

Final CRADA Report for
CRADA Number NFE -09-02189

**Magnetic Processing – A Pervasive Energy Efficient Technology for Next
Generation Materials for Aerospace and Specialty Steel Markets**

Gail Mackiewicz Ludtka, Principal Investigator
Gerard M. Ludtka, Co-Investigator
Oak Ridge National Laboratory

Patrick Ray, Co-Investigator
John Magee, Co-Investigator
Carpenter Technologies, Inc.

September 10, 2010

Prepared by
Oak Ridge National Laboratory
Oak Ridge, TN 37831
managed by
UT-BATTELLE, LLC
for the
U.S. Department of Energy
Under contract DE-AC05-00OR2225

Funding for this project was provided in part by the Department of Energy's Office of Energy Efficiency and Renewable Energy's Technology Commercialization and Deployment Program's Technology Commercialization Fund and by Carpenter Technologies, Inc. under CRADA No. NFE-09-02189.

UNLIMITED CRADA



ORNL-27 (4-00)

DOCUMENT AVAILABILITY

Reports produced after January 1, 1996, are generally available free via the U.S. Department of Energy (DOE) Information Bridge.

Web site <http://www.osti.gov/bridge>

Reports produced before January 1, 1996, may be purchased by members of the public from the following source.

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone 703-605-6000 (1-800-553-6847)
TDD 703-487-4639
Fax 703-605-6900

E-mail info@ntis.fedworld.gov

Web site <http://www.ntis.gov/support/ordernowabout.htm>

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange (ETDE) representatives, and International Nuclear Information System (INIS) representatives from the following source.

Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Telephone 865-576-8401
Fax 865-576-5728
E-mail reports@adonis.osti.gov
Web site <http://www.osti.gov/contact.html>

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Final CRADA Report for

CRADA No. NFE-09-02189 with

Carpenter Technologies, Inc.

Magnetic Processing – A Pervasive Energy Efficient Technology for Next Generation Materials for Aerospace and Specialty Steel Markets

ABSTRACT

Thermomagnetic Magnetic Processing is an exceptionally fertile, *pervasive and cross-cutting technology* that is just now being recognized by several major industry leaders for its significant potential to increase energy efficiency and materials performance for a myriad of energy intensive industries in a variety of areas and applications. ORNL has pioneered the use and development of large magnetic fields *in thermomagnetically processing (T-MP)* materials for altering materials phase equilibria and transformation kinetics. ORNL has discovered that using magnetic fields, we can produce unique materials responses. T-MP can produce unique phase stabilities & microstructures with improved materials performance for structural and functional applications not achieved with traditional processing techniques. These results suggest that there are unprecedented opportunities to produce significantly enhanced materials properties via atomistic level (nano-) microstructural control and manipulation. ORNL (in addition to others) have shown that grain boundary chemistry and precipitation kinetics are also affected by large magnetic fields. This CRADA has taken advantage of ORNL's unique, custom-designed thermo-magnetic, 9 Tesla superconducting magnet facility that enables rapid heating and cooling of metallic components within the magnet bore; as well as ORNL's expertise in high magnetic field (HMF) research. Carpenter Technologies, Corp., is a US-based industrial company, that provides enhanced performance alloys for the Aerospace and Specialty Steel products. In this CRADA, Carpenter Technologies, Corp., is focusing on applying ORNL's Thermomagnetic Magnetic Processing (TMP) technology to improve their current and future proprietary materials' product performance and open up new markets for their Aerospace and Specialty Steel products. Unprecedented mechanical property performance improvements have been demonstrated for a high strength bainitic alloy industrial/commercial alloy that is envisioned to provide the potential for new markets for this alloy. These thermomechanical processing results provide these alloys with a major breakthrough demonstrating that simultaneous improvements in yield strength and ductility are achieved: 12 %, 10%, 13%, and 22% increases in yield strength, elongation, reduction-in-area, and impact energy respectively. In addition, TMP appears to overcome detrimental chemical homogeneity impacts on uniform microstructure evolution.

STATEMENT OF OBJECTIVES

The primary goal of this project was to develop, mature and transition the High Magnetic Field Processing (HMFP) Technology beyond a laboratory novelty into a commercially viable and industrially scalable Manufacturing Technology by capitalizing on ORNL's Materials Processing Group's unique thermo-magnetic facilities and expertise. In this project, ORNL and Carpenter

Technologies, Inc. have collaborated on the research and development of magnetic processing effects for the purpose of manipulating microstructure and the application specific performance of two alloys provided by Carpenter (their Custom 465 alloy, and their bainitic high strength alloy steel). Some specific industrial and commercial applications areas considered were cases where HMFP can be used to provide significant energy savings and improve materials performance include using HMFP to: 1.) Increase the strength of their PH stainless grades by 10% without sacrificing ductility and toughness. 2.) Improve the high strength and toughness of their high strength alloy steel via HMF processing to obtain a lower cost, higher energy efficient ultra-fine bainite structure. Mechanical property performance improvements in these two industrial/commercial alloys were evaluated with the goal of expanding Carpenter's current market for these alloys.

BENEFITS TO THE FUNDING DOE OFFICE'S MISSION

The key mission of the US DOE, Office of Energy Efficiency and Renewable Energy (EERE), Industrial Technologies Program, Energy Intensive Program (EIP) is to improve the energy efficiency and energy utilization in energy intensive US industries. The goal of this project was to improve the energy efficiency of processing specific alloys of commercial interest to US industries using HMFP to provide significant energy savings and improve materials performance. The Superconducting magnets being used in this CRADA High Field Magnetic Processing (HMFP) technology project provide a more energy efficient materials processing technology than other conventional and/or currently available materials processing alternatives.

TECHNICAL DISCUSSION OF WORK PERFORMED BY ALL PARTIES

In order to accomplish the objectives of this project, ORNL and Carpenter have collaborated to improve the mechanical performance of two specific alloys selected by Carpenter. Carpenter provided ORNL the initial baseline/starting pedigrees for the materials for each material, for example, the processing history, as-received material microstructural characterization (optical/SEM metallography, grain size), the current baseline core microstructure mechanical properties, and the materials needed to conduct the experiments agreed upon. Since CCT information did not exist for the bainitic high strength alloy steel, Carpenter provided ORNL dilatometer specimens of the bainitic high strength alloy material, to define the martensite start temperature in order to generate these data in order to initiate Task 2.

Carpenter fabricated the mechanical property test specimens for ORNL to Thermo-Magnetically process and Carpenter performed all the mechanical testing. ORNL determined via dilatometry how the martensite start temperature shifted with magnetic processing. This effort was necessary in order to define the process control parameters for the HMF experiments. Knowing the CCT data prior to HMF processing aided in guiding ORNL in determining the thermo-magnetic processing temperatures needed to obtain the proper/optimized heat treatment practices.

Carpenter Technologies staff, upon review of their ferrous alloy systems, down-selected two candidate alloys for initial proof-of-principal HMFP experiments. One was their Custom 465

stainless steel alloy, the other was a new, high strength bainitic alloy. The materials characterization results for these alloys are detailed below.

HIGH STRENGTH BAINITIC ALLOY

The high strength bainitic alloy has the chemistry noted below in Table 1. This alloy is well documented and typically is used in the austenitized + quenched + refrigerated + tempered condition. . The primary goal for this alloy was to develop a more energy-efficient T-MP processing sequence that would eliminate the energy-intensive cryogenic processing step that is currently needed to control and limit the amount of retained austenite in this alloy. The mechanical properties and performance of this alloy are strongly influenced by the % retained austenite present in this alloy. Table 1 lists the nominal alloy composition for this alloy.

TABLE 1 CHEMISTRY OF SUPER BAINITIC ALLOY (HEAT 010964)

Element	C	Mn	Si	P	S	Cr	Ni	Cu	V	Ti	Al	N [ppm]	O [ppm]
wt. %	0.36	0.78	0.94	<.005	<.0005	1.26	3.81	0.52	0.30	<.003	.004	<10	<10

MATERIALS CHARACTERIZATION

First, in order to determine/establish the important phase transformation temperatures prior to planning the targeted TMP experiments for this material, CarTech provided some mechanical and dilatometer test samples to ORNL, ORNL conducted and completed high speed quenching dilatometry experiments on the dilatometer samples using a high quench rate (@ 20 psi) on Carpenter's high strength alloy samples. Figure 1 shows that the martensite start temperature was determined to be ~238C. As a comparison, the martensite start temperature was also estimated by using the standard Andrews equation, i.e.,

$$Martensite\ start(K) = 785 - 453C - 16.9Ni - 15Cr - 9.5Mo + 217C * C - 71.5C * Mn - 67.6C * Cr \text{ (eqn 1)}$$

Using this equation, the Ms was estimated to be ~516.4K (nominally 243C), which shows excellent agreement between the predicted/estimated and actual experimental values determined for the martensite start temperature.

Also, at the beginning of this CRADA, ORNL ran initial baseline type TMP trials/experiments on a more standard Carpenter alloy grade material both with and without a magnetic field. These test samples were significantly larger in diameter and length (and hence, sample mass) than previously tested ones, and hence, the sample handling and quench tube design required both heating coil redesign and sample handling modifications to heat and rapidly quench these samples. ORNL designed and fabricated a sample holder and appropriate fixturing capable of handling the larger diameter (~0.55-inch diameter) samples requested by Carpenter. Using magnetic saturation (M values) for a 52100 steel alloy, the extraction force was estimated to be on the order of 250 – 275 lbs., which is nearly 40% higher than the extraction force exerted on the magnet for previous samples that were 0.5 inches in diameter and only 3.5 inches long. This significant increment in the extraction force required a change out on our linear motion robotic platform to achieve a maximum gear head load capacity of 400 lbs. In addition, to achieve the

required high quench rates for this alloy with this larger mass sample also required the use of a stainless gas manifold on the inlet side of the sample tube endcap.

ORNL performed metallographic evaluations using DOE funding from a DOE-based project in which Carpenter is a supporting in-kind partner. Materials characterization of the samples processed with no-field vs. with magnetic field processing demonstrated a profound response during aging treatments. Figure 2 shows the striking distinction in the microstructural response of this alloy by aging with and without a magnetic field imposed. Aging in the presence of a magnetic field appears to essentially eliminate the obvious “banding” that results following aging this alloy without a magnetic field imposed during aging. Consequently, aging under the influence of a magnetic field appears to significantly reduce the banded/ periodic structure that resulted without a magnetic field imposed during aging. In other alloys, this type of banding is typically associated with local chemistry variations (apparent alloy segregation). Consequently, TMP appears to overcome detrimental chemical homogeneity impacts on uniform microstructure evolution.

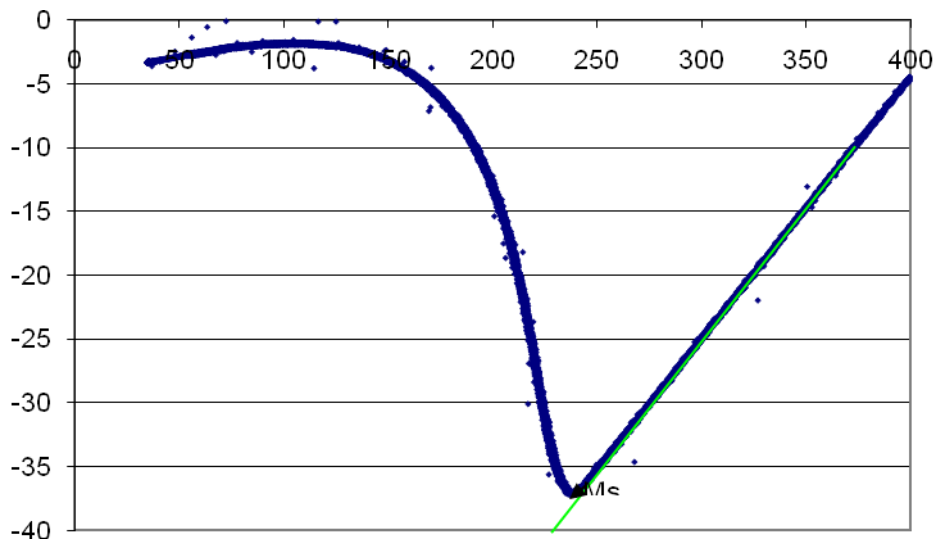


Figure 1 Plot depicting the experimentally determined martensite start (Ms) phase transition temperature (238C) for a baseline steel composition using high speed quenching dilatometry techniques.

MECHANICAL PROPERTIES

Using the experimentally determined (discussed above) martensite start (Ms) phase transition temperature (238C) for another steel alloy, a preliminary test matrix was developed to investigate and determine the influence of thermomechanical processing (TMP) during austempering on its mechanical properties. Tensile and Charpy impact tests conducted on samples with and without TMP demonstrated that the samples TMP had higher yield strength, lower ultimate strength, higher % elongation and % reduction in area, and better Charpy impact properties compared to the no-field (NF) trials.

For the 9T thermomagnetically processing runs, the tensile and Charpy samples were processed as follows:

- Austenitized at 885C_under a 9T field for 30min;

- Helium-gas-quenched at 90psi to 250C;
- Held at 250C_8hrs under a 9T magnetic field;
- HeQ to room temperature.

For the No-Field (NF), 0T processing runs, the tensile and Charpy samples were processed as follows:

- Austenitized at 885C at 0T/NF for 30min;
- Helium-gas-quenched at 90psi to 250C;
- Held at 250C_8hrs at 0T/NF;
- HeQ to room temperature

While the lower ultimate strength and better ductility and toughness values could be explained by the temperature difference between the two trials, the higher yield strength means that the magnetic field narrowed the gap between the yield strength and the ultimate tensile strength. This narrower gap is considered favorable for some industrial applications. Table 2 summarizes these data and demonstrates that HMFP results in unprecedented improvements in mechanical property performance. Figure 3 demonstrates the relative mechanical property (Charpy V-notch and toughness index) performance improvements developed in this alloy by employing ThermoMagnetic Processing. This figures shows that thermomagnetically processing this high-strength (low alloy) bainitic steel enables this latter alloy to outperform a much higher (a Co-containing) alloy, Maraging 250 steel,.

It is envisioned that these alloy property improvements will provide unique opportunities by expanding the potential markets for this alloy and TMP is anticipated to provide similar performance enhancements and similar market expansions for many other alloys. These TMP results represent a major and significant breakthrough in materials property enhancements not previously attained. Namely, both strength and ductility are simultaneously improved. These mechanical property results are unprecedented, and cannot be achieved by any other processing method. These results demonstrate that TMP can provide simultaneous improvements in yield strength and ductility. For example, for this alloy, 12 %, 10%, 13%, and 22% increases in yield strength, elongation, reduction-in-area, and impact energy, respectively are achieved. In addition, as demonstrated above, TMP appears to overcome detrimental chemical homogeneity impacts on uniform microstructure evolution.

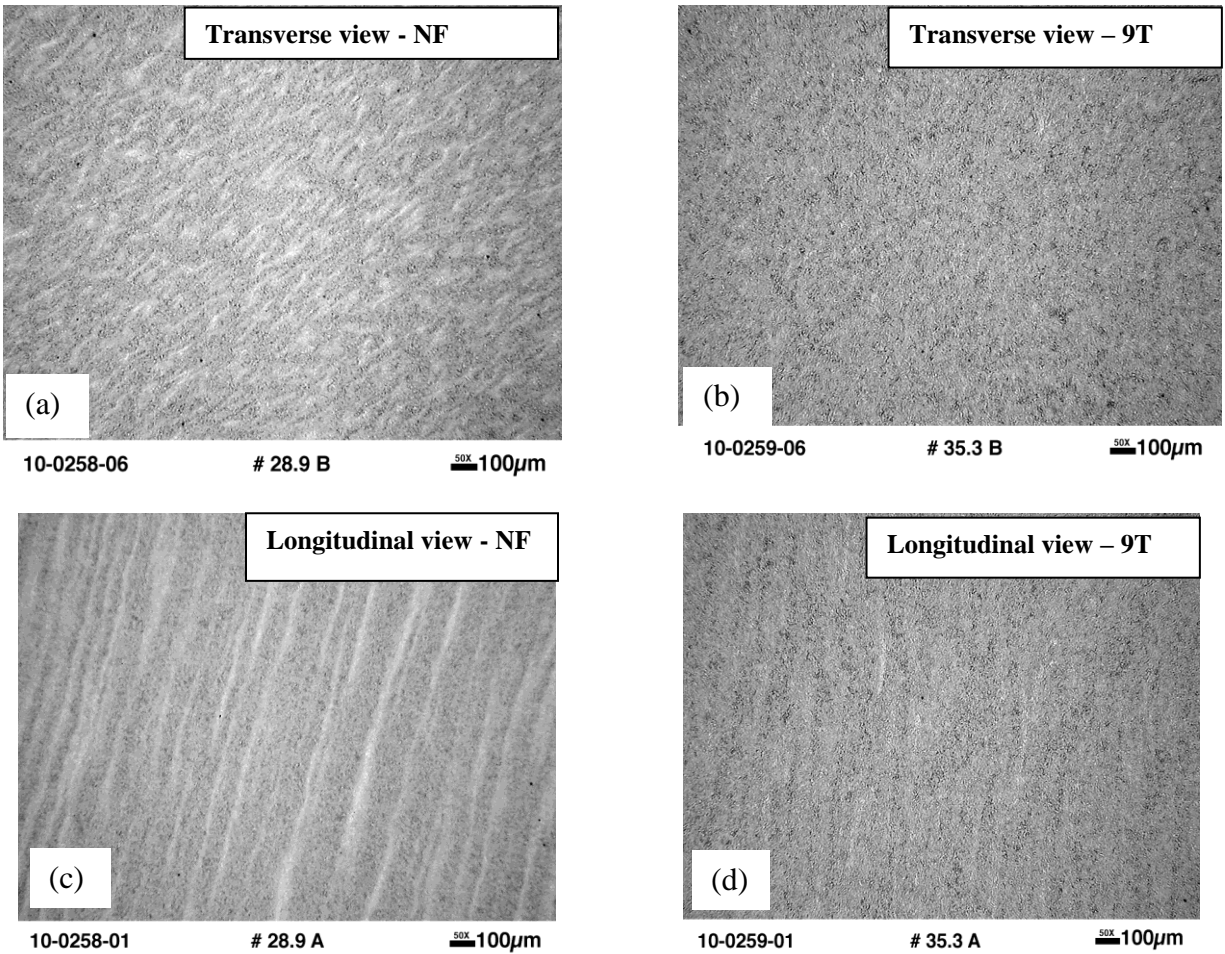


Figure 2 Preliminary metallographic micrographs of a high strength bainitic alloy austenitized and austempered for 8 hrs without (Fig. 1 a & c), the No Field (NF) condition and with (Fig. 1 b & d) a magnetic field (9T) indicate that magnetic field processing appears to refine the microstructure ((Fig. 1 a vs. b: transverse view) and significantly reduce the banded structure ((Fig 1 c vs. d: longitudinal view) when compared to the no-field conditions. I think we used Ralph's etch, but I'm still checking on this.

Table 2 Mechanical Property Results for this High Strength Bainitic Alloy demonstrate that T-MP Processing Produces Unprecedented, and Simultaneous Improvements in both Yield Strength and Ductility.

	<u>0.2% Yield strength (ksi)</u>	<u>Ultimate Tensile Strength (ksi)</u>	<u>% Elongation</u>	<u>% Reduction in Area</u>	<u>Charpy V-notch (ft-lbs)</u>	<u>Hardness HRC</u>
<u>No field</u>	172.69	250.49	15.3	52.08	28.9	49.0
	164.05	250.67	13.8*	49.27*		49.0
Average	168.37	250.58	15.3	52.08	28.9	49.0

* Note: specimen broke very near line mark. % Elongation and % R.A. are unreliable

	<u>0.2% Yield strength (ksi)</u>	<u>Ultimate Tensile Strength (ksi)</u>	<u>% Elongation</u>	<u>% Reduction in Area</u>	<u>Charpy V-notch (ft-lbs)</u>	<u>Hardness HRC</u>
<u>9 T Mag Field</u>	189.45	243.65	16.8	58.49	35.3	49.0
	188.6	241.42	16.9	59.52		49.0
Average	189.025	242.535	16.85	59.01	35.3	49.0
Property Change with H-field	12.30%	-3.20%	10%	13%	22.10%	0.0

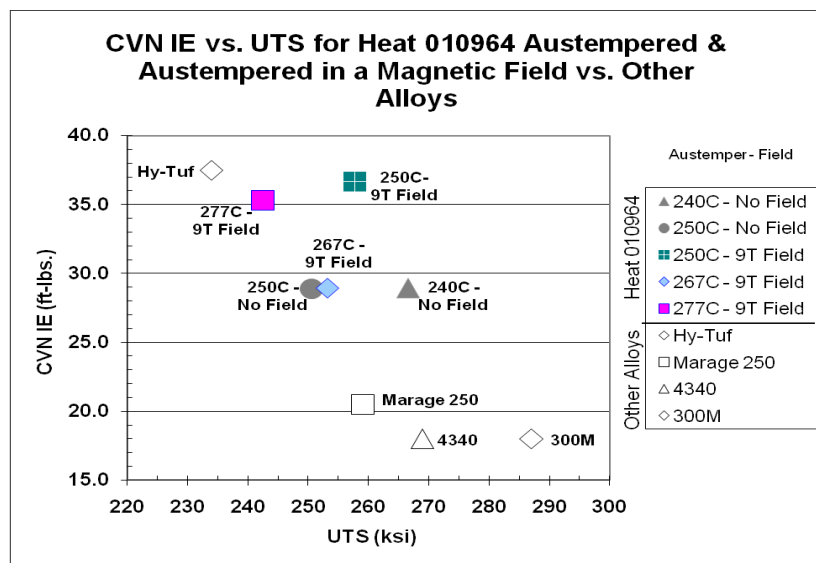
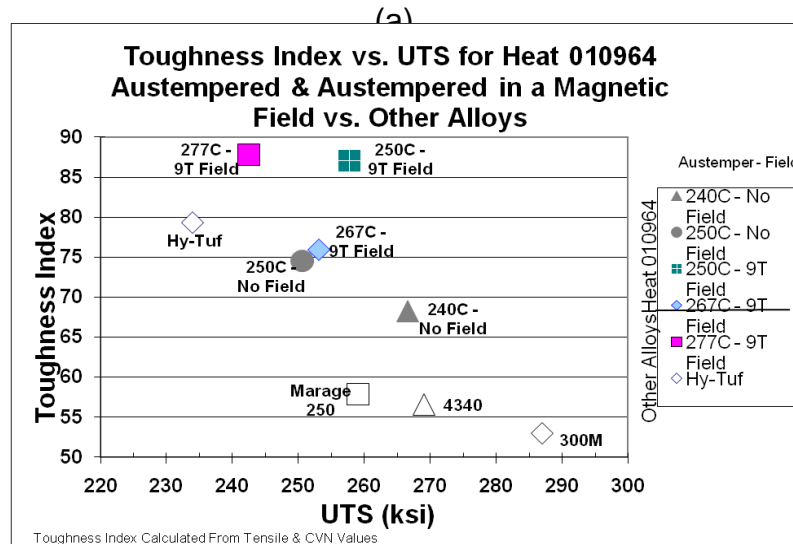


Figure 3 Plots depicting the relative performance improvement in (a) Charpy V-Notch and (b) superior toughness index ranking of the thermomagnetically processed high strength bainitic steel. This latter alloy outperforms a Maraging 250, a Co-containing alloy steel.

CUSTOM 465

Custom 465 stainless is premium melted, martensitic, age-hardenable alloy capable of ultimate tensile strength in excess of 250 ksi in the overaged (H950) condition. This alloy was designed to have excellent notch tensile strength and fracture toughness in this condition. The nominal chemistry of this alloy is indicated below in Table 3.

TABLE 3 CHEMISTRY OF CUSTOM 465 ALLOY

Element	C	Mn	Si	P	S	Cr	Ni	Mo	Ti
wt. %	<.02	<.25	<.25	<.015	<.01	11.75	11	0.52	1.65

The goals of HMFP experiments for the Custom 465 alloy was to determine whether T-MP could be used to: 1.) increase the UTS by 10%; and 2.) eliminate the otherwise energy-intensive cryogenic processing step that is needed to achieve the desired microstructure, mechanical properties and performance needed for this alloy. In actual production processing of this alloy, the alloy chemistry and the large size ingots require low (air-cooling) conditions. Although we attempted to experimentally simulate these slow cool conditions using helium gas to control the cooling rate in our current sample handling and containment set-up, upon X-ray characterization of these samples, it was determined that both the samples processed *with a 9T magnetic field* and those processed *without a magnetic field (i.e., the No-Field (NF) condition)* responded identically. That is, we achieved low percentages of retained austenite for both the field and no-field processing conditions.

The T-MP steps followed for the Custom 465 alloy are as follows:

- Austenitized at 1800 F (982 C) for 60 min followed by super-quench in Helium at 125 psi
- He gas cooled quickly and reproducibly; T:(980-->200C) in 8-19 sec
 - Temperature range at end of quench to typically 150 C (± 25 C).

Future experiments (perhaps, in a follow-on study as part of a future project) would have to be developed and more carefully designed so that we can adjust the experimental, laboratory cooling rates (associated with helium gas flow rate) to more closely match the cooling rate(s) achieved during production processing. In addition, we could also investigate using magnetic field processing during the aging treatment without the deep freeze processing step to determine if this latter step could be eliminated.

MATERIALS CHARACTERIZATION

Material evaluations were performed on samples processed with and without TMP. During aging treatments on a specialty steel alloy material, some samples were aged with and some were aged without a magnetic field imposed on them. Subsequently a subset of these samples received a deep-freeze treatment commonly used commercially to reduce detrimental amounts of retained austenite in these alloys. Both hardness nor X-ray analyses were conducted on these samples. As mentioned above, although we attempted to experimentally simulate these slow cool conditions using helium gas to control the cooling rate in our current sample handling and containment set-up, upon X-ray characterization of these samples, it was determined that both the samples processed *with a 9T magnetic field* and those processed *without a magnetic field (i.e., the No-Field (NF) condition)* responded identically.

These results are documented in Tables 4 and 5 below.

TABLE 4 COMPARISON OF HARDNESS OBTAINED FOR CUSTOM 465 WITH AND WITHOUT MAGNETIC FIELD PROCESSING, AND WITH AND WITHOUT A SUBSEQUENT CRYOGENIC TREATMENT WERE INCONCLUSIVE DUE TO ISSUES WITH MATCHING LABORATORY EXPERIMENTAL COOLING RATES WITH PRODUCTION COOLING RATES.

			1	2	3	4	5	6	7
		ST only							
	Aging temp		0	900	925	950	975	1000	1100
A	mag field-subzero	Avg	29.58	52.78	51.88	51.38	50.8	48.84	43.52
		Stdev	0.48	0.68	0.13	0.19	0.59	0.09	0.16
B	mag field-no sub zero	Avg	28.98	52.18	51.84	51.1	50.24	48.62	43.54
		Stdev	0.031	0.79	0.4	0.25	0.13	0.13	0.23
C	no mag field - subzero	Avg	30.08	52.64	51.78	51.64	50.48	48.92	43.58
		Stdev	0.8	0.39	0.56	0.15	0.23	0.11	0.28
D	no mag field - no subzero	Avg	29.94	52.6	51.9	51.54	50.56	48.66	43.46
		Stdev	0.21	0.46	0.37	0.21	0.21	0.35	0.42

TABLE 5 COMPARISON OF THE % RETAINED AUSTENITE OBTAINED FOR CUSTOM 465 WITH AND WITHOUT MAGNETIC FIELD PROCESSING, AND WITH AND WITHOUT A SUBSEQUENT CRYOGENIC TREATMENT WERE INCONCLUSIVE DUE TO ISSUES WITH MATCHING LABORATORY EXPERIMENTAL COOLING RATES WITH PRODUCTION COOLING RATES.

Mag Field	Sub-zero	% Austenite				
		Aging Treatment (°F for 4 hrs)	None	900	950	1100
Y	Y		<1	4.3	6.9	25.3
N	Y		<1	5.3	10.4	18.2
Y	N		<1	<1	6.6	23.9
N	N		<1	4.8	7.5	20.4

SUBJECT INVENTIONS

No new intellectual property was generated under this CRADA.

COMMERCIALIZATION POSSIBILITIES

- 1.) The results of this preliminary investigation indicated that the thermomagnetic processing technology has major potential commercialization applications from process energy efficiency improvement perspectives as well as making major improvements in component performance metrics (properties) for the high strength bainitic alloy.
- 2.) For the Custom 465 alloy, additional work is needed in a future study to match laboratory cooling rates with actual production cooling rates.

Future collaborations (next section) with Carpenter and potential equipment suppliers (AjaxTOCCO [induction heating equipment] and American Magnetics Inc [superconducting magnet technology] will be pursued to determine potential commercial possibilities.

PLANS FOR FUTURE COLLABORATIONS

Comparisons of the % Retained Austenite Obtained for Custom 465 with and without Magnetic field Processing, and with and without a Subsequent Cryogenic Treatment were inconclusive due to issues with matching laboratory experimental cooling rates with production cooling rates. Additional work is needed in a future study to match laboratory cooling rates with actual production cooling rates.

CONCLUSIONS

- 1.) Thermomagnetic processing has been shown to make significant and unprecedented, simultaneous improvements in microstructure, strength and ductility for the high strength (low alloy) bainitic alloy. Further comparisons (e.g., CVN and Toughness Index) with the no-field references cases and other higher alloy performance metrics demonstrate that by magnetically processing the High Strength Bainitic Alloy you can attain the strength of 250 Maraging steel with significantly better CVN Impact toughness. In addition, this can be accomplished with an inexpensive alloy that does contain cobalt. Alternatively, the Hy-Tuf alloy can be replaced with T-MP high strength bainitic alloy, and provide the same toughness but considerably more strength.
- 2.) Comparisons of the % Retained Austenite Obtained for Custom 465 with and without Magnetic field Processing, and with and without a Subsequent Cryogenic Treatment were inconclusive due to issues with matching laboratory experimental cooling rates with production cooling rates. Additional work is needed in a future study to match laboratory cooling rates with actual production cooling rates.