4 | 0 T | 1254°C, 30 min.; quench to 550°C; 810°C, 3 min.; quench |
| 5 | 0 T | 1254°C, 30 min.; quench to 550°C; 840°C, 3 min.; quench |
| 6 | 9 T | 1254°C, 30 min.; quench to 550°C; 840°C to 810°C, 3 min.; quench |

The processed samples were shipped to Arnold where their magnetic properties were measured (Figure 12 and tables 2-4) and compared to unprocessed samples from the same batch of material.

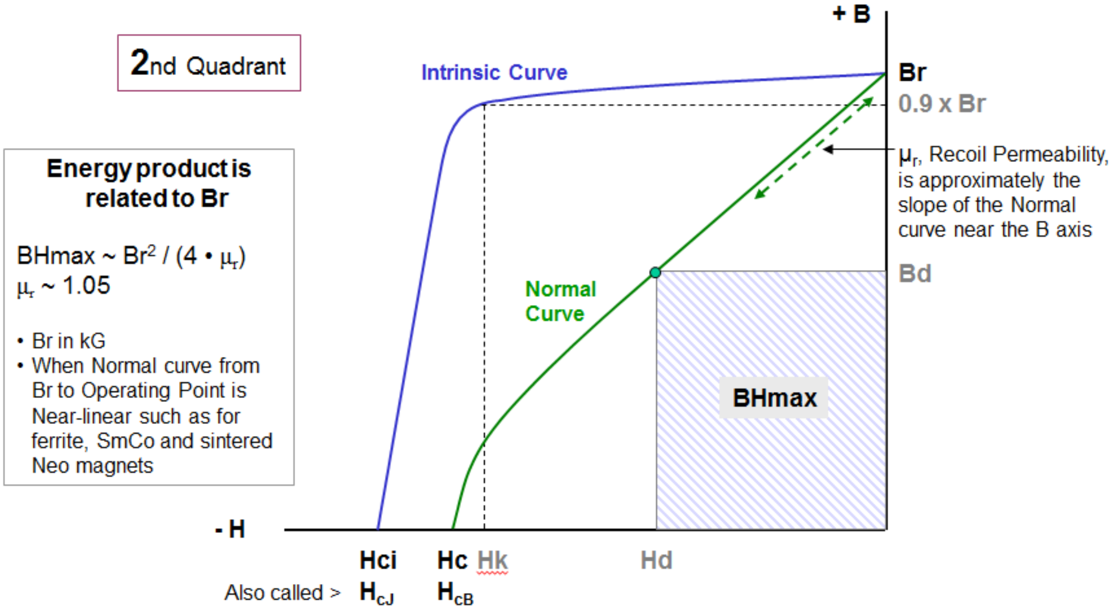

**Figure 12 - Measured magnetic properties.**

Magnetic property measurements reported are shown in the representative plot. Br, Hk, Hcj, and BHmax are compared to show the effect of the following: 1. The effect of aging temperature at 0T, 2. Change in field at constant temperature. Magnetic hysteresis is plotted in two curves, normal and intrinsic. These curves plot the magnetic induction, B, against the applied magnetic field, H. The intrinsic curve is a plot of the magnetic induction from just the sample being measured while the normal curve is a plot of the sum of the magnetic induction from the sample and the applied magnetic field. Br is the residual induction and represents the induction remaining in the material when the applied magnetic field is reduced to 0 after magnetizing the sample to saturation. Hk is the applied magnetic field value on the intrinsic curve corresponding to when the magnetic induction of the material has been reduced to 90% of Br. Hcj is the field that must be applied to fully demagnetize a sample after magnetizing it to saturation. BHmax is the maximum energy product of the material. The energy product is the amount of energy that the sample can supply to an external operating circuit, such as a motor or generator and is calculated by multiplying values of B and H on the normal curve.

**Table 2 - Physical properties of measured samples.**

| Magnet ID | Outside Dia. in | (M) Height in | Pole Area $cm^2$ | Volume cc | Weight g | Density g/cc |
|---|---|---|---|---|---|---|
| 1 | 0.3510 | 0.7020 | 0.6243 | 1.1131 | 7.9000 | 7.097 |
| 2 | 0.3500 | 0.7050 | 0.6207 | 1.1115 | 7.9100 | 7.116 |
| 3 | 0.3490 | 0.7020 | 0.6172 | 1.1005 | 7.9300 | 7.206 |
| 4 | 0.3500 | 0.7030 | 0.6207 | 1.1084 | 7.8600 | 7.092 |
| 5 | 0.3500 | 0.7060 | 0.6207 | 1.1131 | 7.9700 | 7.160 |
| 6 | 0.3480 | 0.7010 | 0.6136 | 1.0926 | 7.8900 | 7.221 |

**Table 3 - Summary plot comparing the effects of temperature at 0T and the effect of high magnetic fields.**

| Hysteresigraph | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Magnet ID | Br G | Hcb Oe | Hk Oe | Hcj Oe | BHmax MGOe | Js G | Hs Oe | Br/Js (ratio) | Sq'ness Hk/Hci |
| 1 | 9,798 | 724 | 157 | 750 | 2.43 | 11,745 | 6,941 | 0.83 | 0.21 |
| 2 | 11,280 | 1,074 | 672 | 1,087 | 6.87 | 11,837 | 6,731 | 0.95 | 0.62 |
| 3 | 10,460 | 519 | 172 | 525 | 2.22 | 11,858 | 6,447 | 0.88 | 0.33 |
| 4 | 6,204 | 418 | 83 | 438 | 0.84 | 11,740 | 7,127 | 0.53 | 0.19 |
| 5 | 6,997 | 446 | 123 | 461 | 1.23 | 11,832 | 7,000 | 0.59 | 0.27 |
| 6 | 9,951 | 501 | 174 | 511 | 2.11 | 11,673 | 6,526 | 0.85 | 0.34 |

**Table 4 - Percent increase of magnetic properties for selected sample sets**

| Samples | Br | Hk | Hcj | Bhmax |
|---|---|---|---|---|
| 4-5 | 13% | 48% | 5% | 47% |
| 4-1 | 58% | 89% | 71% | 189% |
| 1-2 | 15% | 328% | 45% | 183% |
| 2-4 | 82% | 710% | 148% | 718% |

### 1.2.6 Effect of Aging Temperature

Minor changes in the aging temperature can have a significant effect on the magnetic properties of Alnico. It was revealed that a 30°C increase in processing temperature from 810°C to 840°C can coarsen the spinodal decomposition products resulting in inferior magnetic properties (Figures 13 and 14). The energy product was shown to decrease from 1.23 to 0.84 MGOe, This resulted in a general decrease in the residual magnetization along with a decrease in the coercivity and the squareness of the demagnetization curve. This was attributed to a coarse spinodal decomposition.

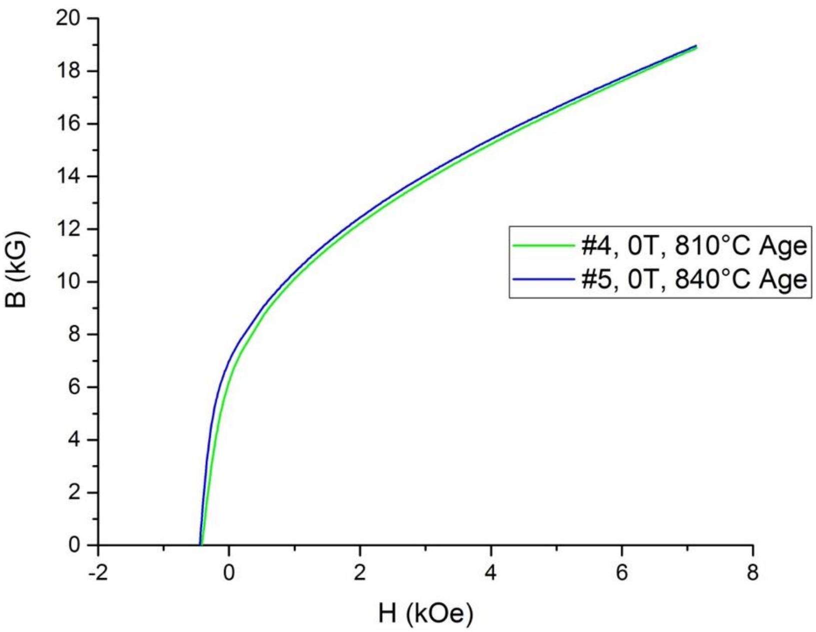

**Figure 13 - Hysteresis plot of samples 4 & 5.**

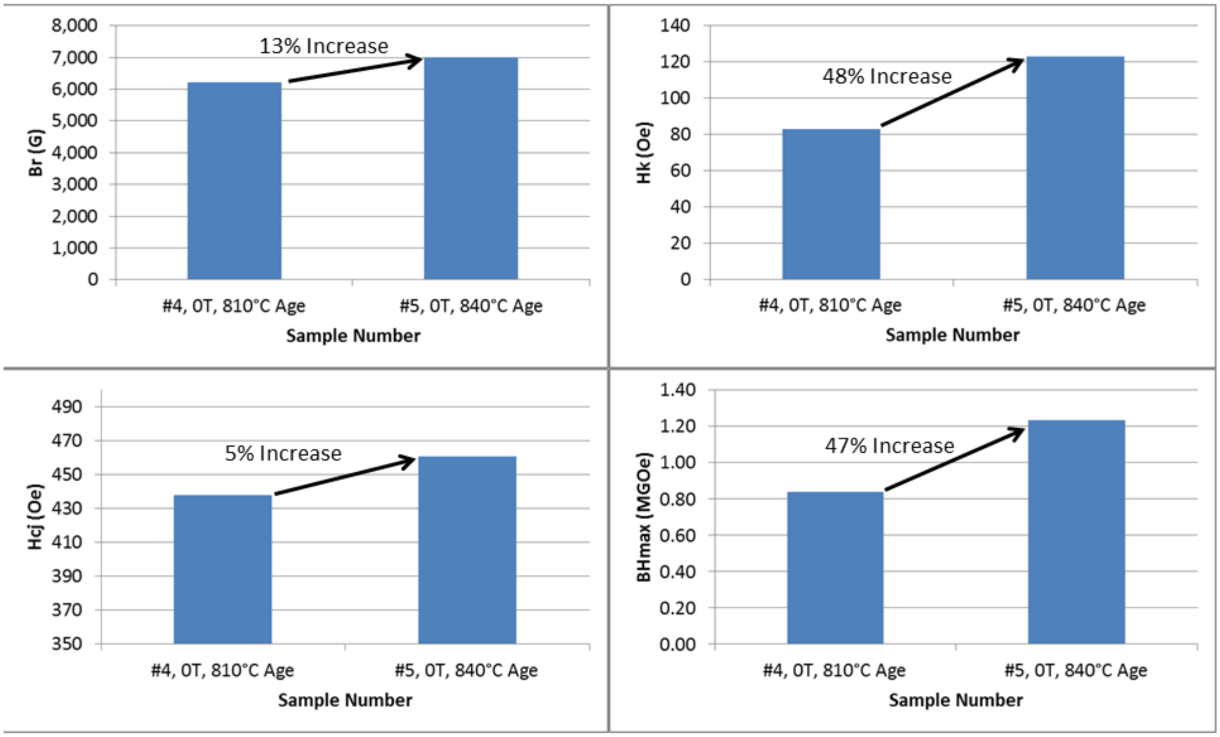

**Figure 14 - Br, Hk, Hcj, & BHmax for samples processed at 810°C and 840°C showing a slight improvement in residual magnetization and a 46% increase in energy product. The majority of the improvement in magnetic properties is attributed to improved squareness of the demagnetization curve as evident in Hk.**

### 1.2.7. Effect of High Magnetic Fields

Thermomagnetic processing of Alnico at Arnold Magnetics occurs fields less than 1T. The current study investigates the highest fields obtainable with commercially relevant superconducting magnetic processing systems (9T) and an intermediate field of 2T. The intermediate field has been shown to be compatible with large bore superconducting magnets.

The effect of field is evident with an increase in the BHmax of the resulting magnets (Figure 15). Interestingly small fields (2T) have a strong effect on Br (58% increase) while larger fields (9T) have a significant yet weaker effect on Br (25% increase). Hk however increases by over 300% at 9 Tesla and only 89% at 2 Tesla. The energy product increase by over 700% to a maximum of 6.87 MGOe (Figure 16). The maximum energy product approaches that of optimally processed Alnico. Although a full optimization and evaluation is well outside the scope of this study these results indicate that further optimization using thermomagnetic processing under high magnetic fields could provide a path to higher energy product Alnico.

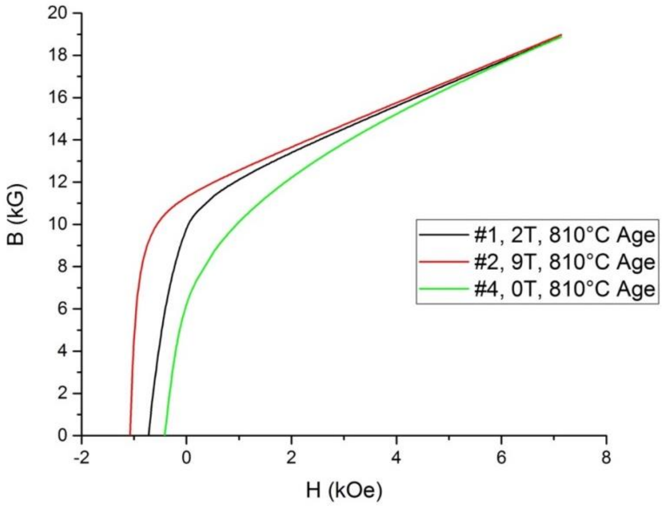

**Figure 15 - Hysteresis plot of samples 1, 2, & 4.**

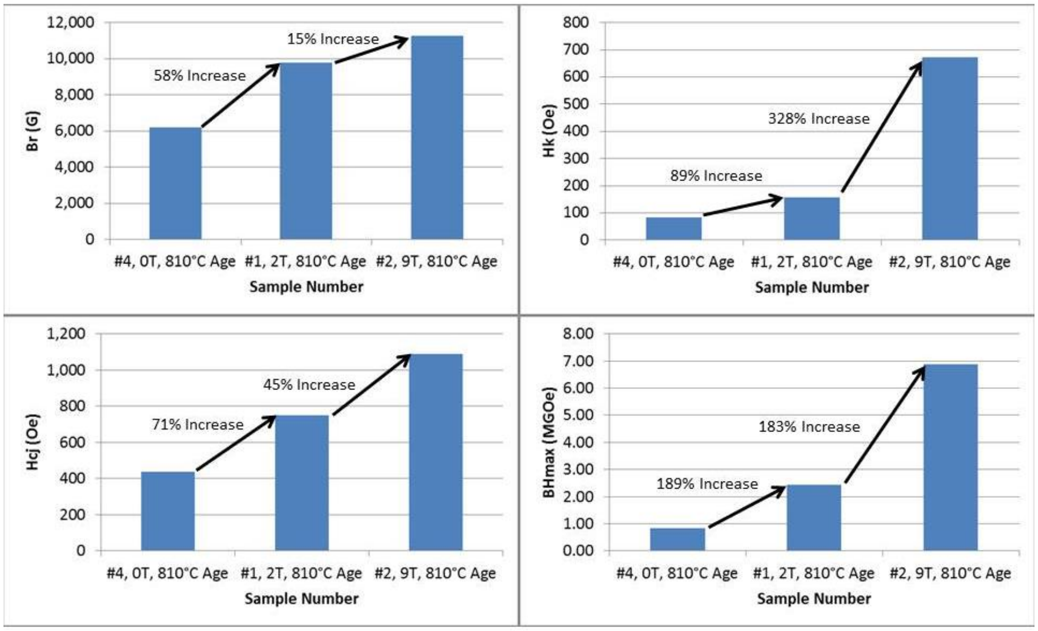

**Figure 16 - Br, Hk, Hcj, & BHmax for samples processed at 810°C and at 0T, 2T and 9T. A significant improvement in the energy product is found with increasing field.**

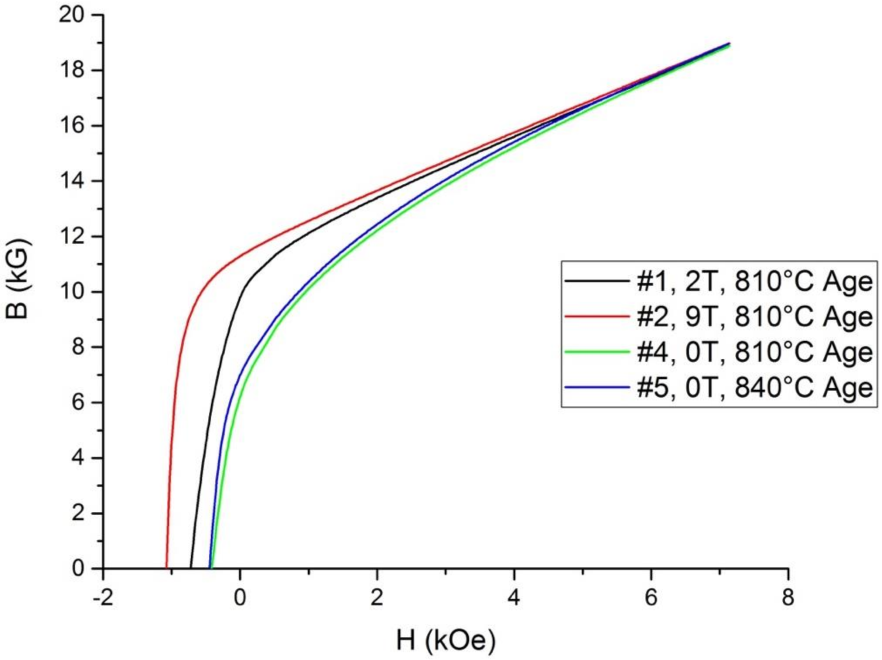

**Figure 17 - Hysteresis plots for selected samples.**

## 1.3 IMPACTS

This project indicates that high magnetic fields have the potential to improve the magnetic performance of Alnico magnets. Alnico magnets are already produced using thermomagnetic processing. Although the results are promising, further investigations are required to justify the investment required for the adoption of superconducting technologies for thermomagnetic processing at high fields. Arnold Magnetic Technologies has not upgraded its thermomagnetic processing facilities in over 40 years however they operate two daily manufacturing shifts. The results of this study indicate that the higher magnetic fields available with superconducting magnets are a potential candidate for improved products, production rates and energy efficiency. The current study provided some evidence however a more comprehensive study is required to make the business case for significant investments in new materials processing.

Alnico was invented in 1931 and has been commercially available on a global basis since then. Alternative materials developed between 1955 and 1995 (ferrite, samarium cobalt, samarium iron nitride, and neodymium iron boron) have provided greater resistance to demagnetization, an important characteristic for permanent magnet motors and generators. On the other hand, alnico benefits from 1) moderately priced and widely available raw materials, 2) no rare earth content, 3) high saturation magnetization, 4) superior physical strength and toughness, and 5) very good corrosion resistance. If a way can be found to increase intrinsic coercivity to resist demagnetizing fields, alnico's energy product will rise rapidly approaching maximum values which can be calculated as follows: Room temperature optimistic maximum of 41 MGOe (326 kJ/m$^3$) and more likely maximum of 28 MGOe (222 kJ/m$^3$). Alnico magnetic induction changes slowly with a change in temperature resulting in energy products at 200°C of 38 (optimistic) and 27 MGOe (likely) (302 and 215 kJ/m$^3$ respectively). At 200°C alnico of even "likely" energy product will outperform the best neodymium iron boron and alnico has the potential to perform above 500°C.

Raw materials used in manufacturing alnico magnets are available from many companies in many countries. While prices of all raw materials can be expected to vary with market conditions, none of the alnico constituent materials is considered rare or difficult to obtain.

Estimates of actual and potential permanent magnet output are presented in this table. Data of actual neodymium iron boron and alnico output has been obtained from numerous sources many of which are confidential. The following assumptions have been made.

- Output of neodymium iron boron would be greater if adequate supplies of dysprosium were available at an acceptable price
- Enhanced alnico would cannibalize a portion of existing alnico (legacy) business
- Enhanced alnico would take up to or more than 20% of neodymium iron boron business by 2020
- Enhanced alnico could be introduced in a short time (18 months) as required processing equipment and methodologies are quickly extensible
- A portion of the enhanced alnico production would be applied to applications at temperatures above those which could be served by neodymium iron boron and where the coercivity of enhanced alnico permits its use

Table 5 - Current and project demand showing the potential for a large market for Alnico

| Year | 2010 | 2012 | 2014 | 2016 | 2018 | 2020 |
|---|---|---|---|---|---|---|
| Sintered NdFeB, tons | 61,710 | 57,341 | 65,025 | 79,300 | 87,500 | 87,500 |
| Standard Alnico, tons | 5,555 | 5,893 | 6,252 | 6,500 | 5,000 | 4,500 |
| Enhanced Alnico, tons | | | | 4,000 | 13,100 | 17,500 |
| Total Alnico, tons | 5,555 | 5,893 | 6,252 | 10,500 | 18,100 | 22,000 |
| Alnico average sales value, $/kg | 30 | 30 | 32 | 35 | 38 | 40 |
| Sales value of Alnico, $millions | $ 167 | $ 177 | $ 200 | $ 368 | $ 688 | $ 880 |
| NdFeB + Standard Alnico, tons | 67,265 | 63,234 | 71,277 | 85,882 | 92,447 | 91,947 |
| NdFeB + total Alnico, tons | 67,265 | 63,234 | 71,277 | 89,851 | 105,564 | 109,437 |

Applications which might use enhanced alnico include wind power generators and high power density automotive motors and generators. Enhanced alnico could also replace neodymium iron boron in high performance industrial motors.

Alnico is the only commercially viable alternative to rare earth magnets in elevated temperature applications.

## 1.4 CONCLUSIONS

Magnetic fields (2T) were found to have a strong effect on Br (58% increase over 0T) while larger fields (9T) have a significant yet weaker effect on Br (15% increase over 2T). This indicates that, while processing under a magnetic field is beneficial and results in a stronger magnet, the effect does not scale linearly with the field strength. Hk however increases by over 300% at 9 Tesla and only 89% at 2 Tesla. This indicates that processing under a high magnetic field results in a magnet that is much harder to demagnetize than one that is processed under a lower magnetic field. The coercivity was increased and as a result the energy product increased by over 700% to a maximum of 6.87 MGOe.

### 1.4.1. Future Work (Phase 2)

The results of phase 1 proved that both solutionizing, quenching and ageing under a high magnetic field can improve the properties of Alnico. The preliminary study used materials that had already undergone a thermal cycle. Phase 2 will more closely match the production cycle by including large production magnets in the as-cast state. These are materials that Arnold does not typically release. However this CRADA provides a mechanism for closer interactions with industry.

Phase 2 will consist of developing optimized processing parameters for high performance alnico magnets. We propose a series of samples of alloys 5-7, 8 and 9 where samples are rapidly cooled from 1250°C to 810°C, the anneal temperature previously determined in Phase 1, by non-contact electromagnetic Curie point measurements (+/- 10°C) with and without the applied field. A second set of samples will be processed with and without the applied field during the quench. These samples will be characterized by TEM to evaluate the crystallographic orientation of nanoscale precipitates that form during the quench. Our team will include the use of high throughput transient processing under high magnetic fields. The transient processing methods include rapid heating, high magnetic fields and in-situ gas/water quenching. The results of Phase 1 will be analyzed and used to guide the process development. Arnold Magnetics has extensive expertise in Alnico alloys and will guide the process development and analysis while the ORNL MDF team will focus on efforts on scalable high magnetic field processing methods and advanced process control. Magnetic materials, and specifically the processing of Alnico, are quite complex. Therefore a partnership with a world leading manufacturer and materials experts is expected to accelerate the development of this technology and provide for an objective analysis. A follow-on project would be to look at Alnico 9 with some variable offset from perfect alignment to see if coercivity can be improved with a small amount of disrupted spinodal.

## 2. PARTNER BACKGROUND

Arnold Magnetic Technologies currently employs 775 persons and is a world leading manufacturer of Alnico with production facilities in the USA in Marengo, Illinois. Development of a higher performance Alnico will expand both the domestic and global market for Arnold’s products as well improve the competitiveness of several alternative energy technologies. Arnold Magnetic Technologies, headquartered in Rochester, N.Y., is a global manufacturer of high performance magnets, precision magnetic assemblies, flexible magnetic material, and thin metals. Arnold has 6 manufacturing facilities in the United States, 2 locations in Europe and 2 locations in Asia. Arnold’s largest manufacturing facility and only thermomagnetic processing facility is located in the USA. Arnold’s high performance, permanent magnets and magnetic assemblies have a wide variety of applications including generators on military and commercial aircraft, magnetic torque-coupled pumps , traveling wave tubes (radar), and precision thin alloy foil (magnetic and non-magnetic). Arnold can handle tasks ranging from relatively simple mechanical assemblies to complex electromechanical parts and components requiring extreme precision. Arnold custom produces Samarium Cobalt (RECOMA® SmCo), Alnico, Injection molded, and Flexmag rubber magnets. When required, Arnold supplies Neodymium Iron Boron magnets from licensed manufacturers. Arnold’s diverse markets allow us to keep our technologies on the leading edge of innovation.