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Study of Fe-C-based alloys by dynamic methods of thermal analysis

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ABSTRACT

Purpose: of this paper is to determine the temperatures of liquidus/solidus temperatures for multicomponent Fe-C-based alloys (industrially produced steel grades). The obtained results could be used in settings of conditions of steel casting and/or in the numerical simulations of processes occurring during casting and solidification of steel.

Design/methodology/approach: Two modern apparatus for dynamic thermal analysis were used. Measurements of liquidus/solidus temperatures were realized by two thermal analysis methods. Experiments by the differential scanning calorimetry were done using the new one Setaram Multi High Temperature Calorimeter with 3D sensor (smaller samples about 2.6 g). The direct thermal analysis was used for large samples (23 g) at the STA 449 F3 Jupiter equipment.

Findings: The differences between calculated and experimentally obtained values of liquidus/solidus temperatures were found. Also temperatures of solidification process are different than for "equilibrium" conditions.

Practical implications: Presented results will be implemented into steel production practice – lowering of superheating of steel during ingot casting. The obtained temperatures will be implemented also into numerical simulations of ingot solidification.

Originality/value: Two thermal analysis methods with different sample mass of steel was used under conditions of one research team. The direct cooperation between steel plant experts and university research team was applied. The utilization of results is the next phases of cooperated research of the authors.

Keywords: Steel; Solidification; Thermal analysis; Liquidus temperatures; Solidus temperatures

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1. Introduction

Modern steel production technology needs to keep better control of the entire production cycle - from selection of quality raw materials, through proper control of primary and secondary metallurgy processes, and finally, the optimum settings of casting and solidification conditions. In the refining processes, optimizing the slag regimes [1,2], thermal and chemical homogenization of the melt [3] or filtration of steel [4,5] is very important to solve. In the casting and solidification of steel studies, works toward optimizing the process of solidification of heavy forging ingots [6] are currently being implemented.

VÍTKOVICE HEAVY MACHINERY a.s. (VHM) is traditional producer of large machinery components. The typical products of this company are crankshafts, propeller and connecting shafts, rotor shafts for wind power plants, forged parts for the container of pressurizers, steam generators, heat exchangers and collectors for both conventional and nuclear power engineering. For these products it is necessary to cast heavy steel ingots - up to 200 tons. Typically steel grades for these products are structural carbon-manganese, low alloyed, middle alloyed and tool steels [7].

The methods of study of metallurgical processes are based on knowledge of thermodynamic properties of materials occurring in a given technology nodes. Knowledge of solidus and liquidus temperatures of the studied steels is one of the most important factors - especially in dealing with the processes involved in the casting and solidification. These temperatures are critical parameters for proper adjustment of models (physical or numerical) or in the final stage of applied research of the real process. It is significantly affecting the final quality of the as-cast steel (billets or ingots).

Therefore, this paper is devoted to discussion of findings obtained during the utilization of dynamic thermal analysis methods to identify the solidus and liquidus temperatures.

2. Thermal analysis

The term Thermal Analysis [8] actually means the set of methods that allow us to monitor changes in the substance being studied by the measurement of certain (appropriately chosen) physical properties depending on the time or temperature (phase transformation, heat capacity, dehydration, dissociation, etc.). In the steel industry, thermal analysis is often used to determine the solidus and liquidus temperatures.

The methods of Thermal Analysis present in particular the dynamic processes for which it is typical to obtain information on the changes in the sample's state. These procedures require a non-isothermal temperature regime, which is usually achieved by constant heating or cooling of the sample [8,9]. Changes in the state of the studied material are determined either directly by measuring selected physical properties or indirectly by measuring the properties of the environment surrounding the sample.

Several tens of thermo analytical methods exist, and three of them are the most significant. These three methods are used in half to three-quarters of all professional works in the field of thermal analysis [8-12]. Among these methods belong DTA, DSC, TG, respectively TG/DTA and TG/DSC. The direct method, or the so-called direct measurement of sample temperature during cooling mode [13] was widely used in the past, especially for measuring the solidus and liquidus temperatures in metallic materials.

As already mentioned in previous work [14], new Laboratory for Modelling of Processes in the Liquid and Solid Phases within the project RMSTC was formed at the Faculty of Metallurgy and Materials Engineering. This laboratory has also acquired new equipment for high-temperature thermal analysis - JUPITER (Fig. 1a). The second, also new, equipment used for thermal analysis was Setaram MHTC (Fig. 1b).

a) b)

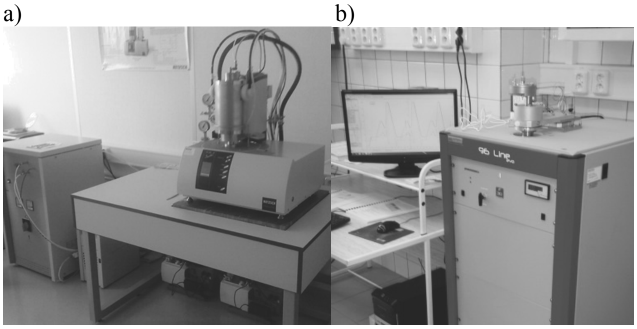


Fig. 1. Used measuring equipment: a) Netzsch STA 449 F3 Jupiter, b) Setaram MHTC

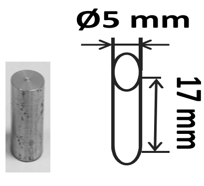
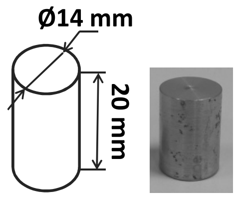
During the first year after the installation of new equipment JUPITER, dozens of measurements to define and subsequently to use the practical potential of this device - especially given by the opportunity to study the thermodynamic properties of the material on the "big" steel samples (over 20 g) - have already been done. Despite that Setaram MHTC with samples (over 2.5 g) and 3D DSC sensor with high sensitivity was installed during January 2012; it is fully implemented to thermal analysis of steels now.

This paper discusses the utilization of above mentioned equipment and methods: direct thermal analysis and differential scanning calorimetry for determination of liquidus (T_L) and solidus (T_S) temperatures of complex multicomponent Fe-C system such as special grades of steels - Table 1.

Table 1.
Chemical composition of steel grades according to specification

Elements; wt.%	Grade of Steel	
	S34MnV	20MnMoNi5-5
C	0.33- 0.39	0.17- 0.23
Mn	1.20- 1.50	1.20- 1.50
Si	max. 0.30	0.15- 0.30
P	max. 0.020	max. 0.012
S	max. 0.020	max. 0.008
V	max. 0.12	---
Cu	---	max. 0.12
Ni	---	0.50- 0.80
Cr	---	max. 0.20
Mo	---	0.40- 0.55
Al	---	0.010-0.040

Table 2.
Steel samples with dimensions specified for each analysis

<table>
<tr><th>Sample for method:</th><th>Setaram MHTC</th><th>STA 449 F3 Jupiter</th></tr>
<tr><td>Dimensions:</td><td>
</td><td>
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The samples of studied steel grades were taken and adapted (Table 2) for measuring by selected methods of thermal analysis.

2.1. 3D differential scanning calorimetry

B type HF DSC measuring probe (thermocouple: PtRh 6% / PtRh 30%) was used to obtain temperatures of phase transformations at the Setaram MHTC equipment. Samples were analysed in alumina (Al_2O_3) crucibles with a capacity of 0.7 ml. Weight of analysed steel samples was approximately 2.6 g. Constant dynamic atmosphere - inert helium with purity of 99.9999% - was maintained during measurements.

3D differential scanning analysis was used to determine the temperatures of solidus and liquidus temperatures close to the equilibrium in the frame of studied steel grades. Utilisation of 3D sensor with high sensitivity enabled to obtain correct data about occurring phase transformation. The heating rates 1 and 2°C·min^{-1} in the critical temperature range were used to obtain the relevant phase transformation temperatures. Example of the DSC curve obtained and analysed for the steel grade 20MnMoNi5-5 is shown on Fig. 2.

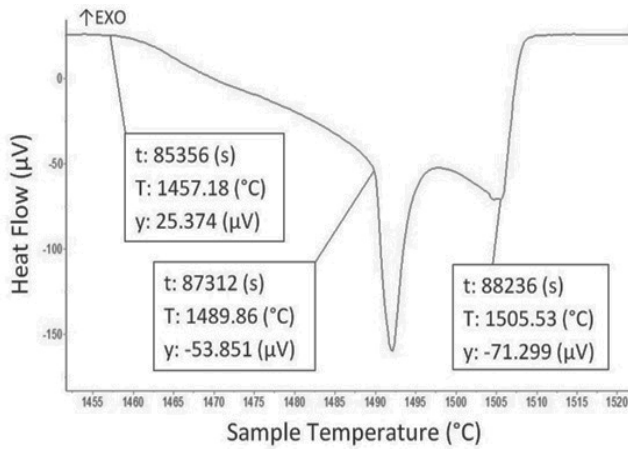

Fig. 2. Example of DSC curve from Setaram MHTC, steel grade 20MnMoNi5-5, heating rate 1 °C·min^{-1}

2.2. Direct thermal analysis

S type measuring rod for TG (thermocouple: Pt/PtRh 10%) and STA 449 F3 Jupiter equipment was used for obtaining of phase transformation temperatures. Samples were analysed in corundum (Al_2O_3) crucible with a capacity about 4 ml. Weight of analysed samples was about 23 g. Constant dynamic atmosphere - inert argon with purity of 99.9999% - was maintained during measurements. Example of measured and subsequently analysed curve obtained from direct thermal analysis measurement for steel S34MnV is shown on Fig. 3.

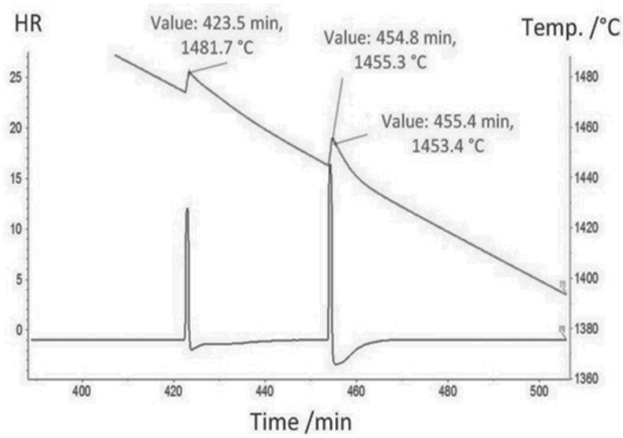

Fig. 3. Example of curve from direct thermal analysis (JUPITER), steel grade S34MnV, cooling rate 1 °C·min^{-1}

Direct thermal analysis was used to determine the solidus and liquidus temperatures for the conditions corresponding to the solidification process of studied real steel grades. This method was chosen intentionally, it allows us to study the behaviour of complex structures contained in "large" samples of steel. Measurements were carried out for the cooling rate 1°C·min^{-1}.

3. Results of thermal analysis

The results obtained during thermal analysis of steel samples by above described methods were evaluated. Finally, the liquidus and solidus temperatures for nearly equilibrium and for solidification process of studied steel grades (S34MnV, 20MnMoNi5-5) were determined. Details are briefly discussed below (see Fig. 4 and Fig. 5).

3.1. Liquidus and solidus temperatures for the steel grade S34MnV

Fig. 4 summarizes the obtained liquidus and solidus temperatures for S34MnV steel grade. This steel is used for crankshafts production.

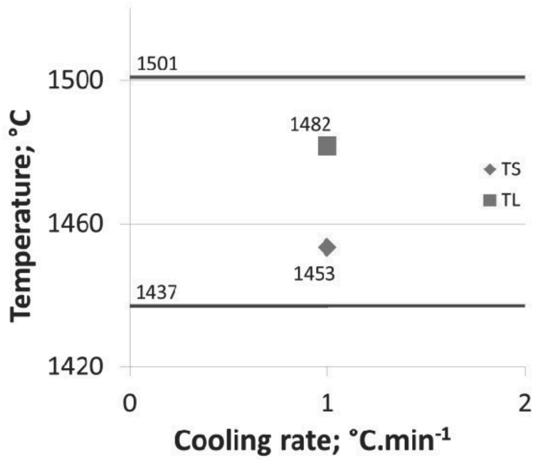

Fig. 4. Determined liquidus and solidus temperatures: lines presents the "equilibrium" temperatures, points are for 1 °C·min^{-1} cooling rate; steel grade S34MnV

Fig. 4 shows the liquidus and solidus temperatures (horizontal lines) determined by 3D DSC measurement at the Setaram MHTC equipment. Smaller 2.6 g samples of S34MnV steel were used under condition of slow heating (heating rates: 1 and 2°C·min^{-1}). These temperatures T_L = 1501°C; T_S = 1437°C should be called the "equilibrium" temperatures.

The liquidus and solidus temperatures for large (23 g) steel samples (points at the Fig. 4) were obtained by direct thermal analysis at the JUPITER equipment.

Cooling rate 1°C·min^{-1} was chosen as optimal based on previously performed numerical modelling of steel ingot solidification. These temperatures of liquidus (T_L = 1482°C) and solidus (T_S = 1453°C) differ from the "equilibrium" temperatures. Processes occurring during the cooling of large steel sample significantly narrow two-phase region between the T_L and T_S.

The "equilibrium" T_L is 19°C higher than non-equilibrium T_L. The "equilibrium" T_S is 16°C lower than non-equilibrium T_S. Whole two-phase region is 35°C (almost 55%) shorter due to cooling than for "equilibrium" state.

3.2. Liquidus and solidus temperatures for the steel grade 20MnMoNi5-5

Fig. 5 summarizes the obtained liquidus and solidus temperatures for 20MnMoNi5-5 steel grade. This steel is used for production of components for nuclear power plants.

Fig. 5 shows the liquidus and solidus temperatures (horizontal lines) determined by 3D DSC measurement at the Setaram MHTC equipment. Smaller 2.6 g samples of 20MnMoNi5-5 steel were used under condition of slow heating (heating rate: 1°C·min^{-1}). Temperatures T_L = 1506°C; T_S = 1456°C should be called the "equilibrium" temperatures.

The liquidus and solidus temperatures for large (23 g) steel samples (points at the Fig. 5) were obtained by direct thermal analysis at the JUPITER equipment.

Also for this steel grade 1 °C·min^{-1}cooling rate was chosen. These temperatures of liquidus (T_L = 1486°C) and solidus (T_S = 1454°C) differs from the "equilibrium" temperatures. Processes occurring during the cooling of large steel sample narrow two-phase region between the T_L and T_S as previously discussed steel grade.

The "equilibrium" T_L is 20°C higher than non-equilibrium T_L. The "equilibrium" T_S is only 2°C higher than non-equilibrium T_S. For this steel grade, whole two-phase region is 18°C (almost 36%) shorter due to cooling than for "equilibrium" state.

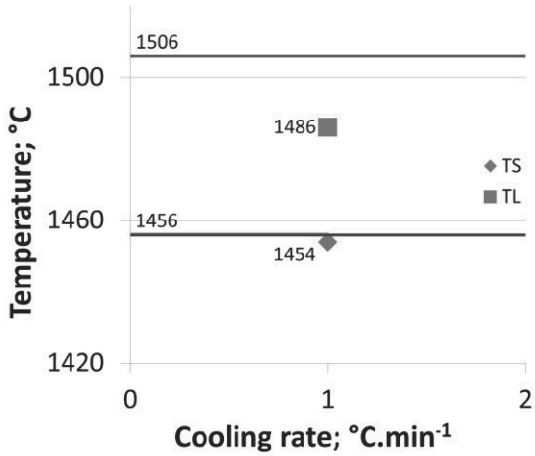

Fig. 5. Determined liquidus and solidus temperatures: lines presents the "equilibrium" temperatures, points are for 1°C·min^{-1} cooling rate; steel grade 20MnMoNi5-5

4. Comparison of "equilibrium" temperatures with calculated values

The theoretical calculations of equilibrium liquidus and solidus temperatures of both studied steel grades were performed. The aim was to compare such values with temperatures determined by thermal analysis measurements.

Ten different generally used equations and CompuTherm SW was used for prediction of liquidus temperature. Only one relevant equation was found for calculation of solidus temperature. The CompuTherm SW was used too - see Table 3.

Table 3.
Comparison of "equilibrium" temperatures

Steel grade	Source	"Equilibrium" temperatures	
		Liquidus; °C	Solidus; °C
S34MnV	Equations	1490 to 1504	1425
	CompuTherm	1497	1429
	Thermal Analysis	1501	1437
20MnMoNi5-5	Equations	1495 to 1508	1451
	CompuTherm	1503	1444
	Thermal Analysis	1506	1456

For S34MnV steel grade, Table 3 shows that liquidus temperature determined by thermal analysis measurements lies in the 14°C wide temperature interval obtained from different calculated predictions. Measured solidus temperature is 12/8°C higher than theoretical calculated/CompuTherm values.

Similarly, liquidus temperature of 20MnMoNi5-5 steel grade experimentally determined by thermal analysis lies also inside 13°C wide calculated temperature interval. Measured solidus temperature is 5/12°C higher than theoretical calculated/CompuTherm values.

5. Conclusions

The thermal analysis of Fe-C based alloys, two real steel grades (S34MnV; 20MnMoNi5-5), was performed by two methods. The differential scanning calorimetry was done by Setaram MHTC equipment with 3D DSC sensors around approx. 2.6 g steel sample in alumina crucible. Measurements were realized under conditions of slow heating (heating rates: 1; 2°C·min^{-1}).

1) The "equilibrium" liquidus and solidus temperatures were determined:
   - S34MnV: T_L = 1501°C; T_S = 1437°C;
   - 20MnMoNi5-5: T_L = 1506°C; T_S = 1456°C.

The direct thermal analysis by JUPITER equipment was performed (approx. 23 g steel samples) for conditions close to solidification process of heavy ingots. Cooling rate 1°C·min^{-1} was chosen based on previously realized numerical modelling of ingot solidification.

2) Non-equilibrium liquidus and solidus temperatures that differ from "equilibrium" temperatures were determined:
   - S34MnV: T_L = 1482°C; T_S = 1453°C;
   - 20MnMoNi5-5: T_L = 1486°C; T_S = 1454°C.
3) It was found that during cooling process of ingots the liquidus and solidus temperatures are not the same as the "equilibrium" temperatures. Whole two-phase region between liquid and solid steel is up to 55 % less than under equilibrium conditions. This fact could be taken into account when study of solidification processes is performed. The settings of boundary conditions should significantly affect the results of numerical simulations.

The comparison of "equilibrium" liquidus and solidus temperatures determined by thermal analysis (3D DSC) and calculated by different equations and by CompuTherm SW was performed in this paper.

4) Calculated liquidus temperatures for studied steel grades are different based on selected calculation methods.
5) Finally, the intervals of such obtained liquidus temperatures were found for both steel grades:
   - S34MnV: 1490 to 1504°C;
   - 20MnMoNi5-5: 1495 to 1508°C.
6) In the frame of this paper, only one equation and CompuTherm SW were used for calculation of solidus temperatures. Both predictions are different about 10 °C from measured values.
7) It is evident that experimentally determined liquidus and solidus temperatures are very useful for precise settings of research connected with steel casting and solidification.

Thus, the results obtained by thermal analysis are implemented into boundary conditions settings of numerical modelling of mentioned steel grades casting and solidification. This integration of determined liquidus and solidus temperatures will lead to the more proper results of simulations.

Finally, acquired information could be used for optimization of casting temperatures of selected steel grades directly in real plant conditions.

Next research should be concerned to better understanding the reason and mechanism of differences between "equilibrium" and non-equilibrium temperatures of liquidus and solidus in multicomponent Fe-C systems.

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