REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 09/27/2021	**2. REPORT TYPE** Technical Report	**3. DATES COVERED** *(From - To)* 09/01/2017-08/31/2021

4. TITLE AND SUBTITLE
Understanding the Solidification and Refinement of Steels

5a. CONTRACT NUMBER
N00014-17-1-2766

5b. GRANT NUMBER
GRANT12253654

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Tuttle, Robert

5d. PROJECT NUMBER
4720003736

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Saginaw Valley State University
7400 Bay Road
University Center, MI 48710-0001

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
SVSU

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
This purpose of this project is to continue to develop our understanding of solidification based grain refinement in steels and the solidification of steels in general. This project will focus on rare earth and titanium based grain refining materials. Cooling curve thermal analysis will be conducted to determine how the presence of rare earth or titanium containing inclusions change the solidification path of 1030, 4130, and HY80 steels. This analysis will provide a better background on how these alloys solidify and how inclusions act as nuclei for steels. This work will enable the creation of stronger and more ductile steels.

15. SUBJECT TERMS
steel, solidification, grain refinement

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Robert Tuttle
				32	**19b. TELEPHONE NUMBER** *(Include area code)* (989) 964-4676

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Final Report for Understanding the Solidification and Refinement of Steels

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What were the major goals and objectives of the project?

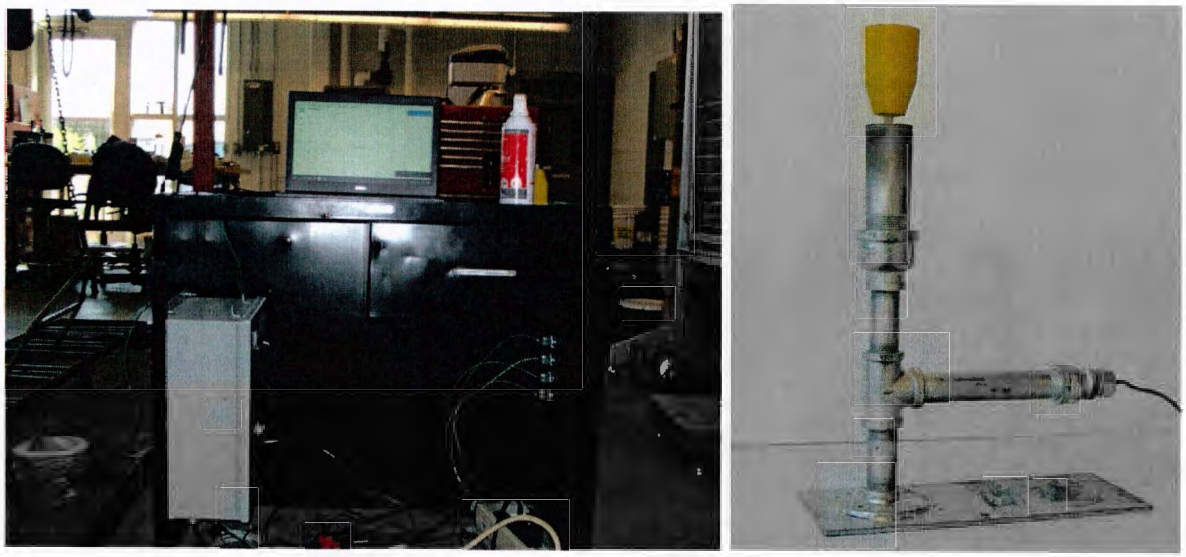
This project broadly focuses on improving the current state of steel solidification and grain refinement knowledge. While research has been done in the area of grain refinement, it has mainly employed room temperature microstructure and mechanical property testing. These techniques can determine if refinement occurred but provide a limited ability in revealing the underlying mechanisms. Improving the understanding of the mechanisms requires a new tool. A major thrust of this project is the development of a thermal analysis technique that can improve our understanding of steel solidification and be eventually used as a process control. The second major thrust is to use thermal analysis to improve rare earth based grain refinement.
The major tasks for the project are as follows:

1. Development of thermal analysis experimental procedure and analysis
2. Baseline thermal analysis experiments for 1030, 4130, and HY100
3. Thermal analysis experiments on 1030, 4130, and HY100
4. Experiments on titanium refined 1030, 4130, and HY100
5. Development of a rare earth master alloy with improved efficiency
6. Experiments on a rare earth master alloy additions to 1030 and 4130

What was accomplished towards achieving these goals?

All tasks in the original proposal were accomplished. Results from the project have been published and presented in various journals and conferences. What follows is a summary of the results from each task.

Task 1 consisted of purchasing a thermal analysis (TA) system and developing the experimental procedure. Figure 1A shows the system purchased, while Figure 1B shows the stand with a cup in it. The system records the cooling curve, can calculate up to the fifth derivative, and use the various derivatives to detect phase reactions.



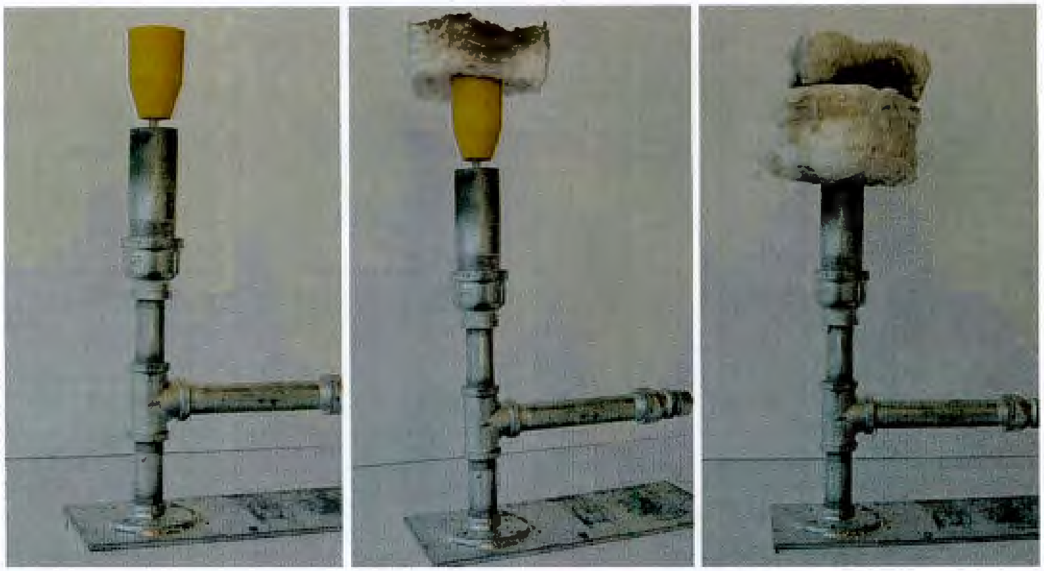
A) System B) TA cup and stand

Figure 1 MeltLab System for Thermal Analysis of Steels

To help determine the system capabilities and develop the proper experimental procedures, initial experiments were conducted. Twenty-three kilogram heats of 4130 steel were melted in a 3 kHz induction furnace. The initial charge consisted of 1010 punchings, FeCr, and FeMo. At 1700°C additions of FeSi, FeMn, graphite, and aluminum shot occurred. Heating continued to 1730°C where a portion of the heat was poured into a 2.3 kg hand ladle. An additional 1g piece of aluminum was added in the hand ladle to maintain deoxidation. The hand ladle then poured a TA cup. For these initial experiments six cups were poured per run. Three different experimental treatments applied to the cups (See Figure 2). These produced different cooling rates in the TA cups. Examining slower cooling rates was done due to MeltLab's experience with analyzing certain cast iron alloys. Two cups of each type were poured. The covers and wrap were made from an alumino-silicate fiber refractory blanket 5 cm thick with a density of 128 kg/m^3. In addition to the TA cups, a spectrometer sample was poured. The average chemical analysis of these heats is presented in Table 1.

Table 1 Average chemical analysis of initial 4130 heats (wt.%)

C	Si	Mn	P	S	Cr	Mo	Al
0.321	0.25	0.473	0.013	0.01	0.952	0.236	0.0215



Normal Covered Wrapped & Covered

Figure 2 TA Cup Conditions of Initial Experiments

Figure 3 depicts a typical set of cooling curves recorded using the TA system. There is good agreement between the overall shape and phase reaction temperatures in the cooling curves.

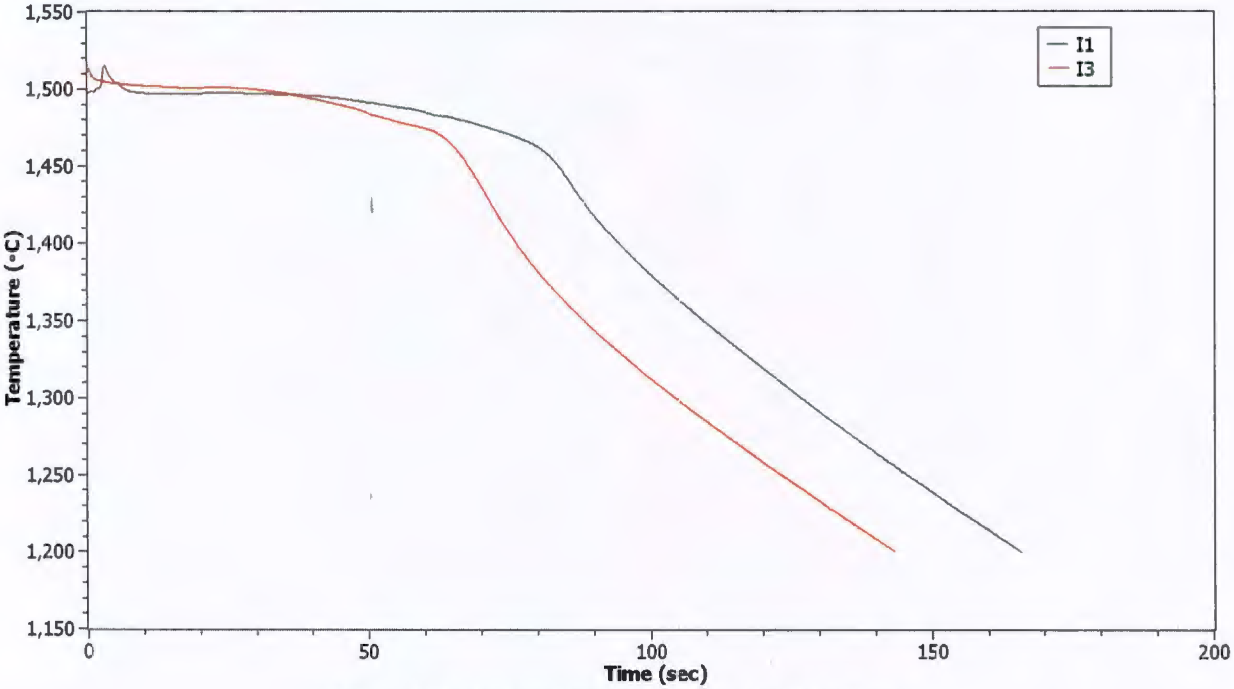


Figure 3 Typical cooling curves from the TA system

Of more interest are the cooling rate, first derivative, curves for each sample. These curves make phase reactions more evident than the temperature curves. Data from the normal cups are illustrated in Figure 4. The liquidus and solidus are easily detected using the current analytical methods in the MeltLab software.

There is no existing code for the peritectic. However, the peritectic was easily detected in the normal cup cooling curves. Peritectic temperatures are currently being manually determined from the peak of the peritectic reaction (See Figure 4).

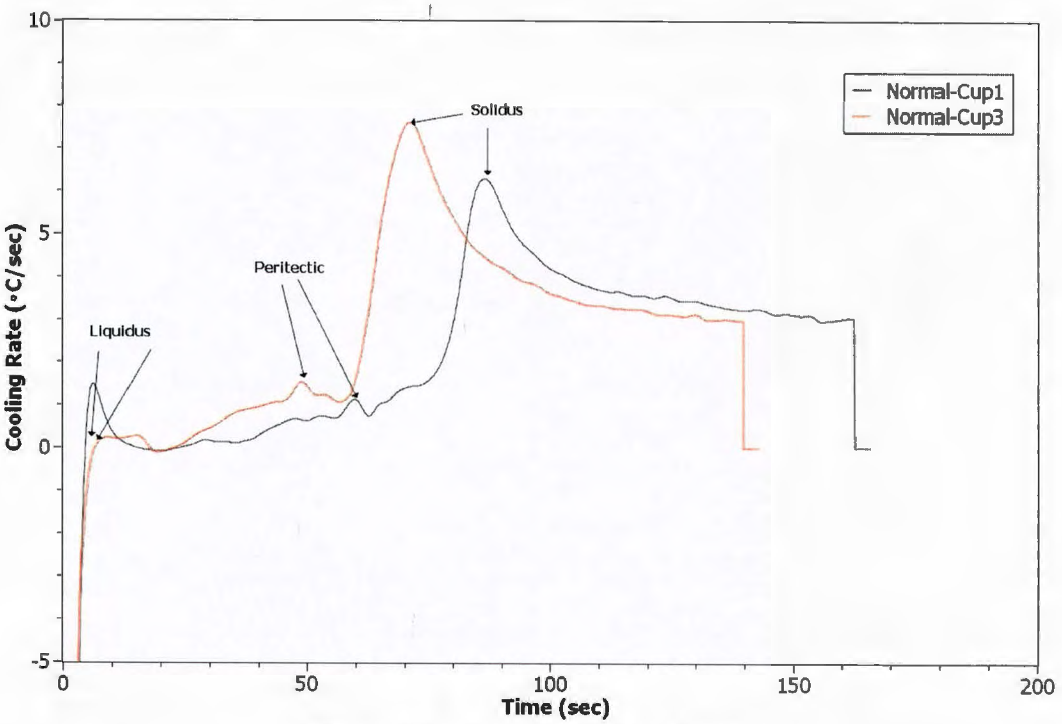


Figure 4 Cooling rate for Normal cups

As part of benchmarking the system, the liquidus and solidus values were compared to thermodynamic predictions and a set of reference data. The thermodynamic predictions were done using ThermoCalc using the TCFE9 database. Reference data was taken from *A Guide to the Solidification of Steels*, which is an atlas of thermal analysis data produced by Jenkortoret in 1977.[1] This reference data uses a somewhat similar technique to the one used in this work. The main difference is that the measurements are made inside a small furnace so the cooling rate could be controlled.

Tables 2 through 4 present the measured values for each condition, thermodynamically predicted value, and reference data. The liquidus values agree considerably well between techniques. The slight difference between values is within the typical measurement error of a thermocouple. Thus, it appears they are equivalent. Examination of the solidus reveals a significant issue. The reference data and thermodynamic predictions are approximately 20°C from each other (See Table 3). The data from the TA system appears to be closer to the reference data, but still slightly high. The peritectic also appears to have a significant discrepancy in value (See Table 4). Again, the thermodynamic predictions and reference data have a significant difference, about 10°C. The TA system tended to find a higher temperature.

Table 2 Liquidus values

Thermodynamic predictions (°C)	**Liquidus from the reference (°C)**[1]	**Liquidus from DAQ (°C)**	**Condition**
1499.97	1501	1498.75	Normal
		1505.75	Covered
		1500.15	Wrapped & Covered

Table 3 Solidus values

Thermodynamic predictions (°C)	**Solidus from the reference (°C)**[1]	**Solidus from DAQ (°C)**	**Condition**
1402.02	1420	1431.1	Normal
		1424.7	Covered
		1423	Wrapped & Covered

Table 4 Peritectic values

Thermodynamic predictions (°C)	**Peritectic from the reference (°C)**[1]	**Experimental values (°C)**	**Condition**
1474.1	1460	1484.5	Normal
		1486	Covered
		1465	Wrapped and Covered

The discrepancy between the thermodynamic calculations and the reference data indicates that there are some issues in the open literature. Thus, the TA systems variance from these may not indicate that there is a problem with the system. Examining *Computational Thermodynamics: The CALPHAD Method* reveals that most of the thermodynamic databases use differential scanning calorimetry (DSC) as the main method for determining phase reactions.[2] DSC has been used in the study of steel solidification and probably represents the bulk of the data sets in the thermodynamic databases.[3–10] However, detecting the solidus can be problematic in DSC.[11] Solidus determination can be so problematic that in some cases there is no peak on the DSC curve indicating this portion of the reaction.[10] Obviously, if the solidus is hard determine with DSC then the values will scatter considerably. Overall, it was determined that the system produces data within acceptable limits.

Task 2 focused on creating baseline data for interpretation of the cooling curves in 1030, 4130, and HY100. Baseline 4130 data was recorded while conducting the work for Task 1 and was outlined previously. For 1030 and HY100, separate heats were poured using the same procedure defined under Task 1. The only change was with regard to pouring only four TA cups. Two cups were in the normal condition and two were in the covered condition. Covered conditions were poured in these experiments since the cause of the discrepancies in the solidus and peritectic were still under investigation at the time these were poured.

A typical cooling rate curve for the 1030 data is presented in Figure 5. The liquidus and solidus were easily identified by the system. Two additional peaks were observed between the liquidus and solidus. It appears the system detected the start and end of the liquid+BCC+FCC region predicted by ThermoCalc.

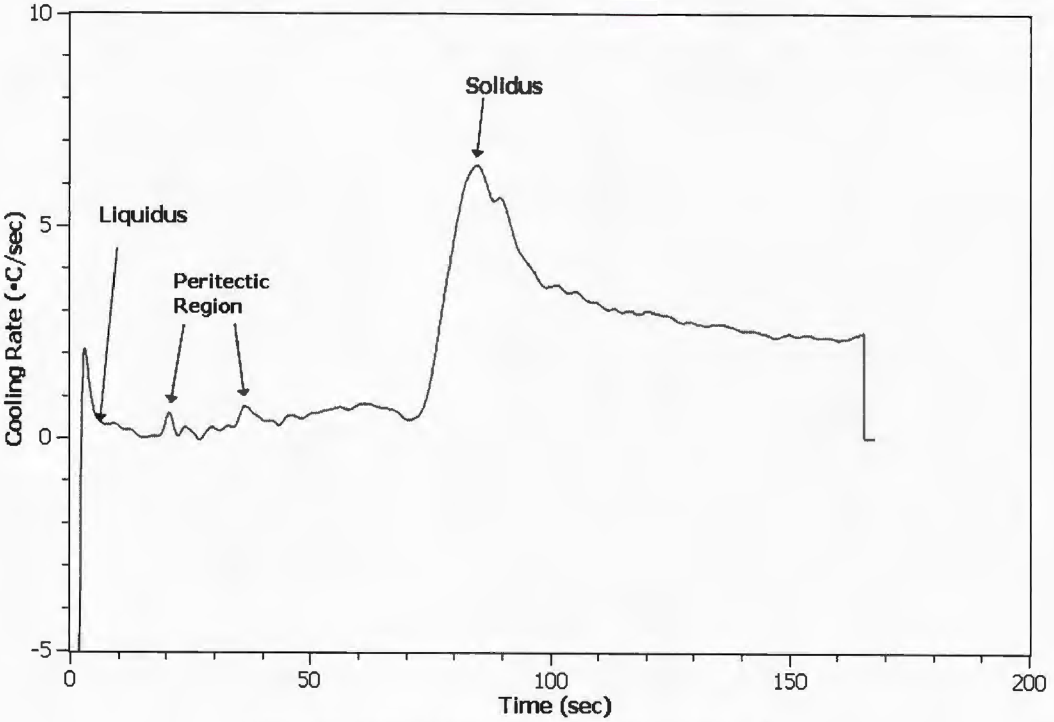


Figure 5 Cooling rate curve for 1030 baseline data

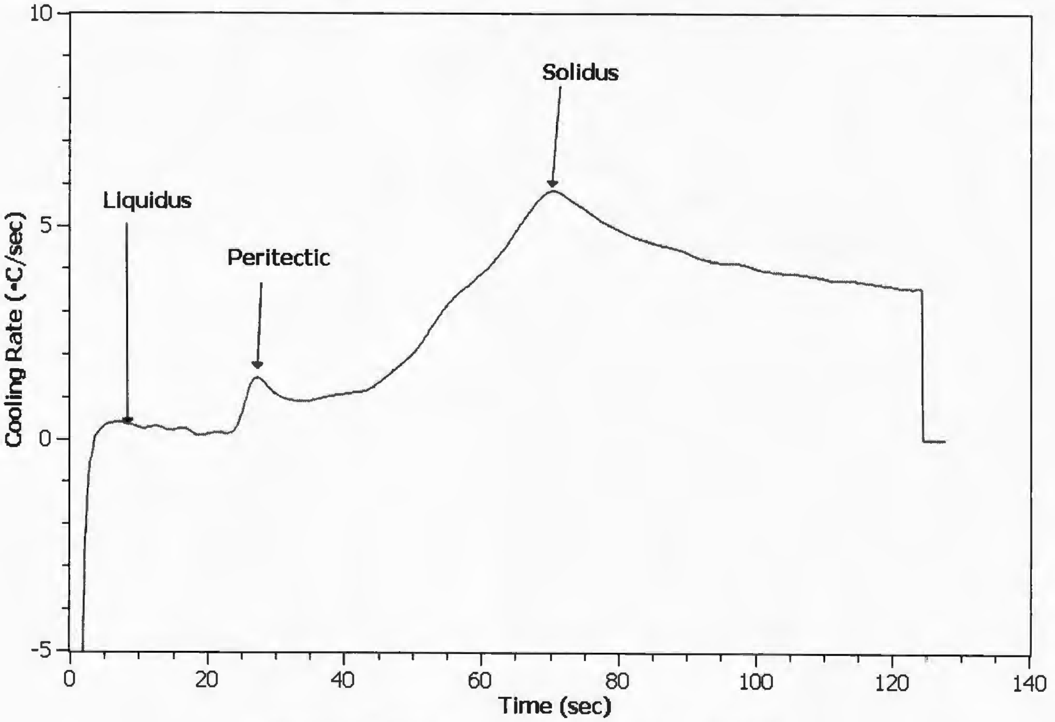


Figure 6 Typical cooling rate curve for HY100

Examination of the data for HY100 also indicates that several peaks are identifiable (See Figure 6). Again, the liquidus and solidus are easily found. The peritectic reaction also provided a strong peak. The presence of the single peritectic related peak makes sense for this alloy since thermodynamic calculations predict a shift from a liquid+BCC region to a liquid+FCC region just prior to the completion of solidification. The correct identification of this and the peaks in the 1030 data does indicate that the thermodynamic predictions can be helpful in interpreting the data collected by the TA system. It is also evident that the ability to detect the peritectic as first observed in the 4130 data continued to be true for different alloys.

Task 3 consisted of experiments for examining how rare earth (RE) additions changed the solidification of 1030, 4130, and HY100 through the use of thermal analysis. Melting for the experiments consisted of heating 23 kg of the target steel alloy in a 3 kHz induction furnace under an air atmosphere. The initial charge consists of 1010 punchings and nickel pellets, FeCr, or FeMo if the alloy requires them. Once the melt reaches 1700°C, final additions of FeSi, FeMn, graphite, aluminum shot, and either nothing, 0.3 wt. % RE silicide, or 0.3 wt. % EGR were added. The melt continued heating until 1750°C was reached where a portion of the heat was tapped into a 2.3 kg capacity hand ladle that had 1 g of aluminum shot for maintaining deoxidation. A thermal analysis (TA) cup was then poured using the hand ladle and the cooling curve recorded. Measurements by the data acquisition system (DAQ) started at 1050°C and continued until the specimen cooled to 1200°C. Readings were taken at a rate of 38.4 kHz using an S-type thermocouple in a shell core cup. After cooling to room temperature, the TA cup was removed and a new one placed on for testing. Four cups per heat were poured. Once at room temperature, the TA cups were sectioned 20 mm from the bottom and polished and etched with a 25% HNO_3 and 75% H_2O solution. The resulting macrostructure could then be related to cooling curve changes.

Figure 7 illustrates the cooling rate data for the Baseline heat. The liquidus and solidus were detected using the existing algorithms from MeltLab's DAQ system. Unlike differential scanning calorimetry (DSC) curves, the solidus appeared as a large peak.[12] The peritectic appeared as a small peak prior to the solidus. The TA technique being used provides a clearer peak than DSC based experiments which is consistent with observations by other researchers.[13,14] As expected from the cooling curve shape change, additional phases were observed to form during the solidification of the treated steels (See Figures 8). The phases have been labeled Ce_2O_2S and Ce_2S_3 based on ThermoCalc predictions using the TCFE9 database. The PI must note that these are estimations of the phases being evolved and not definitive.

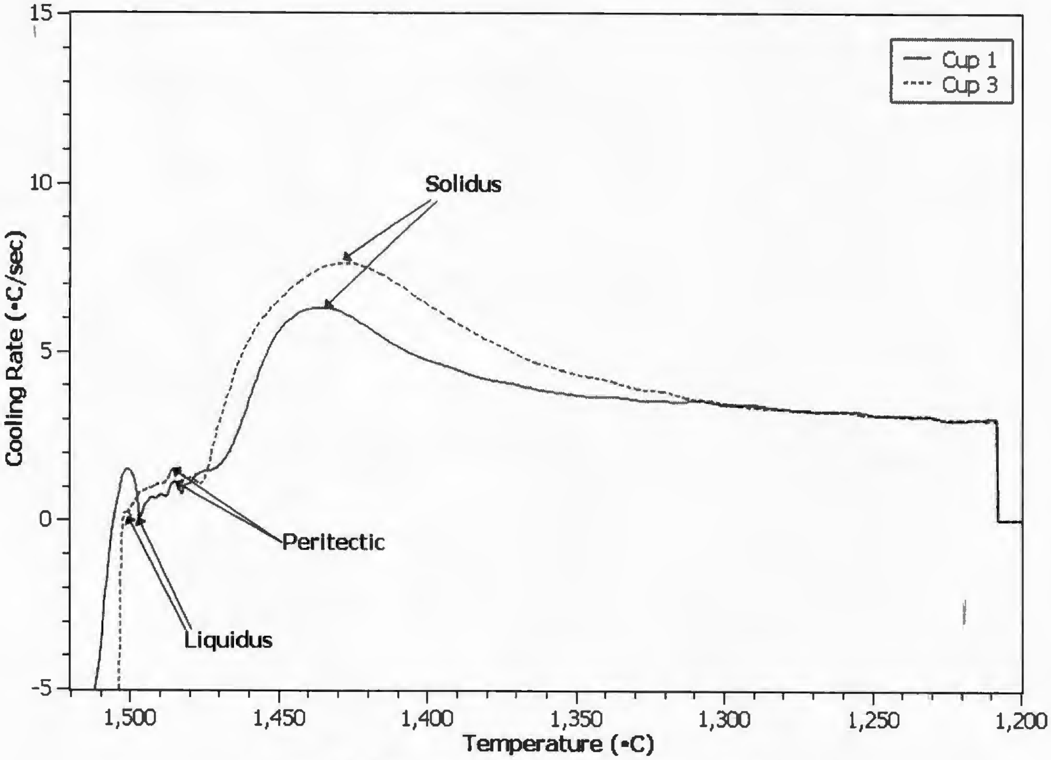


Figure 7 Cooling rate curves for Baseline 4130.

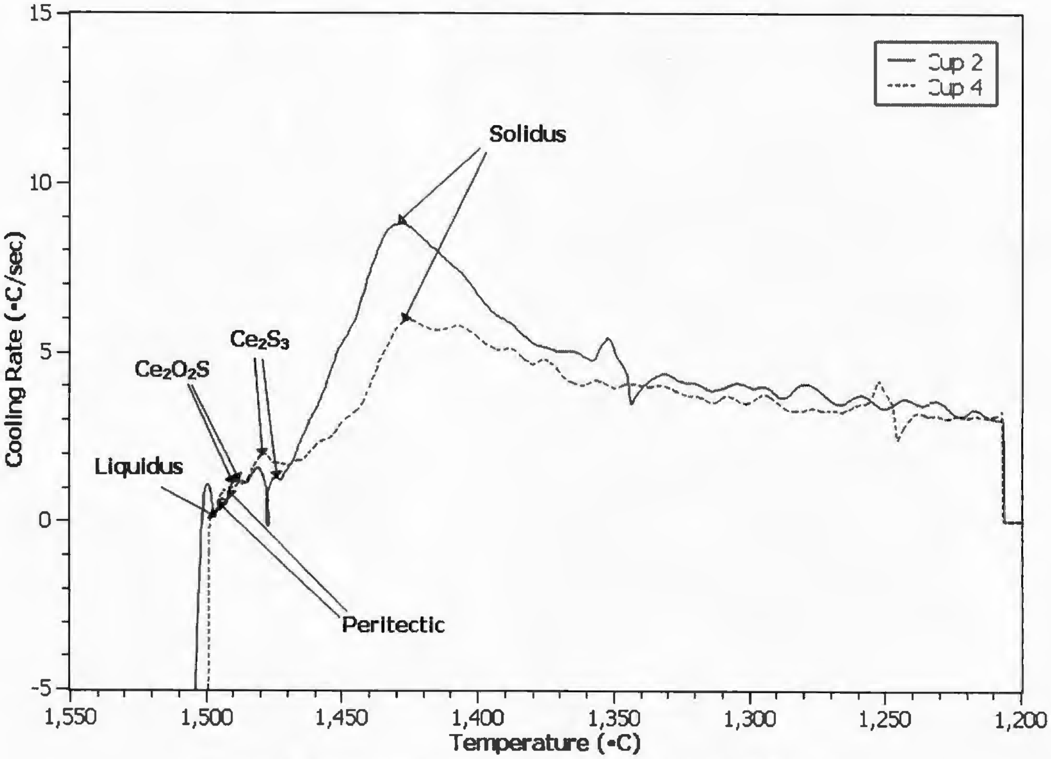


Figure 8 Cooling rate curve for 0.3 wt. % RE silicide 4130.

Tables 5 through 8 list temperature measurements for various reactions and predictions for those reactions from ThermoCalc and data from *A Guide to the Solidification of Steels*, referred to as the reference data.[15]

The liquidus data from all three appear to be very close. However, the solidus data has some significant disagreement (See Table 6). This disagreement may be related to the relative sizes of the samples and thermocouple placement in the original experiments. Peritectic reaction temperatures and the expected values also demonstrate some disagreement in the open literature (See Table 7). However, the experiments also demonstrate that the addition of RE silicide or EGR raises the peritectic reaction temperature. The measured peritectic temperature appears the same between the two additions. This increase would be consistent with the presence of an inclusion within the melt that acts as a heterogeneous nuclei for austenite.[16–19] It also corresponds to the formation of the finer macrostructures in the TA cups.

Table 5 Liquidus data for 4130 TA only experiments.

Liquidus from ThermoCalc (°C)	*Liquidus from reference (°C)*	*Liquidus from DAQ (°C)*	*Condition*
1506	1501	1499	Baseline
		1504	0.3 wt. % RE Silicide
		1497	0.3 wt. % EGR

Table 6 Solidus data from 4130 TA only experiments.

Solidus from ThermoCalc (°C)	*Solidus from reference (°C)*	*Solidus from DAQ (°C)*	*Condition*
1409	1420	1431	Baseline
		1423	0.3 wt. % RE Silicide
		1405	0.3 wt. % EGR

Table 7 Peritectic data from 4130 TA only experiments.

Peritectic from ThermoCalc (°C)	*Peritectic from reference (°C)*	*Peritectic from DAQ (°C)*	*Condition*
1483	1460	1487	Baseline
		1493	0.3 wt. % RE Silicide
		1495	0.3 wt. % EGR

Table 8 Cerium inclusion temperatures for 4130.

Reaction	*Prediction (°C)*	*0.3 wt. % RE (°C)*	*0.3 wt. % EGR (°C)*
Ce_2O_2S	1463	1486	1487
Ce_2S_3	1425	1477	1476

Table 8 lists the measured and predicted temperatures for Ce_2O_2S and Ce_2S_3 formation. The measurements in these experiments are higher than those predicted by ThermoCalc. This might be true for two different reasons. One is that the inclusion of cerium in the TCFE database has been relatively recent and may be less accurate than other phase data. A second explanation might be that Ce_2O_2S and Ce_2S_3 form on existing nuclei that are highly effective. This might be more likely since previous work by the PI indicates that the observed RE inclusions have a very complex structure and may contain multiple phases.[20]

Task 4 focused on conducting thermal analysis experiments on titanium additions to 1030, 4130, and HY100. The experimental procedure was similar to Task 3, but with titanium additions instead. Cooling curve data found that the solidus peaks were smaller when titanium was added, but still easily detectable, across all the alloys. Table 9 provides representative data from this task from HY100 experiments. No upward shift in the liquidus appeared, which indicates that the titanium additions did not result in heterogeneous nucleation. In fact, the liquidus decreased due to the addition of titanium. The peritectic and solidus appear to be identical (See Table 9).

Table 9 Solidification reaction temperatures for 0.1 wt. % Ti HY100.

Source	**Liquidus (°C)**	**Peritectic (°C)**	**Solidus (°C)**
Baseline	1515	1484	1437
0.1 wt. % Ti	1494	1490	1436

These trends were observed throughout the titanium addition experiments in this task. It appears that the TiC and TiN particles reported by various researchers are likely formed during the final 5% of solidification and the main refinement mechanism is actually grain growth restrictions.

Task 5 consisted of the creation of various RE and TiC based master alloys. The main purpose was to enable the creation of specific nuclei within the alloy to test their ability to act as heterogeneous nuclei. Single point equilibrium and Scheil calculations in ThermoCalc provided basic information on designing these alloys. Single point equilibrium calculations provided a quick method for examining multiple alloy compositions, while Scheil predictions provided verification and melting information to ensure the alloy could be made using equipment on hand. Figure 9 presents data for a master alloy designated 0.2RE 100ppm O. The calculations indicate the formation of Ce_2O_3 inclusions within the alloy. A different alloy, 0.1RE 200 O, was designed to primarily contain CeO_2 inclusions. Both Ce_2O_3 and CeO_2 have been theorized to act as heterogeneous nuclei for austenite.[21-24] However, they have been reported to assist alloys that initially solidify as δ-ferrite.[22,25]

TiN and TiC have also been examined as possible nuclei for steel since the early work on heterogeneous nucleation theory.[26] This stems from their excellent fit with δ-ferrite. Again, master alloy design occurred by utilizing ThermoCalc to evaluate phase stability via single point equilibrium and Scheil calculations. Figure 10 depicts a Scheil calculation for an alloy with 20% TiC. The creation of the TiC master alloy was conceived based on the fact that other work on titanium additions has led to TiC formation late in solidification.[27-29] Late formation results in the carbides not acting as nuclei and embrittling the alloy due to their size. Addition of a master alloy containing TiC particles may enable their survival in the melt long enough to act as heterogeneous nuclei.

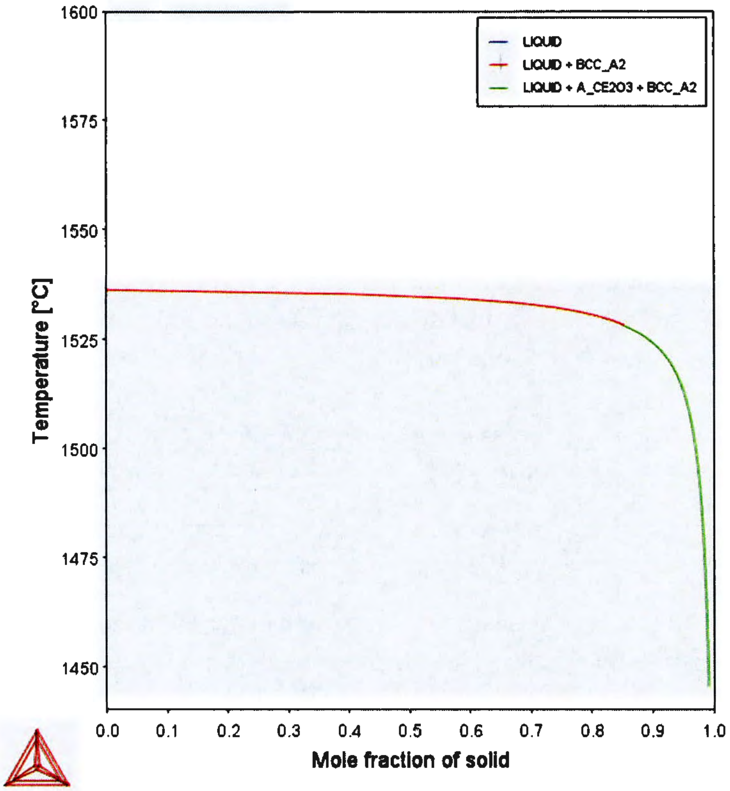


Figure 9 Scheil calculation results for a master alloy containing Ce_2O_3

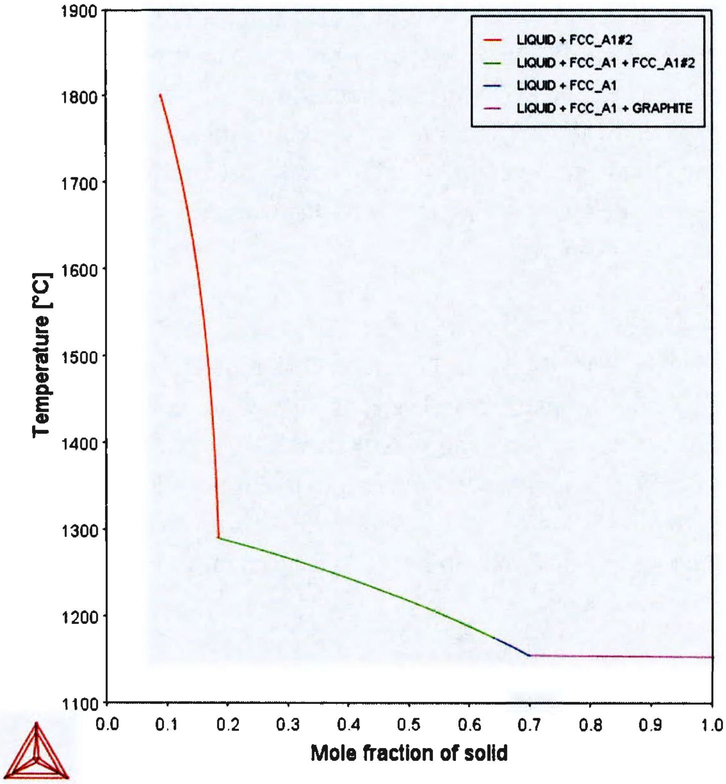


Figure 10 Scheil results for a 20% TiC containing master alloy

Master alloy creation was accomplished in a smaller resistance furnace capable of 1600°C. Electrolytic iron, ferrocerium rod, pure titanium, graphite, or Fe_2O_3 were used as charge materials. These were placed into a small alumina crucible with a lid to create the desired master alloy. The small crucibles were placed in a larger alumina crucible with a lid. Graphite was packed around these to ensure a reducing atmosphere occurred and only the desired quantity of oxygen was present by the use of Fe_2O_3. A heating rate of 10°C/min until achieving 1570°C was employed. After holding for half an hour, the samples cooled at a rate of 10°C/min. Three samples could be produced at a time.

Once the master alloys were created, representative samples were mounted and polished for microstructure characterization. Figure 11 depicts the structure of the 0.1RE 200 O master alloy. The primary iron-rich dendrites appeared to be surrounded by a rare earth (RE) rich region that contained the RE oxides. This structure agreed with the predicted solidification route from ThermoCalc. Scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS) characterized the regions and confirmed the iron-rich and RE rich regions. Table 10 details the oxide composition. The inclusions were not as pure as predicted by ThermoCalc. There were significant amounts of aluminum and iron detected by the EDS. The iron content could come from the surrounding matrix, the aluminum would not. The aluminum likely came from reduction of the alumina crucible. The overall composition had a higher oxygen content than CeO_2 (18 wt. % O, 82 wt %. Ce). This oxygen may have also come from the reduction of the alumina crucible. Supporting the theory that the master alloy and crucible interaction occurred was the observation that the master alloy could only be removed by breaking the alumina crucible, indicating the melt attacked the crucible.

Examination of the 0.2 RE 100 O alloy found a similar structure to the 0.1 RE 200 O alloy. Primary iron-rich dendrites were surrounded by a RE rich metallic region with RE oxides towards the center of these regions (See Figure 12). Again, consistent with ThermoCalc predictions. SEM/EDS analysis found a composition with high levels of aluminum and iron. The oxygen content was higher than the predicted amount for the Ce_2O_3 (15 wt. % O, 85 wt. % Ce) inclusions. The aluminum and excess oxygen likely came from the alumina crucible. These master alloys also required the destruction of the small crucibles due to attack by the melt.

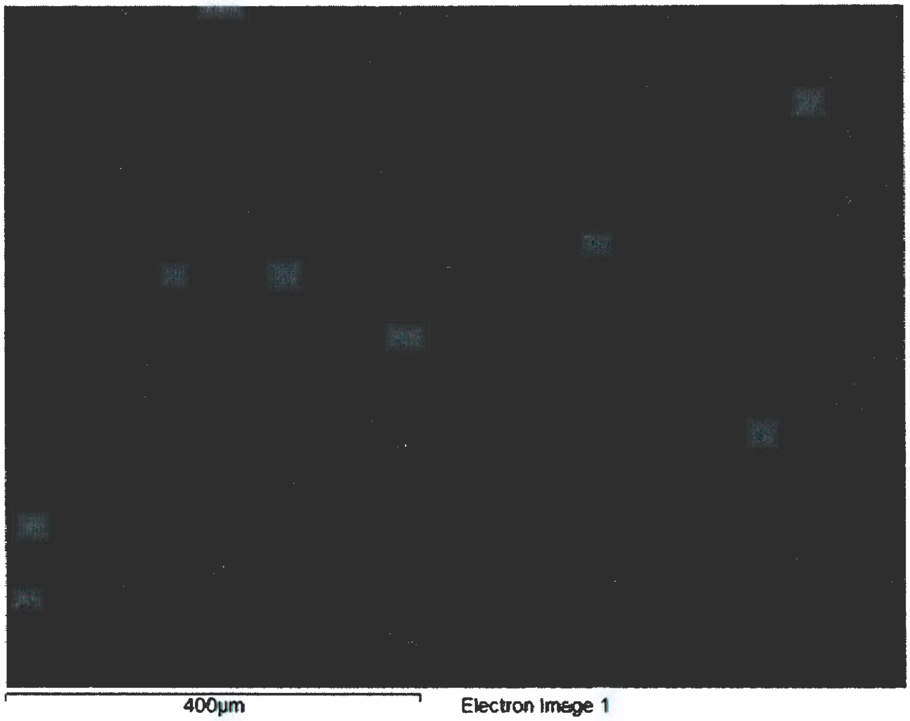


Figure 11 Microstructure of the 0.1 RE 200 O master alloy.

Table 10 Composition of the RE oxides from 0.1 RE 200 O master alloy.

Element	**Weight %**
O	37.15
Al	1.77
Fe	6.68
La	38.15
Ce	16.25

Table 11 0.2 RE 100 O master alloy inclusion composition

Element	**Weight %**
O	40.36
Al	35.09
Fe	4.26
La	14.66
Ce	5.62

Figure 12 Example microstructure for the 0.2 RE 100 O master alloy

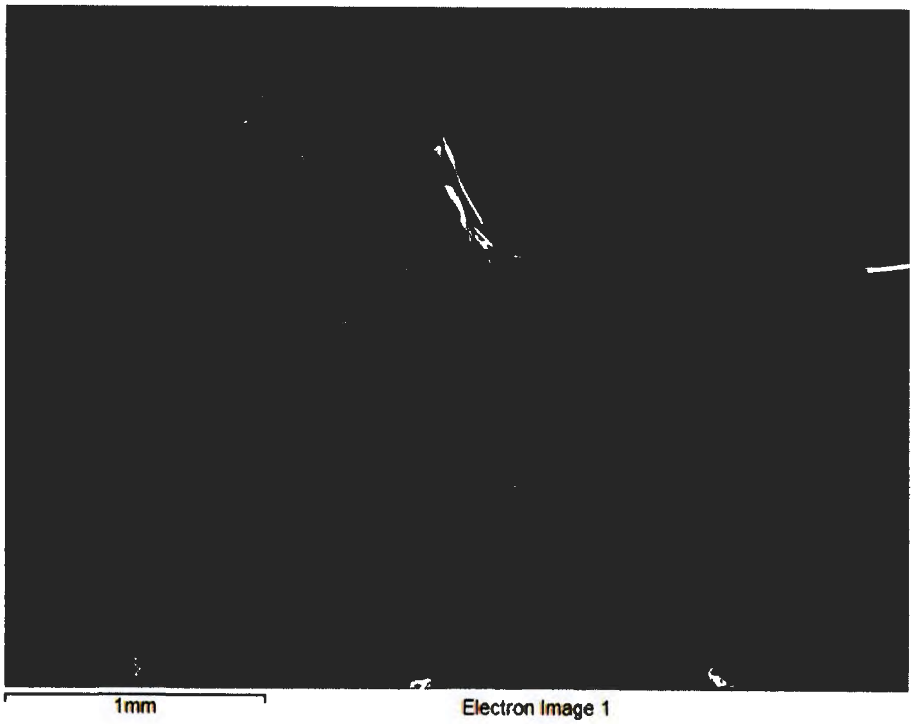


Figure 13 Microstructure of a TiC master alloy.

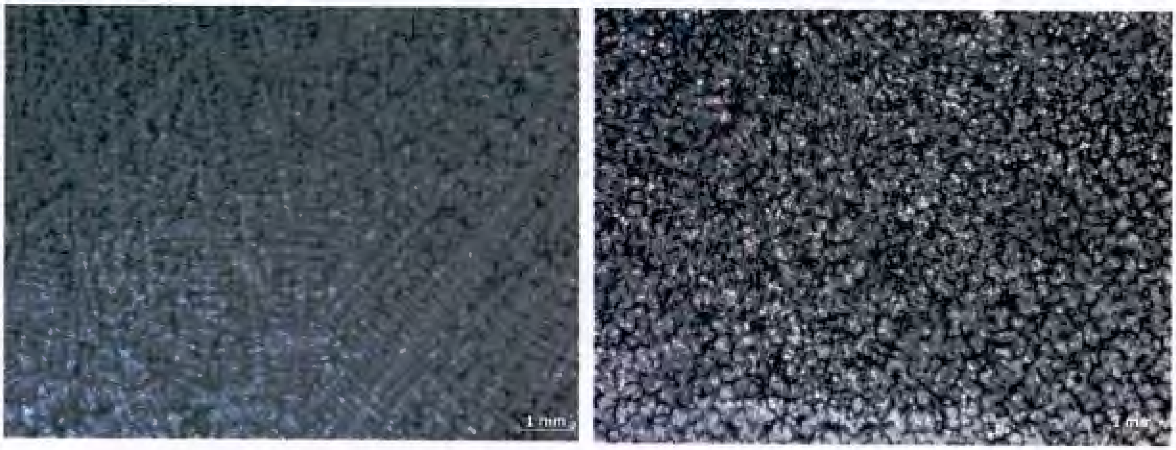
Table 12 EDS analysis of TiC particle

Element	Weight %
C	9.26
Ti	90.74

Figure 13 depicts the microstructure of the TiC master alloys, while Table 12 confirms the composition matches TiC. The structure consisted of large TiC particles (~ 1mm) surrounded by a metallic iron matrix. A large particle size was desired due to the tendency for TiC and TiN particles to dissolve in a melt. The theory was that larger particles might take longer to dissolve and remain in the melt when solidification began. The master alloys here differed by the volume fraction of TiC particles formed.

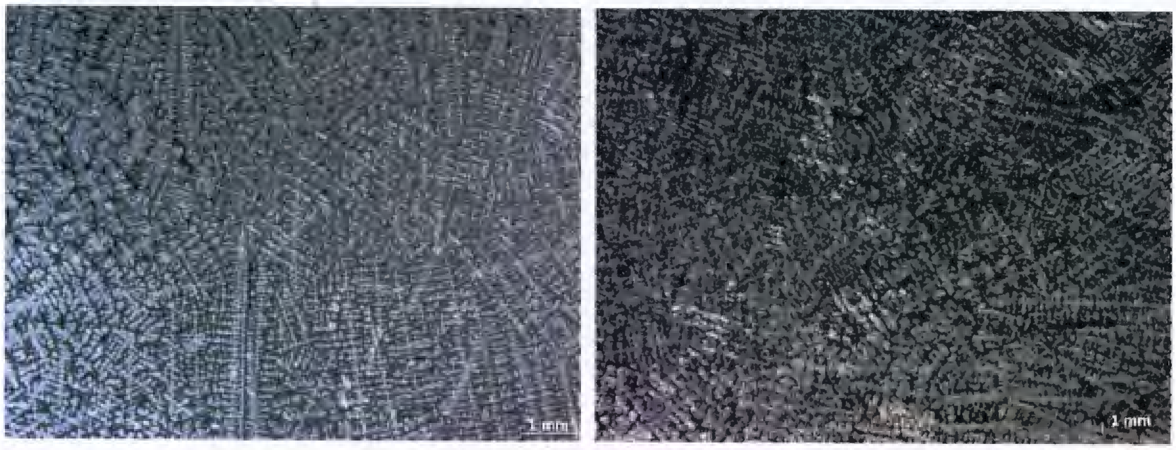
Task 6 consisted of conducting thermal analysis only experiments and thermal analysis-mechanical property experiments with the various master alloys from Task 5. For brevity, only the thermal analysis-mechanical property experimental results will be discussed. For these experiments, a 3kHz induction furnace melted 60 lb heats consisting of 1010 punchings, 316L punchings or ferroalloys depending on the alloy being made. At 1650°C, ferrosilicon, ferromanganese, and graphite were added to the melt. At 1700°C, the melt was tapped into a 150 lb capacity ladle and aluminum shot and the designated master alloy were added. A small portion was then poured from the tapping ladle into a 5 lb hand ladle. This hand ladle was utilized for pouring the TA cup and single bar casting. The single bar casting contained a small amount of FeP to improve macroetching response to Oberhoffer's etch. ASTM A781-05 keel block castings were made from green sand molds and poured at 1590°C from the tapping ladle. The castings cooled for 25 minutes before shakeout and then further cooling to room temperature. Tensile bar blanks, spectrometer samples, and metallographic samples were sawed from the keel blocks. The tensile bar blanks were then machined into 0.5 inch diameter tensile bars and tested on a 500 kip capacity hydraulic frame in accordance with ASTM E8-04.

Additions of the 30 RE 1.5S master alloy were carried out in 4130, 1030, and HY100. Only data from the 1030 and HY100 experiments will be presented for brevity. Figure 14 depicts the macrostructures of the 1030 heats. The 30RE 1.5S structures was considerably finer than the baseline heat. Some refinement was observed in the HY100 30 RE 1.5S heat (See Figure 15). The PI notes that this is the first time macrostructure refinement was observed in HY100.[30–32] Table 13 lists the mechanical property testing data for the baseline and addition heat. The yield strength and ultimate tensile strength (UTS) were lower for both materials. However, the 1030 had a higher elongation. The elongation was very low for HY100. In fact, the addition of the 30 RE 1.5S master alloy tended to create considerable porosity in addition to the lower properties. Sulfur and sulfides have been well documented to have a dramatic impact on the properties of HY100.[33–35] This impact is partially due to the fact that HY100 is used in a quench and temper condition and the tempered martensite microstructure tends to be mover sensitive to both porosity and sulfur embrittlement which likely explains the poor mechanical properties.



Baseline ***30RE 1.5S Treated***

Figure 14 Macrostructure of 1030 heats.



Baseline ***30RE 1.5S Treated***

Figure 15 Macrostructure of the HY100 heats.

Table 13 Mechanical properties from 30RE 1.5S experiments.

Material	Yield Strength (MPa)	UTS (MPa)	% Elongation
1030 Baseline	335	570	19.5
1030 30RE 1.5S	307	543	28.8
HY100 Baseline	796	886	10.2
HY100 30RE 1.5S	197	197	0.4

Inclusion analysis found similar trends in the 1030 and HY100 treated steels. Only HY100 data is presented here for brevity. RE oxysulfides were observed (See Figure 16). Table 2 lists the typical composition. Significant clustering was also found (See Figure 17). A reduction in distance between sulfur containing inclusions increases their detrimental impact on ductility in HY100.[33] These clusters are likely a significant reason for the poor ductility observed in the mechanical testing. This clustering behavior was not observed in the 1030 treated heat. Close examination of Tables 13 and 14 reveals a significant difference in oxysulfide composition. Significant amounts of iron, nickel, and manganese were present in the treated HY100 heat. These were not present in the master alloy. Additionally, the sulfur content was higher than in the master alloy.

It appears the oxysulfides in the master alloy reacted with the melt to form a different inclusion composition. Another explanation might be the inclusions observed in the treated steel formed by reactions between the RE rich metallic regions and the melt during tapping. Either mechanism would explain why no master alloy composition inclusions were observed.

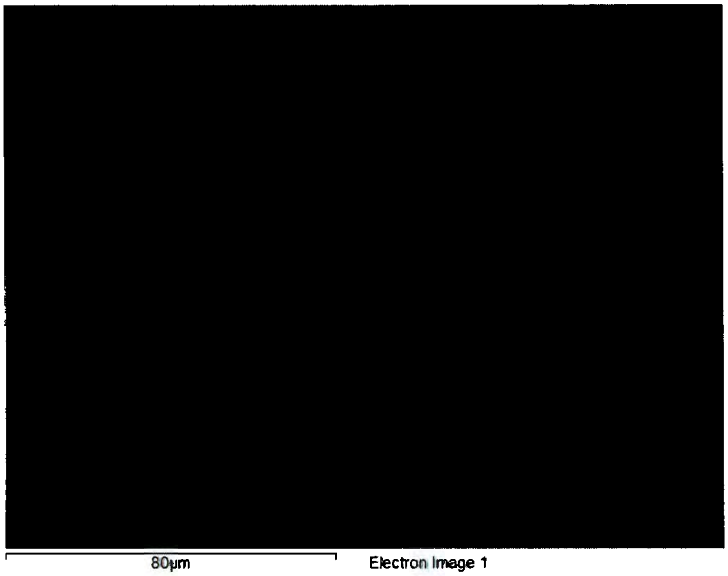


Figure 16 Typical RE sulfide from 30 RE 1.5S treated HY100.

Table 14 Quantitative EDS analysis of inclusion from Figure 16.

Element	Weight %
O	16.70
Al	17.97
S	5.10
Mn	2.15
Fe	43.64
Ni	1.60
La	3.81
Ce	9.04

Table 15 Composition of the oxysulfide from the 30 RE 1.5S master alloy.

Element	Weight %
O	35.46
Al	5.01
S	1.23
Fe	4.57
La	29.56
Ce	24.17

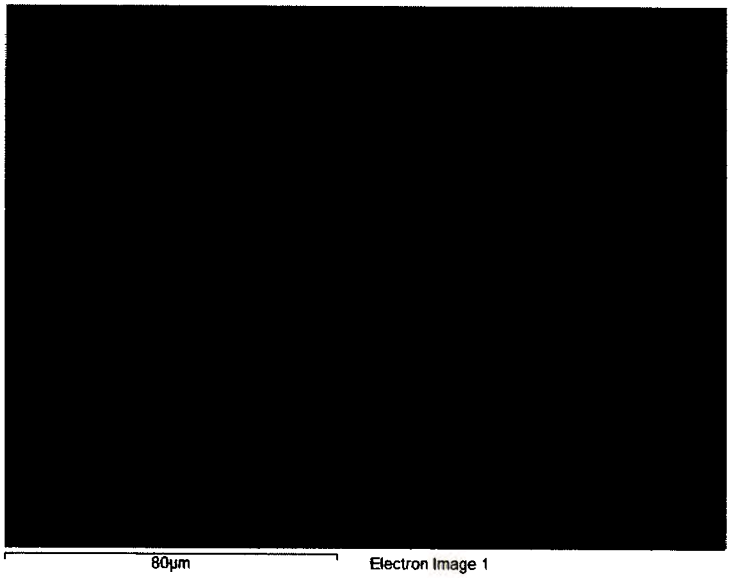
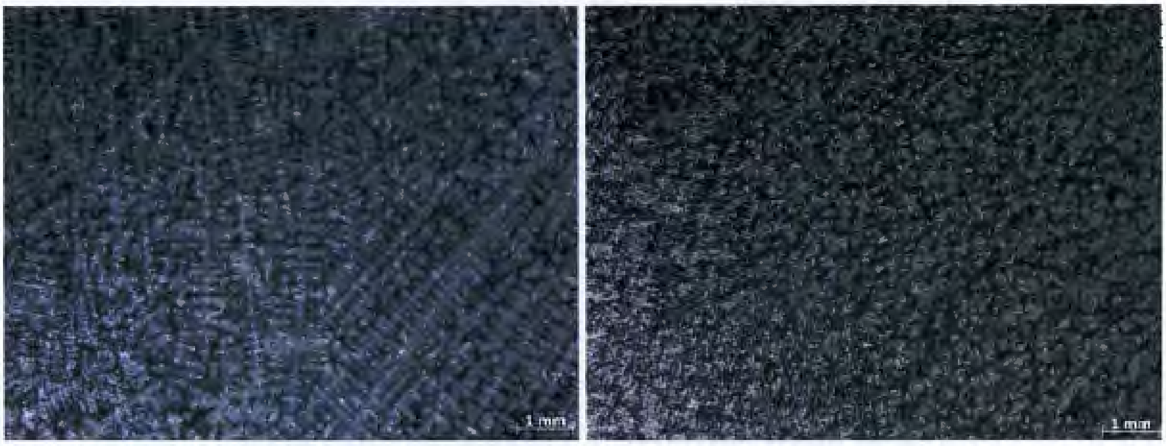


Figure 17 RE oxysulfide cluster in HY100 treated steel.

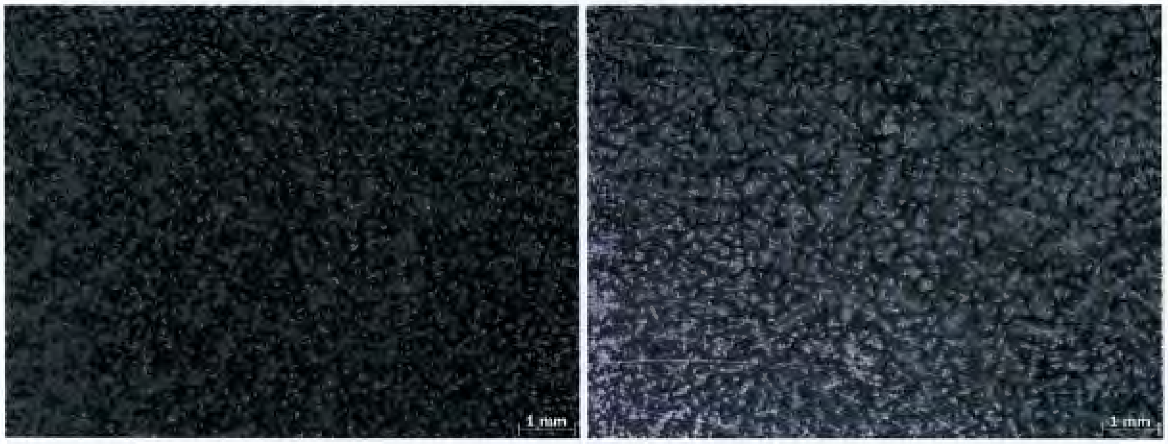
In addition to the originally planned experiments, the PI conducted a series of experiments using a combination of magnesium and titanium additions.[27,36–38] A significant issue has been the late formation of Ti(C,N) inclusions in the last 5% of the solidification range. Formation at this point does not lead to heterogeneous nucleation and an improvement in ductility.[27] However, recent research has found that the addition of magnesium followed by titanium can result in the formation of Ti(C,N) in a melt prior to solidification.[28,29,39]

The PI conducted a series of TA and mechanical property experiments as part of the project. These used the same melting, sampling, and analysis procedures as outlined previously. The magnesium addition was carried out by adding FeSiMg nodulizer into the melt just prior to tapping, while titanium was added in the ladle. No aluminum shot was added. Additions of only titanium or magnesium were also done to ensure that the change as not simply due to one or the other addition.

Experimentation in 1030 found that Ti, Mg, or Mg+Ti additions refined the as-cast structure (See Figure 18) Mechanical testing found that only the Mg+Ti had higher strengths and elongation (See Table 16). In the two titanium treated steels, TiN particles were observed. The Mg+Ti heat contained smaller TiN particles that surrounded magnesium containing oxides (See Figure 19). The role of these inclusions was not clear. Both the Ti and Mg+Ti steels had a higher yield strength. But, only the Mg+Ti steel had higher strength and ductility as would be expected for TiN inclusions acting as heterogeneous nuclei.



Baseline Ti



Mg Mg+Ti

Figure 18 1030 solidification structure with Mg or Ti additions.

Table 16 Mechanical properties for Mg, Ti, and Mg+Ti treated 1030

Heat	Yield Strength (MPa)	UTS (MPa)	% Elongation
Baseline	336	570	19
Ti	351	553	19
Mg	321	556	23
Mg+Ti	393	596	26

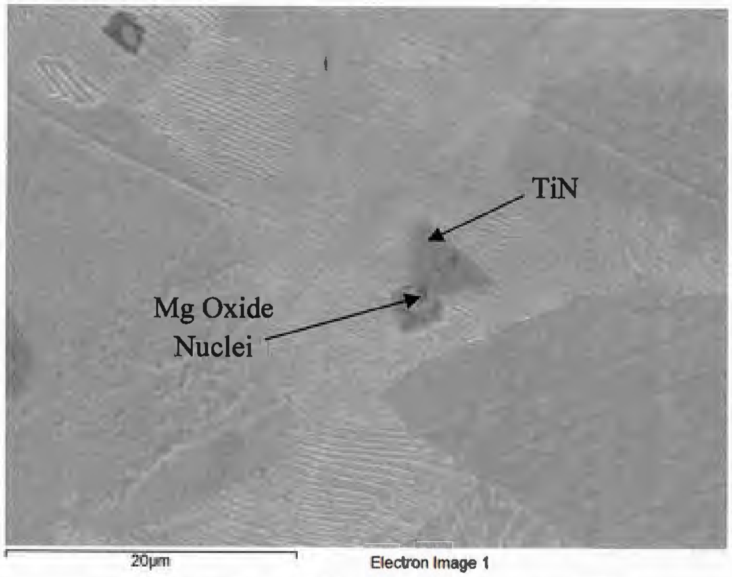


Figure 19 Typical TiN particle in the Mg+Ti steel.

TA results found no increase in liquidus. Interestingly, the Mg+Ti heat appeared to have a significantly lower liquidus than the Baseline heat. Oddly, the magnesium containing heats had higher solidus temperatures. Based on the results, this appears to be due to magnesium, but the cause is not obvious. ThermoCalc calculations did not predict this trend.

Table 17 1030 solidification reaction temperatures.

Heat	**Liquidus (°C)**	**Peritectic (°C)**	**Solidus (°C)**
Baseline	1500	1488	1415
Ti	1495	1494	1412
Mg	1495	1487	1431
Mg+Ti	1491	1482	1432

It was not apparent from the data when the TiN inclusions were formed. The TA data, mechanical properties, and macrostructures hint that they may have still formed late in solidification. The elevated strength of the Ti heat while still having lower elongation and liquidus temperatures hint at late stage solidification formation. If TiN particles formed in the melt and acted as heterogeneous nuclei, then the liquidus would increase. The fact it did not, appears to indicate they were not present at this stage. It appears that in both the Ti and Mg+Ti heats that the TiN particles restricted grain growth during cooling and improved the strength of the alloy. The difference in elongation performance between the Ti and Mg+Ti heats may be attributed to the size of the TiN particles. The Mg+Ti heat had smaller particles, likely due to the presence of magnesium containing oxides that acted as nuclei. These particles were small enough to restrict grain growth while not impacting ductility. While it appears that the nucleation of TiN in the melt did not occur, the presence of magnesium oxide nuclei for TiN may still provide a methodology for controlling particle size allowing the use of this approach for grain refinement.

All of the originally planned tasks plus and extra series of experiments have been completed. This occurred within the originally planned budget and the one year COVID extension.

References

1. Jernkontoret, *A Guide to the Solidification of Steels* , Jenkortoret, Stockholm, 1977,
2. Lukas, H. L., Fries, S. G. & Sundman, B., *Computational Thermodynamics: The CALPHAD Method* , Cambridge University Press, Cambridge ; New York, 2007,
3. Gryc, K., Smetana, B., *et al.*, "Determination of Solidus and Liquidus Temperatures for S34MnV Steel Grade by Thermal Analysis and Calculations," *Metalurgija*, Vol. 53, 2014, pp. 295–298.
4. Han, Z., Liu, J., He, Y., Li, K., Ji, Y. & Liu, J., "Determination of the Liquidus and Solidus Temperatures of FeCrAl Stainless Steel," *International Journal of Minerals, Metallurgy, and Materials*, Vol. 22, No.11, 2015, pp. 1141–1148.
5. Likvidusnih, D. S., Metodami, R. J. & Analize, D., "Determinationa of the Solidus and Liquidus Temperatures of the Real-Steel Grades with Dynamic Thermal-analysis Methods," *Materiali in tehnologije*, 2013, pp. 7.
6. Wielgosz, E. & Kargul, T., "Differential Scanning Calorimetry Study of Peritectic Steel Grades," *Journal of Thermal Analysis and Calorimetry*, Vol. 119, No.3, 2015, pp. 1547–1553.
7. Sun, S.-H., Zhao, A.-M., Ding, R. & Li, X.-G., "Effect of Heat Treatment on Microstructure and Mechanical Properties of Quenching and Partitioning Steel," *Acta Metallurgica Sinica (English Letters)*, Vol. 31, No.2, 2018, pp. 216–224.
8. Fang, D., Jun-mao, Q. & Hao-hua, D., "Study on Thermal Physical Properties of 304 Stainless Steel," *6th International Symposium on High-Temperature Metallurgical Processing*, 2015, pp. 99–104.
9. Binczyk, F., Cwajna, J. & Gradoń, P., "ATD and DSC Analysis of IN-713C and ZhS6U-VI Superalloys," *Archives of Foundry Engineering*, Vol. 17, No.1, 2017
10. Arvola, D., O'Malley, R., Lekakh, S. N. & Bartlett, L. N., "Effect of Phase Solidification Sequence in Stainless STeel on Grain Refining Efficiency," *AISTech 2018 Proceedings*, Vol. III, 2018, pp. 2651–2662.
11. Carlson, K. D. & Beckermann, C., "Determination of Solid Fraction-Temperature Relation and Latent Heat Using Full Scale Casting Experiments: Application to Corrosion Resistant Steels and Nickel Based Alloys," *International Journal of Cast Metals Research*, Vol. 25, 2012, pp. 75–92.
12. Boettinger, W. J., Kattner, U. R., Moon, K. & Perepezko, J., *NIST Recommended Practice Guide: DTA and Heat-flux DSC Measurements of Alloy Melting and Freezing*, Vol. Special Publication 960-15 , NIST, Gaithersburg, MD, 2006,
13. Dojka, M., Dojka, R. & Studnicki, A., "Development of a New ATD-P Tester for Hard Wear Resistant Materials," *Archives of Foundry Engineering*, Vol. 17, No.1, 2017
14. Binczyk, F., Cwajna, J. & Gradoń, P., "ATD and DSC Analysis of IN-713C and ZhS6U-VI Superalloys," *Archives of Foundry Engineering*, Vol. 17, No.1, 2017, pp. 13–16.
15. Jernkontoret, *A Guide to the Solidification of Steels* , Jenkortoret, Stockholm, 1977,
16. Stefanescu, D., *Science and Engineering of Casting Solidification* , Springer, New York, NY, 2015,
17. Gajewski, M. & Kasinska, J., "Rare Earth Metals Influence on Mechanical Properties and Crack Resistance of GP240GH and G17CrMo5-5 Cast Steels," *Archives of Foundry Engineering*, Vol. 9, 2009, pp. 37–44.

18. Lan, J., He, J., Ding, W., Wang, Q. & Zhu, Yanping., "Effect of Rare Earth Metals on the Microstructure and Impact Toughness of a Cast 0.4C-5Cr-1.2Mo-1.0V Steel," *ISIJ International*, Vol. 40, 2000, pp. 1275–1282.
19. Gruzleski, J. E., *Microstructure Development During Metalcasting* , American Foundrymen's Society, Inc, Schaumburg, IL, 2000,
20. Tuttle, R. & Song, K., "Characterization of Rare Earth Inclusions from Cast 1010 Steel," *International Journal of Metalcasting*, Vol. 9, No.1, 2015, pp. 23–31.
21. Bartlett, L. N. & Avila, B. R., "Grain Refinement in Lightweight Advanced High-Strength Steel Castings," *International Journal of Metalcasting*, Vol. 10, No.4, 2016, pp. 401–420.
22. Tuttle, R. B., "Grain Refinement in Plain Carbon Steels," *Transactions of the American Foundry Society*, Vol. 118, 2010, pp. 425–435.
23. Suito, H., Ohta, H. & Morioka, S., "Refinement of Solidification Microstructure and Austenite Grain by Fine Inclusion Particles," *ISIJ International*, Vol. 46, 2006, pp. 840–846.
24. van der Eijk, C. & Walmsley, J., "Grain Refinement of Fully Austenitic Stainless Steels Using a Fe-Cr-Si-Ce Master Alloy," *59th Electric Furnace and 19th Process Technology Conferences*, 2001, pp. 51–60.
25. Guo, M. & Suito, H., "Influence of Dissolved Cerium and Primary Inclusion Particles of Ce2O3 and CeS on Solidification Behavior of Fe-0.20 Mass%C-0.02 Mass%P Alloy," *ISIJ International*, Vol. 39, 1999, pp. 722–729.
26. Bramfitt, B. L., "Effect of Carbide and Nitride Additions on the Heterogeneous Nucleation Behavior of Liquid Iron," *Metallurgical Transactions*, Vol. 1, 1970, pp. 1987–95.
27. Tuttle, R. B., "Role of Titanium on the Grain Refinement of 1030 Steel Castings," *Transactions of the American Foundry Society*, Vol. 119, 2011, pp. 561–571.
28. Park, J. S., Lee, C. & Park, J. H., "Effect of Complex Inclusion Particles on the Solidification Structure of Fe-Ni-Mn-Mo Alloy," *Metallurgical and Materials Transactions B*, Vol. 43, No.6, 2012, pp. 1550–1564.
29. Kimura, K., Fukumoto, S., Shigesato, G. & Takahashi, A., "Effect of Mg Addition on Equiaxed Grain Formation in Ferritic Stainless Steel," *ISIJ International*, Vol. 53, No.12, 2013, pp. 2167–2175.
30. Tuttle, R. B., "Influence of Rare Earth Additions on the Structure of HY100," *Transactions of the American Foundry Society*, Vol. 126, 2018, pp. 335–343.
31. Tuttle, R. B., "Thermal Analysis of Rare Earth Additions to HY100," *Journal of Materials Engineering and Performance*, Vol. 28, No.5, 2019, pp. 2707–2715.
32. Tuttle, R., "Comparison of Rare Earth Refinement in 4130 and HY100," *Metals*, Vol. 11, No.4, 2021, pp. 540.
33. Everett, R. K. & Geltmacher, A. B., "Spatial distribution of MnS inclusions in HY-100 steel," *Scripta Materialia*, Vol. 40, No.5, 1999, pp. 567–571.
34. Sampath, K., "Meeting specification, failing expectations,", 2004, pp. 425.
35. Phillips, R. H. & Metzbower, E. A., "Laser beam welding of HY80 and HY100 steels using hot welding wire addition," *Welding Research (Miami, FL, United States)*, 1992, pp. 201.
36. Ferry, M., Hunter, A., Strezov, L. & Mukunthan, K., "Influence of titanium inoculation on the as-cast microstructure of ferritic stainless steel strip.," *Eng. Mater. 2001, Proc.*, 2001, pp. 2/33-2/38.

37. Malla, K. C., Chakrabarti, A. K. & Galgali, R. K., "Deoxidation and Strengthening of Steels Using Fe-Ti-C Master Alloy," *Ironmaking and Steelmaking*, Vol. 25, 1998, pp. 168–172.
38. Church, N., Wieser, P. & Wallace, J. F., "Control of Cast Grain Size of Steel Castings; Effect of Grain Refinement on Properties," *Modern Castings (1956-66)*, Vol. 49, 1966, pp. 129–44.
39. Arvola, D., O'Malley, R., Lekakh, S. N. & Bartlett, L. N., "Effect of Phase Solidification Sequence in Stainless Steel on Grain Refining Efficiency," *AISTech 2018 Proceedings*, Vol. III, 2018, pp. 2651–2662.

What opportunities for training and professional development did the project provide?

A primary goal of the Foundry Research Group at SVSU is to build the skills of its members and accomplishing this several ways. Each member experiences formal safety training, exposure to new analytical techniques, mentoring, design skill development, manufacturing process training, and attendance at conferences. Thus, members experience a broad range of developmental activities that prepare them for a successful career after graduation.

Safety has always been the number one priority of the SVSU Foundry Research Group. Each member goes through a rigorous safety training procedure upon entering the group. The first portion focuses on understanding the safety hazards related to molten metal explosions and proper induction furnace practice. This information is presented in a series of online safety videos they must watch. A quiz on molten metal safety is taken by members to ensure they understand the hazards. Online training on heat exhaustion is also done so each member recognizes this medical risk. Additionally, online chemical hazard training has been implemented to provide additional familiarization with potential hazards. These online courses are followed by an aluminum pour and a cast iron pour. The pours are designed to ensure that all personnel are familiar with pouring procedures and have a chance to work together since the cohesiveness of a pouring crew is vital. Aluminum is done first followed by cast iron. These are done since they are progressively hotter metals. Safety training continues during their entire time; however, this initial training ensures they begin thinking about safety while working. It also establishes that students will be responsible for the safety of others when they work. The training offered follows similar procedures at local companies so it acclimates them to industry standards.

While the undergraduate programs at SVSU attempt to provide a large exposure to various experimental, manufacturing, and theoretical areas, coverage of every topic is never possible. Students working in the research group learn advanced topics or gain practical experience related to their coursework. Microscopy receives minor coverage in undergraduate coursework. The students learn in their *Principles of Engineering* course how to etch a sample and capture an image. The students assist in polishing, etching, and capturing microstructure images which drastically expands their experience. This exposure assists them in developing a broader background in metallography. They also learn how to conduct quantitative microscopy measurements by conducting grain size measurements. Changes in areas being sampled and the interpretation of the microstructure are also covered. These quantitative microcopy topics are not covered in the normal undergraduate program. Another area where significant materials education occurs is the area of sand testing. Every member of the group learns how to run compactibility, green compressive strength, moisture, and methylene blue tests. These are used in controlling the green sand system to assure molds made in the foundry are the same each experiment. This data and its interpretation are also discussed as problems arise.

Conducting the research in this project requires a wide variety of manufacturing processes. The most evident process is the metalcasting process itself. Students learn moldmaking techniques that cannot be taught in the classroom, such as the jolt/squeeze machine or resin bonded mold making. They also learn why certain parameters are used at SVSU based on previous or current defect issues. Students learn CNC machining by using the CNC lathe to machine tensile bars, attend TRAKMill training for conversational programing, and using the various CNC mills to create experimental apparatus. Students receive training on how to use drill presses, bench grinders, lathes, mills, welders, and other shop equipment. Some of the training replicates educational experiences in the curriculum, but many go beyond what is covered in coursework. As a regular part of the group's activities, students also build or repair experimental equipment. This exposure to different manufacturing processes provides a strong background for students.

The PI attempts to have each student during their tenure in the group design some type of device related to the research project. This ranges from new equipment to simple fixtures. These projects are necessary for completing the proposed research, but also provide a chance for students to practice concept generation, understand realistic constraints, and hone solid modeling skills. The PI meets weekly or more during the design process to see how it is progressing and provide feedback. This feedback relates both to the project itself, but also the student's work on it. These frequently show small deficiencies in their understanding of engineering topics which are addressed. Finally, the students build their design by themselves or with their peers. This results in immediate feedback on the feasibility of the design from a manufacturability standpoint. Many issues are headed off during the review process with the PI. However, some are purposely left in by the PI to help the students learn from their own mistakes or are unforeseen issues. Again, the students are developing better design and engineering skills by doing engineering, even on a small scale.

The last way in which the SVSU Foundry Research Group develops its members is through plant tours and conference attendance. While there is an active American Foundry Society Student Chapter that conducts tours, group members often travel with the PI to foundries or suppliers around the state when the opportunity arises. These are important in two ways. First, the members see how their work will be integrated by industry and improves their understanding of industry. Second, they develop a broader understanding of industry and a network of contacts for post-graduation employment. Funding from the project ensures each member can attend Metalcasting Congress. This is the premier metalcasting industry conference for North America. Here the students attend workshops and talks on the latest developments in the metalcasting industry. Their attendance increases their knowledge of metalcasting and particularly the current state of the art, and allows them to make contacts for post-graduation employment.

As stated at the start of this section, the Foundry Research Group provides a broad set of developmental experiences to its members. Some experiences are very formal while others are informal. The result of this are a set of people committed to improving themselves and the various experimental processes which helps in producing better research. When members graduate, their employers often comment on the broad set of skills they have, the understanding of current industrial issues, and readiness to work. Many of the former members become key players in both their companies and the industry as a whole. Perhaps the biggest indicator of the successful training and development they received.

How were the results disseminated to communities of interest?

Due to the nature of the project, the results are mostly disseminated through peer reviewed journal publications and conference presentations. However, conversations with two project supporters are also done, Elkem and MeltLab Systems. The journals and conferences are selected based on their target audience. The PI chooses venues that have a significant number of industrial readers/attendees. Since the goal of this research project is to produce a grain refining technology which industry can use, it is critical that industry gains an understanding of the issues and possibilities with the technology. Also, obtaining industrial feedback on the feasibility of the process being developed will ensure issues are addressed at the start of development, not far later.

Recent publications related to this project are the International Journal of Metalcasting, Journals of Materials Engineering and Performance, and Archives of Foundry Engineering. International Journal of Metalcasting (IJMC) is the peer reviewed journal sponsored by the American Foundry Society (AFS) and the World Foundry Organization. IJMC's readership includes the top researchers in the area of metalcasting and a large number of industrial readers. Its designation as the World Foundry Organizations journal has also increased the international readership. Thus papers published here are viewed by the industry that the current research project is trying to work with. The Journal of Materials Engineering and Performance is sponsored by ASM and has a broader readership of academic and industrial researchers. This audience includes researchers working with the larger steelmaking industry and provides a good avenue for the inclusions of commentary from the broader steel and materials research community. The Archives of Foundry Engineering has been added to the list of publication routes since it has a focus on foundry topics. The researchers are primarily Polish but AFE has been expanding its readership across Europe. Another feature of this journal is a larger set of steel foundry related researchers. Again, the targeted journals are all selected to ensure that the results are disseminated to those who need the research results and can provide the most appropriate commentary to improve the work.

The PI regularly presents and attends steel related conferences, the American Foundry Society's Metalcasting Congress, and AISTech. Metalcasting Congress is the largest foundry related conference in North America and covers various alloy systems, design software, management, and molding materials. It has attendees from all over North America and internationally. The focus of the conference is for industrial members, but all of the major metalcasting research groups also attend and present their work. This conference has a peer review process that mimics a high-end peer review journal so the papers presented are of very high quality and include current research and industrial issues. AISTech primarily covers topics related to steelmaking. It has now become the world's largest steel related conference. Attendees are from the steel industry and the major steel research groups. Presentation here ensures that the results are not only disseminated to the foundry industry, but the larger steelmaking community as well. As stated earlier the conference selection has been done to ensure industry members and the key researchers in the field of steelmaking can learn about the results of the project.

Elkem has developed a commercial grain refiner for stainless steels. They have been donating samples of this material to help with grain refining experiments in carbon steels for several years. Copies of published papers are sent to this company to help them understand steel solidification and grain refinement. Additionally, they discuss industrial experiences with their refiners which helps the PI form a better understanding of how refinement work.

MeltLab Systems supplied the thermal analysis system being used in this project. They are also supporting the project by writing software for analyzing the curves. There has been verbal and written communication between the PI and this company as we work together to develop the system. It is hoped that the research conducted in this project will allow MeltLab to offer a product capable of assessing the grain refinement of steels. Such a system will be necessary for controlling industrial processes using grain refining additions.

Project results are being widely disseminated with the goal of educating the industrial base. This broad dissemination also ensures that researchers related to steelmaking are aware of the results and can integrate it in their own work or provide their insight into steel solidification. This approach should make adoption faster and allow the Navy to more easily specify grain refined steels.

What do you plan to do during the next reporting period to accomplish the goals and objectives?

Nothing. This is the final report.

Honors: What honors or awards were received under this project in this reporting period?

- 2019 Steel Division Individual Service Award
- 2021 AFS Steel Division Best Paper

Technology Transfer

No patents or licenses have been issued as part of this project. However, there has been continuing conversations with MeltLab on how to improve their product. This has enabled improved data for this project and better analysis. Those changes have or will be integrated into their product.

Participants

1. Type: Most senior project role
   Faculty
2. Prefix (optional): Dr.
3. First Name: Robert
4. Last Name: Tuttle

5. Middle Name (optional)
6. Suffix
7. Nearest person month worked (a person month equals approximately 160 hours of effort, regardless of funding source): 21
8. National Academy Member? N
9. Country if participant is a foreign collaborator
   If not US based, identify the country of this participant on this project.

Students

Number of undergraduate and graduate STEM participants: 8
Number of participants that received a STEM degree: 6

Products

You have the option of selecting "nothing to report" in this section.

There are no limitations to the number of entries you submit and you can also pull information directly using the publication DOI.

Below is the information detailed for each product submission:

1. Publications (publication reference information (article title, authors, journal, date, volume, issue) can be automatically entered using a DOI)

   a. Article Title: Effect of Rare Earth Master Alloys on 4130
   b. Journal: International Journal of Metalcasting
   c. Authors: R. Tuttle
   d. Keywords: solidification; grain refinement: thermal analysis; rare earth
   e. Distribution Statement: No restriction
   f. Publication Status: Published
   g. Publication Identifier Type: DOI
   h. Publication Identifier: 10.3390/met11040540
   i. Publication Date: 2021
   j. Volume:
   k. Issue:
   l. First Page Number:
   m. Publication Location: N/A
   n. Acknowledgement of Federal Support? Yes
   o. Peer Reviewed? Yes

a. Article Title: Comparison of Rare Earth Refinement in 4130 and HY100
b. Journal: Metals
c. Authors: R. Tuttle
d. Keywords: solidification; grain refinement; thermal analysis; rare earth
e. Distribution Statement: No restriction
f. Publication Status: Published
g. Publication Identifier Type: DOI
h. Publication Identifier: 10.3390/met11040540
i. Publication Date: 2021
j. Volume: 11
k. Issue: 4
l. First Page Number: 540
m. Publication Location: N/A
n. Acknowledgement of Federal Support? Yes
o. Peer Reviewed? Yes

a. Article Title: Thermal Analysis and Properties of 1030 with Mg & Ti Additions
b. Journal: Transactions of the American Foundry Society
c. Authors: R. Tuttle
d. Keywords: solidification, thermal analysis, grain refinement, steels
e. Distribution Statement: No restriction
f. Publication Status: Published
g. Publication Identifier Type: N/A
h. Publication Identifier:
i. Publication Date: 2020
j. Volume: 128
k. Issue:
l. First Page Number: 241
m. Publication Location: N/A
n. Acknowledgement of Federal Support? Yes
o. Peer Reviewed? Yes

a. Article Title: Thermal Analysis Experiments in Titanium and Magnesium Additions to 4130 Steel
b. Journal: Journal of Materials Engineering and Performance
c. Authors: R. Tuttle
d. Keywords: heterogeneous nucleation, metalcasting, rare earth, steel, thermal analysis
e. Distribution Statement: No restriction

f. Publication Status: Published
g. Publication Identifier Type: DOI
h. Publication Identifier: 10.1007/s11665-019-04022-1
i. Publication Date: 2020
j. Volume: 29
k. Issue: 9
l. First Page Number: 5913
m. Publication Location: N/A
n. Acknowledgement of Federal Support? Yes
o. Peer Reviewed? Yes

a. Article Title: Thermal Analysis of Rare Earth Additions to HY100
b. Journal: Journal of Materials Engineering and Performance
c. Authors: R. Tuttle
d. Keywords: heterogeneous nucleation, metalcasting, rare earth, steel, thermal analysis
e. Distribution Statement: No restriction
f. Publication Status: Published
g. Publication Identifier Type: DOI
h. Publication Identifier: 10.1007/s11665-019-04022-1
i. Publication Date: 2019
j. Volume: 2
k. Issue: 5
l. First Page Number: 2707
m. Publication Location: N/A
n. Acknowledgement of Federal Support? Yes
o. Peer Reviewed? Yes

a. Article Title: A System for the Thermal Analysis of Steels
b. Journal: Transactions of the American Foundry Society
c. Authors: H. Kapadia, R, Tuttle
d. Keywords: steel, thermal analysis, solidification, cooling curve analysis, grain refining, mechanical properties
e. Distribution Statement: No restriction
f. Publication Status: Published
g. Publication Identifier Type: None
h. Publication Identifier:
i. Publication Date: 2019
j. Volume: 127
k. Issue:
l. First Page Number: 357
m. Publication Location: N/A

    n. Acknowledgement of Federal Support? Yes
    o. Peer Reviewed? Yes

    a. Article Title: Thermal Analysis of Rare Earth Grain Refined 4130
    b. Journal: International Journal of Metalcasting
    c. Authors: H. Kapadia, R, Tuttle
    d. Keywords: steel, thermal analysis, solidification, grain refinement, cooling curve analysis, macrostructure, rare earth
    e. Distribution Statement: No restriction
    f. Publication Status: Published
    g. Publication Identifier Type: DOI
    h. Publication Identifier: 10.1007/s40962-018-0274-8
    i. Publication Date: 2018
    j. Volume: 13
    k. Issue: 2
    l. First Page Number: 273
    m. Publication Location: N/A
    n. Acknowledgement of Federal Support? Yes
    o. Peer Reviewed? Yes

2. Conference Paper
    a. Title: Effect of RE Master Alloys on AISI 1030
    b. Authors : R. Tuttle
    c. Conference Name: AISTech 2021
    d. Conference Date: July 2021
    e. Conference Location: Nashville, TN
    f. Publication Status: Published
    g. Publication Date: July 2021
    h. Publication Identifier Type: None
    i. Publication Identifier:
    j. Acknowledgement of Federal Support? Yes

    a. Title: Effect of Magnesium and Titanium on the Mechanical Properties of HY100
    b. Authors : R. Tuttle
    c. Conference Name: AISTech 2020
    d. Conference Date: May 2020
    e. Conference Location: Virtual
    f. Publication Status: Published
    g. Publication Date: May 2020
    h. Publication Identifier Type: None
    i. Publication Identifier:

   j. Acknowledgement of Federal Support? Yes
3. Book

   None
4. Book Chapter

   None
5. Thesis
   a. Title: Thermal Analysis of Rare Earth Grain Refined 4130 Steel
   b. Institution: Saginaw Valley State University
   c. Authors: Het Kapadia
   d. Completion Date: May, 2018
   e. Acknowledgement of Federal Support? Yes
6. Website

   None
7. Other Products: Identify any other significant products that were developed under this project. Describe the product and how it is being shared.

   None