

DETERMINATION OF SOLIDUS AND LIQUIDUS TEMPERATURES FOR S34MnV STEEL GRADE BY THERMAL ANALYSIS AND CALCULATIONS

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The paper is devoted to the comparison of the results in the frame of solidus and liquidus temperatures obtained by thermo analytical methods with the generally used empirically based formulas and thermo dynamical Computherm software. The series of thermal analysis measurements of high temperature phase transformations of real steel grade (S34MnV) under conditions of two analytical devices (Netzsch STA 449 F3 Jupiter; Setaram Multi High Temperature Calorimeter (MHTC)) were carried out. Two thermo analytical methods were used (DSC and Direct Thermal Analysis). The different weight of samples was used (2,6 g; 23 g). The liquidus and solidus temperatures for close to equilibrium conditions during heating (DSC: 1 °C/min; 2 °C/min) and during cooling (Direct Thermal Analysis: 1 °C/min) were determined and compared. Then, the discussion on the different values obtained by experiments and empirically based calculation is realised.

Key words: steel, thermal analysis, empirical formula, liquidus temperature, solidus temperature

INTRODUCTION

The methods of study of metallurgical processes are also 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 [1, 2] to identify the solidus and liquidus temperatures of selected steel grade. Generally, it is not so easy to identify the phase transformations occurring in such multicomponent systems like steels [3-5].

THERMAL ANALYSIS METHODS AND STEEL SAMPLES

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 at the VŠB-Technical University of Ostrava in Czech Republic.

This Laboratory has also acquired new equipment for high-temperature thermal analysis – Netzsch STA 449 F3 Jupiter. The conditions for initiation of intensive research activities in the field of dynamic thermal analysis methods for steel are based on years of experience of team members with the issue of laboratory studies of metallurgical processes and the ability to use other equipment of this type - Setaram MHTC.

This paper discusses methods and results of thermal analysis of samples (Table 1). Two methods for dynamic thermal analysis were used to measure the solidus (T_S) and liquidus (T_L) temperatures:

- Differential Scanning Calorimetry (DSC) – Setaram MHTC,
- Direct Thermal Analysis - Netzsch STA 449 F3 Jupiter.

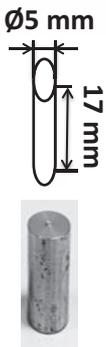
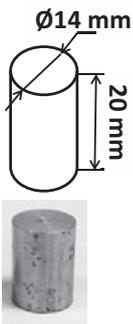
The principles of both methods are described for example in [5]. Results of previous measurements realised by our team you can find for example in [6] where the correct setting of used methodology is presented on other steel grade and also comparison of results realised by Netzsch STA 449 F3 Jupiter with next by our team used method DTA (SETARAM SETSYS 18_{TM}) is realised.

Results from thermo analytical methods

The first method (DSC) was used to determine the T_S and T_L close to equilibrium by the heating of samples (1 °C/min; 2 °C/min) of studied S34MnV steel grade.

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Table 1 Chemical composition of S34MnV steel grade, dimensions of used samples for each method

Chemical composition		Sample dimensions for used methods		
Element	Content / wt.%	Sample for method:	Setaram MHTC	STA 449 F3 Jupiter
C	0,33 – 0,39	Dimensions:		
Mn	1,20 – 1,50			
Si	max. 0,30			
P	max. 0,020			
S	max. 0,020			
V	max. 0,12			

These values will be compared also with results of empirical formulas based calculations in the next chapter of this paper.

The second thermo analytical method, Direct Thermal Analysis, was used to acquire data close to real conditions. Based on numerical simulation of 90 tons heavy forging ingot the cooling rate 1 °C/min was set during measurement.

Figure 1 presents comparison of liquidus (T_L) and solidus (T_S) temperatures (marks) acquired for real plant conditions (cooling) with close to equilibrium temperatures (lines).

It is evident, see Figure 1, that T_L for close to equilibrium conditions (1 501 °C) is about 19 °C higher than the T_L obtained for the controlled cooling conditions (1 482 °C).

Further, the value of T_S for close to equilibrium conditions (1 437 °C) is about 16 °C lower than the T_S for cooling regime (1 453 °C). So, during cooling (close to real plant conditions) the two-phase region between T_L and T_S is narrowed from 64 to 29 °C.

It is important to take into account these differences between close to equilibrium temperatures and real situation for example in solidifying ingot. It should help us to better predict the real processes occurring in steel by numerical modelling and/or technology optimisation.

COMPARISON OF DSC ANALYSIS RESULTS WITH CALCULATIONS

As mentioned, close to equilibrium T_L and T_S acquired by differential scanning calorimetry are suitable to compare with generally used and empirically based formulas (A-K) defined in [6]. Also, a calculation realised by Computherm thermo dynamical software (SW) was applied for this comparison [6].

Computherm SW is able to calculate both studied temperatures. It is possible to choose two microsegregation models (Scheil or Lever). In the case of Lever, the Lever rule has been applied, corresponding to a complete mixing of the solute in the solid (i.e., a very

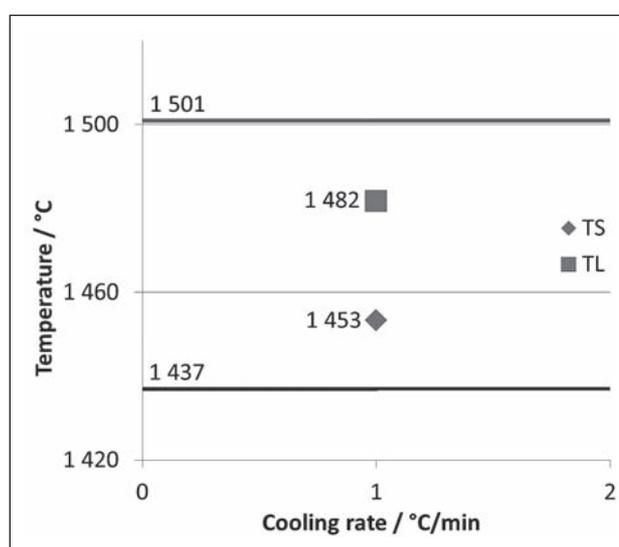


Figure 1 Results of realised thermal analysis measurements for close to equilibrium temperatures and for non-equilibrium conditions – cooling

good diffusion in the solid). On the other hand, the Scheil model corresponds to a no-diffusion model for the solid phase (both models consider a complete mixing of an infinite diffusion in the liquid). The Back-Diffusion model allows for some diffusion in the solid and corresponds thus to the situation in between the Lever rule and Scheil. When the Back-Diffusion model is used, the average cooling rate (corresponding to the representative cooling rate of the casting to be modelled) should be specified in order to determine the amount of back diffusion. For iron and carbon steel, the Lever rule is still recommended.

The Computherm Fe-rich-alloy database has defined the limitations of the chemical composition and recommended composition limits for them. The Lever rule was selected (without the Pb, Sn, As, Zr, Bi, Ca, Sb, B, N contents) for determining T_L and/or T_S in the frame of this paper.

Based on above described thermo-analytical method (DSC) and empirical formulas (A-J) and Computherm

SW [6] T_L was summarized for studied S34MnV steel grade – Table 2.

As standard for comparison with theoretical values of T_L (by calculation) was used the liquidus temperature acquired by DSC experiments realised under conditions close to equilibrium. These differences are quantified in column “Deviation”.

It is evident, see Table 2, that the best agreement (zero deviation) with measured T_L was reached when the formula (I) was used:

$$T_L = 1536 - K \cdot (\%C) - 8 \cdot (\%Si) - 5 \cdot (\%Mn) - 30 \cdot (\%P) - 25 \cdot (\%S) - 1,7 \cdot (\%Al) - 5 \cdot (\%Cu) - 1,5 \cdot (\%Cr) - 4 \cdot (\%Ni) - 2 \cdot (\%V) - 1 \cdot (\%W) - 1,7 \cdot (\%Co) - 12,8 \cdot (\%Zr) - 7 \cdot (\%Nb) - 3 \cdot (\%Ta) - 14 \cdot (\%Ti) - 14 \cdot (\%As) - 10 \cdot (\%Sn) \quad (1)$$

where the K coefficient varies with respect to different contents of carbon:

$$\begin{aligned} C & 2 \% ; & K & = 65 \\ C \in (0,2; 0,5) \% ; & & K & = 88 \end{aligned}$$

Vice versa, the biggest deviation (-11 °C) against measured value of T_L was identified when the formula (C) was applied:

$$T_L = 1537,7 - 100,3 \cdot (\%C) + 22,1 \cdot (\%C)^2 - 13,55 \cdot (\%Si) + 0,64 \cdot (\%Si)^2 - 5,82 \cdot (\%Mn) - 0,3 \cdot (\%Mn)^2 - 4,18 \cdot (\%Ni) - 0,01 \cdot (\%Ni)^2 - 4,2 \cdot (\%Cu) - 1,59 \cdot (\%Cr) + 0,007 \cdot (\%Cr)^2 - 3 \cdot (\%Mo) \quad (2)$$

Table 2 **Liquidus temperatures for S34MnV steel grade determined by the formulas, Computherm and DSC experiments**

T_L based on	T_L / °C	Deviation / °C
A	1 499	-2
B	1 495	-6
C	1 490	-11
D	1 492	-9
E	1 499	-2
F	1 496	-5
G	1 504	3
H	1 493	-8
I	1 501	0
J	1 498	-3
SW	1 497	-4
DSC	1 501	0

In the previous presented study [6], there were compared formulas and SW results with experimental ones for 5 steel grades with different chemical composition. Based on this work can be stated that it is very hard to identify best fit equation or thermo dynamical SW before experimental check-up. Above mentioned best fitting formula (9) for discussed S34MnV steel grade is not automatically the best one for other steel grades [6].

The T_L predicted by Computherm SW were generally in relatively good agreement with measurements, not only for S34MnV steel grade (-4 °C).

Experimentally acquired T_S was compared with only one empirical formula (K) and with Computherm SW [6] – see Table 3.

Table 3 **Solidus temperatures for S34MnV steel grade determined by the formula, Computherm and DSC experiments**

T_S based on	T_S / °C	Deviation / °C
K	1 425	-12
SW	1 429	-8
DSC	1 437	0

It is evident, see Table 3, that calculated T_S differ from experimentally measured T_S much more than when T_L values were compared.

Determination of T_S not only for S34MnV steel grade is very difficult.

CONCLUSION

The comparison of the results in the frame of solidus and liquidus temperatures (S34MnV steel grade) obtained by thermo analytical methods with the generally used empirically based formulas and thermo dynamical Computherm SW was aim of this paper. Two thermo analytical methods were used.

Direct thermal analysis experiments were realised to simulate real cooling process. Moreover, DSC method was used to determine T_L and T_S values for close to equilibrium conditions. Based on a comparison of above mentioned results can be stated:

1. T_L and T_S for close to equilibrium conditions (1 501 °C; 1 437 °C) differ from such values (1 482 °C; 1 453 °C) for simulation of solidifying of heavy forging ingot (cooling).
2. The two phase region (mushy zone) between T_L and T_S is narrowed radically (from 64 to 29 °C).

It is important to take into account these differences between close to equilibrium temperatures and real situation for example in solidifying ingot. It should help us to better predict the real processes occurring in steel by numerical modelling and/or technology optimisation.

Close to equilibrium T_L and T_S acquired by DSC method were then compared with calculations based on empirically based formulas and thermo dynamical Computherm software:

3. Calculated values of T_L/T_S differ from experimentally obtained results.
4. It is very hard to identify best fit equation or thermo dynamical SW before experimental check-up of T_L/T_S .

It is important to verify the theoretical values of the crucial parameters such as the liquidus and solidus temperatures by experimental measurements for optimising the metallurgical process.

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