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Peritectic Determination by a Melt Deck Thermal Analysis System

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Abstract

There has been a growing interest in the peritectic due to increasing productivity, quality, and alloy development. Differential scanning calorimetry (DSC) has traditionally been used to study steel solidification but suffers significant limitations when measuring the solidus and peritectic. This work covers a new thermal analysis system that can characterize the peritectic reaction. Heats of AISI/SAE 1030 and 4130 steel were poured to provide some benchmarking of this new technique. The peritectic was detected and the reaction temperature measured. Measurements agree reasonably well with reference information. A review of the literature and thermodynamic calculations did find some disagreement on the exact temperatures for the peritectic and solidus. Some of this difference appears to be related to the experimental techniques employed. It was determined that the system developed accurately indicates these reaction temperatures. The system provides a unique method for examining steel solidification that can be employed on the melt deck.

Keywords: Thermal analysis, Solidification, Continuous casting, Peritectic

1. Introduction

The peritectic reaction in steel has gained more importance as continuous casting speeds and quality requirements have increased. Developments in advanced high strength steels (AHSS) have also caused renewed interest in this reaction. The reason for this interest in the peritectic reaction centers on the type of solidification a particular steel grade undergoes. In peritectic steels, the end of solidification results in the peritectic reaction occurring (See Equation 1).

$$L + \delta \longrightarrow \gamma \qquad (1)$$
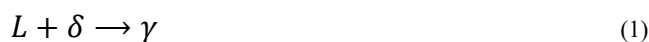
Where L is liquid, δ is delta ferrite, and γ is austenite. The formation of austenite at the end of solidification presents a significant challenge in continuous casting. The reaction results in a volumetric expansion that causes hot tears, surface defects, depression formation, and breakouts [1,2]. Reducing these defects often requires decreasing casting speed. Operational experience with traditional peritectic grades has determined the appropriate casting parameters. However, AHSS grades are not as well known. Additionally, the peritectic reaction has not always been properly predicted in these alloys since they fall outside the thermodynamic datasets used to predict the reaction [3,4].

Traditionally, steel solidification has been done using differential scanning calorimetry (DSC). In this technique, a sample 100 – 200 mg in size is heated inside the device with a reference sample. The difference in energy required to keep the sample at the same temperature as the reference is reported. Temperature deviations occur due to phase reactions in the sample. DSC is a very sensitive technique which can detect many phase reactions. However, determining the solidus temperature can be problematic, especially in steels, since it frequently occurs with a broad peak [5]. Being a heating technique, the detected solidus temperature often depends on the original solidification

structure of the sample [5]. Segregation within the sample can cause the solidus to be lower than it should be. The solidus of steel has also been found to be strongly dependent on cooling rate [5,6]. The peritectic reaction itself presents more difficulties in DSC due to the low energy associated with it [5]. Limited work exists on the peritectic; and because of this, techniques are note fully developed. The work which does exist frequently attempts to identify the reaction's occurrence but do not report the temperature it occurs at [7,8]. Another drawback to the DSC technique is that constructing a system capable of 1600ºC requires costly materials. Thus, DSC systems are also only suitable for laboratory environments.

Thermal analysis (TA) systems consisting of a single thermocouple in a shell core cup provide a possible solution to studying and controlling the peritectic reaction. They have been employed in aluminum alloys to control grain refinement and eutectic modification [9,10]. Their use in cast irons has allowed better control of both inoculation and nodulizing treatments [9,11]. The basis of this technique is that phase transformations cause slope changes in the cooling curves due to the thermal arrests. Computer software can automatically measure the reaction temperatures by examining those slope changes (i.e., the derivative of the cooling curve). It is also possible to measure the energy associated with a reaction [9]. Thus, the technique can provide much of the same data as DSC. A drawback is that precise control of the cooling rate is not easy. While broadly practiced in aluminum and cast iron foundries, the technique has not been as popular in steels. In the late '60s, TA systems were used to determine the liquidus for a steel which then allowed determination of the carbon content for controlling the open hearth process [12–14]. Jernkontoret sponsored work in the '70s using a system contained inside a furnace so controlled cooling rates could be obtained [6]. This TA work provided the first evidence that the solidus in steel varies significantly with cooling rate [6]. More recently some work has been conducted to confirm liquidus and solidus predictions in steels using the TA technique [8,15,16]. The researchers examining these reaction temperatures used the TA technique due to the complications of detecting the solidus in DSC [8,15,16]. They compared the results from TA with DSC and found that the TA method provided better reaction data [8,15,16].

The work presented in this paper used a single thermocouple TA system. Heats of AISI/SAE 4130 and 1030 were examined. While these alloys do not end their solidification with the peritectic reaction, they were selected since a portion of the solidification range has both δ-ferrite and austenite in equilibrium with liquid. This type of solidification makes confirming detection of the peritectic easier so that verifying the system's performance would be more straightforward. Another factor was that these are extremely well characterized alloys. Thus, they provide a good basis for benchmarking.

2. Experimental procedure

A commercially available system from MeltLab Systems was modified for use in steel. This modification consisted of employing S-Type thermocouples and compensation wire in addition to changing some of the software parameters. Fig. 1 illustrates the stand portion of the system where the TA cups were mounted and steel poured into. The cups were S-Type shell core cups from Matrix Sensors that utilized a small quartz tube to protect the thermocouple (See Fig. 1). These cups have a 40 mm inside diameter and 40 mm deep cavity. The S-Type compensation wire connects to the computer-based data acquisition (DAQ) system where data is recorded at a rate of 10 Hz. Acquisition automatically began at 1044ºC and ended at 1200ºC. The system can compute up to the fifth derivative of the cooling curve using proprietary data smoothing techniques. These derivatives are used for automatic identification of phase reaction temperatures. The system's existing algorithms for liquidus and solidus temperatures were utilized for measuring those reactions from the cooling curve.

Twenty-three-kilogram heats of AISI/SAE 1030 and 4130 steel were melted in a 3 kHz induction furnace under an air atmosphere. The initial charge consisted of 1010 scrap. FeCr and FeMo were also a part of the initial charge for the 4130 heat. After heating to 1650ºC, FeSi, FeMn, graphite, and aluminum shot additions were added to achieve the desired final chemistry. A portion of the heat was tapped into a 2.3 kg capacity hand ladle at 1730ºC and poured into a TA cup. Four cups per heat were poured. Two cups were as depicted in Fig. 1. The remaining cups were covered with a 15 cm square, 5 cm thick refractory cover. Covering the cups enabled the author to examine different cooling rates. Excess metal from the first cup in each heat was poured into a small sand mold for use as a spectrometer sample. The spectrometer sample was analyzed by an optical emission spectrometer (OES) to verify the composition. Table 1 lists the composition of the heats.
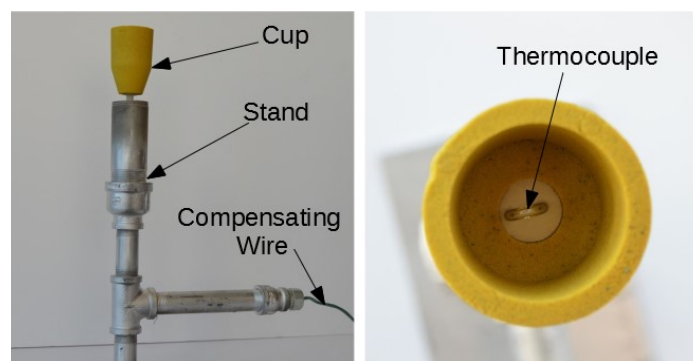

Fig. 1. TA system setup

Table 1.
Chemical composition of each heat in wt. %

Heat	C	Si	Mn	P	S	Cr	Mo	Al
1030	0.28	0.25	0.82	0.008	0.011	0.057	<0.002	0.003
4130	0.32	0.25	0.47	0.013	0.010	0.952	0.236	0.021

3. Results and discussion

While examination of the cooling curves can provide insight into the solidification of an alloy, analysis of the cooling rate or first derivative of the cooling curve, provides easier reaction detection. Phase reactions appear as peaks in the cooling rate. Figs. 2 through 5 illustrate the cooling rate for all samples. The cups original pour order in the experiment are also listed in Figs. 2 through 5. As would be expected, the covered cups for 1030 and 4130 had lower cooling rates due to the slower heat loss. Overall, the covered samples appear to have a higher noise level than the normal cups. This noise can be seen in Figs. 3 and 5 in the regions between the liquidus and solidus and after the solidus. Additionally, the peaks indicating a phase reaction occurred were smaller (See Fig. 3). The peritectic peak in particular tends to disappear (See Figs. 3 and 5). These issues make phase reaction identification and temperature measurement more difficult. It appears that TA cups with no cover provide the best performance in these steels.

As stated earlier, the existing MeltLab algorithms for identifying the liquidus and solidus were utilized in this work. These reactions are labeled on Figs. 3 through 5. A manual approach was necessary for the peritectic was necessary. Close examination of the cooling rate curves indicated a peak just prior to the solidus was typically present. These peak locations also agreed with thermodynamic predictions on the location of the peritectic within the solidification range of the allow. This peak was therefore identified by the author in each curve and reaction temperature at the peak was recorded as the peritectic reaction. The exact peaks chose are noted in Figs. 3 through 5. In the case of 1030, other peak locations were examined, but the resulting reaction temperatures did not make sense and those peak maxima were smaller than the peritectic peaks selected.

To determine the validity of the TA system, the measured reaction temperatures were compared to either ThermoCalc[©] predictions or data from *A Guide to the Solidification of Steels* [6]. The ThermoCalc[©] predictions used the exact chemistry of the heats poured and the TCFE9 database. Table 2 lists the data for 1030, while Table 3 lists the data for 4130. First, it should be noticed that the covered and normal cup data appears very similar across reactions in both alloys. The only exception was in the case of the solidus measurements of the 4130 where the covered samples measured a significantly lower solidus. Liquidus temperatures for the alloys were in good agreement with predictions, especially for the 4130 alloy (See Table 3). There was significant disagreement between the predicted results and that of the solidus (See Tables 2 and 3). The deviations from the ThermoCalc[©] predictions were on the order of 10ºC to 30ºC. It is interesting to note that the thermodynamic predictions and Jernkontoret data for 4130 disagreed by 20ºC. Therefore, it would appear that some discrepancy exists in the literature for this alloy. For 1030, there was also reasonable agreement for the peritectic reaction temperature. However, for the 4130, the peritectic temperature was detected at a higher temperature. And similar to the solidus, there is a significant discrepancy between the ThermoCalc[©] predictions and Jernkontoret data.
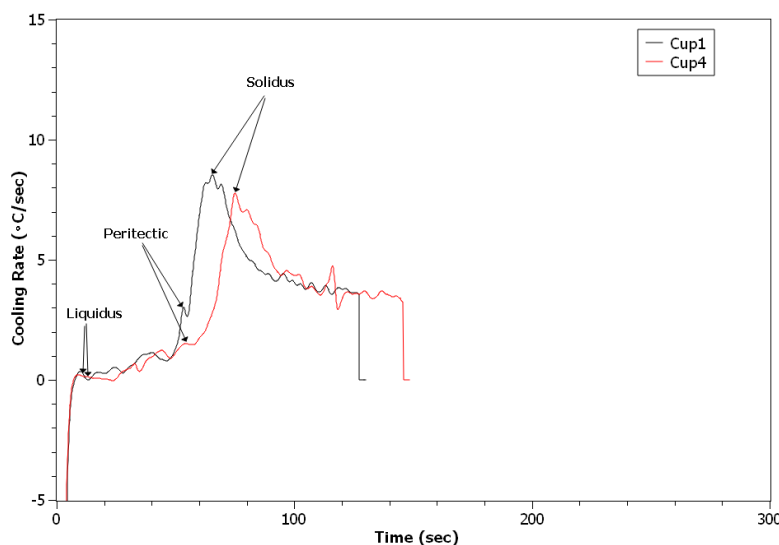

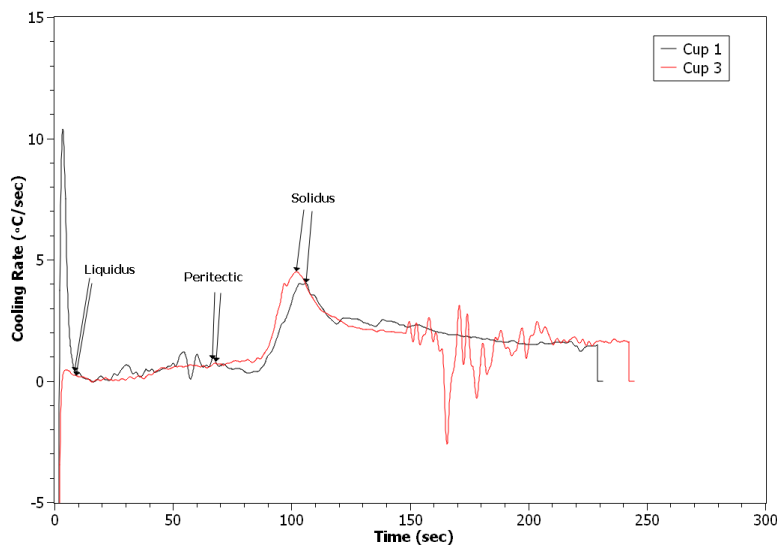Fig. 2. Normal cup cooling rate curves for 1030 samples

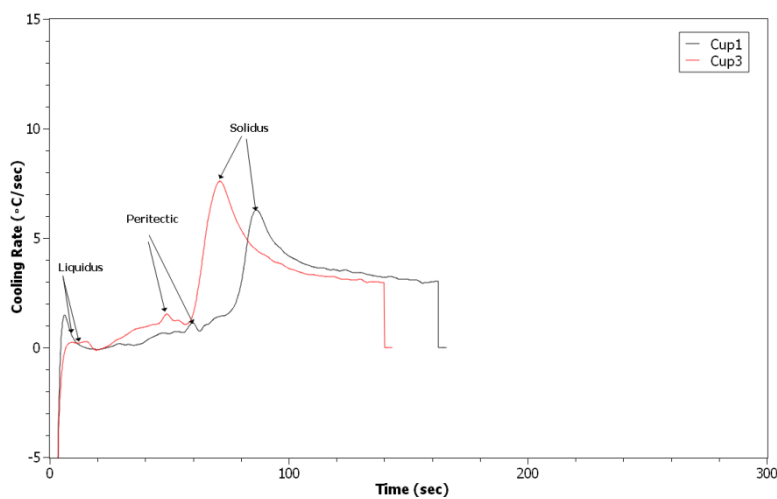Fig. 3. Covered cooling rate cup data for 1030

Fig. 4. 4130 normal cup cooling rate curve

Table 2.
1030 Solidification Parameters

	Liquidus (ºC)	Peritectic (ºC)	Solidus (ºC)
ThermoCalc	1508	1488	1421
Normal	1502	1489	1435
Covered	1502	1483	1436

Table 3.
4130 Solidification Parameters

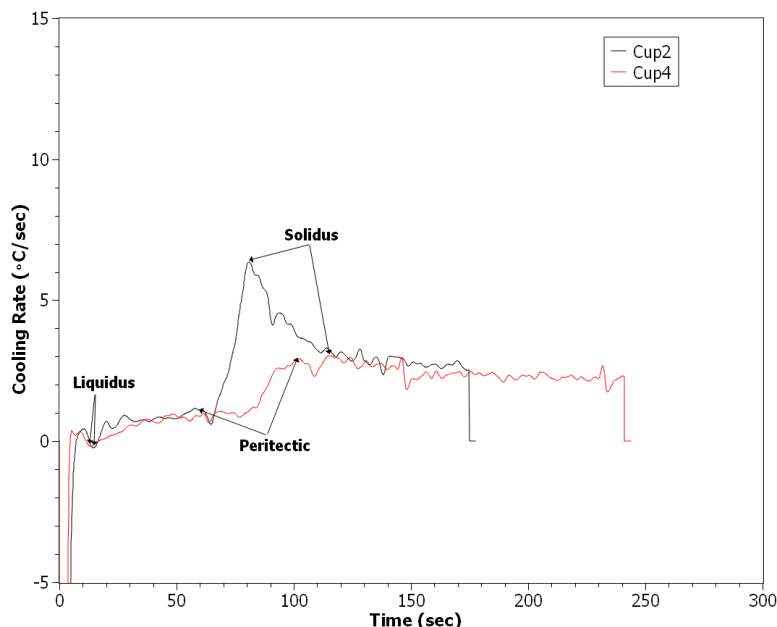|	Liquidus (ºC)	Peritectic (ºC)	Solidus (ºC)
ThermoCalc	1500	1474	1402
Jernkontoret Data[6]	1501	1460	1420
Normal	1499	1484	1431
Covered	1505	1486	1425

Fig. 5. 4130 covered cup cooling rate curve

The discrepancy in the solidus measurements might be explained by several differences in the experimental techniques. Thermodynamic predictions rely on databases of thermodynamic properties for a materials system. The primary basis for this data has been DSC data [17]. Thus, comparisons to thermodynamically predicted values are in many ways a comparison with DSC. As stated earlier, there are several problems with identifying the solidus in DSC. Most DSC work relies on heating the samples while this work and the Jernkontoret work are cooling experiments. It is difficult during heating to identify the onset of liquid formation in a steel sample, especially in DSC. This stems from the fact that, unlike cast irons or even cast aluminum alloys, there is not a major phase reaction like an eutectic to provide a strong signal. Therefore, the broad peak that often occurs provides a very low signal level making detection of the solidus reaction difficult [5]. Additionally, it should be noted that the solidus reaction in steel has been found to be strongly cooling rate dependent [5,6]. The Jernkontoret work observed that the solidus of 4130 decreases from 1450ºC to 1420ºC when the cooling rate increases from 0.1ºC/s to 2ºC/s [6]. However, the trend observed in this work shows the ThermoCalc© predictions tended to be the lowest. This may also be due to the 100-250 mg sample size typical in DSC work. Table 4 lists the average sample size for DSC, the Jernkontoret work, and this work. It also presents the total energy theoretically given off from the heat of fusion. It appears that the sample size might explain the trend in solidus data. The 280 g sample size in this work would be the largest and correlates with the tendency to report a higher solidus temperature (See Table 4).

Table 4.
Sample weight and energy evolved due to solidification

	Average Weight (g)	Energy (J)
TA Sample	281	76334
Jernkontoret Data [6]	35	9520
DSC Samples	0.25	68

The peritectic temperature discrepancies appear to be more complex. The measured peritectic temperature and predicted temperature were very close for the 1030 data. However, there was a significant difference between the 4130 measurements and reference or predicted temperature. There is substantial disagreement between the Jernkontoret data and predicted peritectic. Thus, it seems the disagreement in this peritectic temperature extends beyond the current experimental data. Certainly, a major complicating issue appears to be the smaller quantity of energy evolved during the reaction. This leads to smaller peaks which are much more difficult to analyze. In DSC, little work has been done to develop experimental and analytical techniques for characterizing these reactions [5]. So it is possible that the thermodynamic predictions might be off since DSC data forms the basis of most thermodynamic databases [17]. However, the most significant difference lies between the Jernkontoret data and the measured temperatures from this experiment. Peritectic reactions do involve solid state diffusion as the new solid forms [5]. This diffusion does take time and could be a strong function of the various alloying elements, particularly substitutional elements like nickel and chromium, which may cause a shift in the transformation temperature. Thus, small differences in the Jernkontoret heat chemistries and that of this work might cause the measured reaction temperature differences. 1030 does not have the same levels of alloying and thus would be less affected by such a condition explaining why the measured and predicted values for the peritectic were closer.

Overall, the TA system utilized in this work appears to provide good data. The solidus and peritectic temperatures differ from the predicted and reference data, but those appear related to experimental technique or composition. Identifying the peritectic was relatively easy verses other techniques and the system provides a robust and lower cost solution than other methods. This system can provide a tool for examining changes in the solidification of steels. In future work, the author plans on conducting experiments which examine other alloy compositions.

4. Conclusions

The thermal analysis system utilized in this work was able to detect the liquidus, peritectic, and solidus. The measured liquidus matched closely with the thermodynamic predictions and reference data. The peritectic temperature for 1030 recorded by the system was close to the thermodynamic predictions. For 4130, there was considerable variation between the measured value and thermodynamic predictions and reference data.

The solidus variation may be explained by several factors. First, the solidus is very sensitive to cooling rate. It also appears that sample size differences between experimental techniques may make a difference as well.

For the peritectic, the disagreement revolves primarily around the alloy steel. This may indicate some fundamental behavior in the peritectic reaction in steels or reflect the difficulty in accurately characterizing it regardless of the technique. Examination of the cooling rate curves from the thermal analysis system was relatively easy due to the distinctness of the peritectic peak.

Overall, the system has proven to be capable of determining the liquidus, peritectic, and solidus for steel alloys. It is also a lower cost system capable of steelmaking temperatures. Unlike DSC, solidus detection was trivial The peritectic peak was also large enough for detection. This system also possesses higher mechanical robustness than a laboratory system, so it can be employed on the melt deck. However, a major limitation of the system is that it cannot produce a large variation in cooling rates. A second limitation is that peak identification must be inferred from other data.

Future work will be obtaining data from additional alloys, developing an automatic method for measuring peritectic reactions, and examining the effect of alloy content changes on solidification. A specific area of interest is employing the system to examine how heterogeneous nuclei additions affect solidification reactions.

Acknowledgements

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