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DETERMINATION OF SOLIDUS AND LIQUIDUS TEMPERATURES FOR BEARING STEEL BY THERMAL ANALYSIS METHODS

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Preliminary Note – Prethodno priopćenje

The first part of presented paper is devoted to comparison of solidus and liquidus temperatures determined by two methods of thermal analysis for one real steel grade 100CrMo7. Two modern devices for high-temperature analysis were used. The direct thermal analysis method was used during an experiments realised on large samples (22 g) at NETZSCH JUPITER device. Small bearing steel samples (up to 210 mg) were studied by differential thermal analysis method at Setaram SETSYS 18$_{TM}$.The robustness of both used thermo-analytical methods was documented. Measured results were compared with liquidus and solidus temperatures used in industry and calculated by specialized IDS and ThermoCalc software. Measured temperatures differ from the theoretically calculated by tens for liquidus to more than 100 °C for solidus.

Key words: alloyed steel, bearing steel, thermal analysis, liquidus temperature, solidus temperature

INTRODUCTION

Methods for studying processes related to steel production are based on knowledge of the thermodynamic properties of materials occurring in the technological nodes. A solidus (T_S) and a liquidus (T_L) temperature belong among the most critical parameters especially for casting and solidification of the steel. Exact knowledge of T_L is particularly important with respect to the setting of steel superheat before its casting. T_S is related in particular to the solidification process, when the existence and range of two-phase area between T_L and T_S affect a segregation and other phenomena connected with solidification process. Knowledge of these critical temperatures is important not only for the correct setting of the technology of casting and solidification of the steel intermediate product, but also for precise setting of conditions for modelling of steel solidification.

This paper follows on previous works [1]. Again, it is focused on the possibility of refinement of these temperatures (T_L, T_S) by experimental methods of high temperatures thermal analysis. Concretely, the bearing steel 100CrMo7 was analysed. For this steel grade, it is possible due to high carbon content (1 wt. %) to assume that real T_L value can be significantly different from the theoretical T_L determined by calculation. It is expected that based on more accurate information on the liquidus temperature the casting temperature can be adjusted so as to achieve a higher quality of the ingot, i.e. lower range of porosity and macro-segregation.

THERMAL ANALYSIS AND THEORETICAL CALCULATIONS

The term thermal analysis [2-6] can be explained as group of methods that trace changes in the studied substance by measuring of selected physical properties in dependence on time or temperature (phase transition, heat capacity, dissociation etc.). From the perspective of the steel industry, thermal analysis is mainly used to determine the T_L and T_S.

Thermal analysis methods are essentially dynamic processes aimed at obtaining information about the state change of the sample. These processes require a non-isothermal temperature regime which is generally constant heating or cooling of the sample [2]. Changes in the state of studied material are determined either directly by measuring selected physical properties or indirectly by measuring the properties of the atmosphere surrounding the sample.

There are several tens of thermo-analytical methods. Three of them are the most important. These three methods are used in the range of one half to three-quarters of all professional work in thermal analyses [2-12]. These methods are: differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Methods of simultaneous combinations TG / DTA or TG / DSC exist too. In the past, the method of direct thermal analysis based on di-

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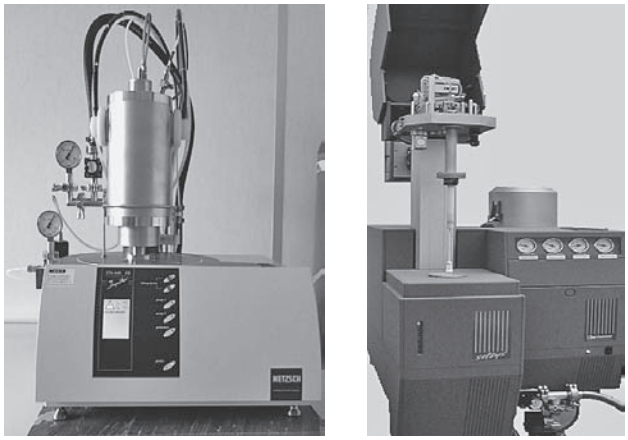
rect measurement of sample temperature changes especially during controlled cooling [7] was used very often. This method was and is used mainly for measurement of T_L and T_S of metallic materials.

As mentioned in the previous work [1], new Laboratory of modelling processes in liquid and solid phase was established within the project RMSTC (Regional Materials Science and Technology Centre) at the Faculty of Metallurgy and Materials Engineering, Technical University of Ostrava. This laboratory was, among other things, equipped with new device for high temperature thermal analysis - Netzsch STA 449 F3 Jupiter (Figure 1a). Next device utilized for high temperature thermal analysis is Setaram SETSYS 18_{TM} (Figure 1b).



a) b)

Figure 1 Devices for high-temperature thermal analysis: (a) Netzsch STA 449 F3 Jupiter, (b) Setaram SETSYS 18_{TM}

On the device Netzsch STA 449 F3 Jupiter, measurements were made using the method of direct thermal analysis (DirTA) - a direct measurement of sample temperature in time dependence (large samples, sample weight of about 22 g).

Liquidus temperatures were obtained at the cooling mode, and also under cyclic experiments (2 cycles were performed under the same cooling conditions). Solidus temperature was not possible to determine with this device and this method (low sensitivity temperature sensor - a vague record on the cooling / heating curve).

Setting the cooling temperature modes were as follows: the sample was heated to a temperature at which the sample is completely in the liquid phase, from this temperature was cooled at 5 or 10 °C/min (first cooling) until complete solidification, and subsequently heated again to complete melting and then re-cooled at 5 or 10 °C/min (second cooling).

Device Setaram SETSYS 18_{TM} with DTA (Direct Thermal Analysis) method (the principle of the method is the measurement of the temperature difference between sample and reference) was used for determining the liquidus and the solidus temperature (small samples, sample weight of about 120 to 210 mg) only during heating. Heating of the sample was carried out at high speed (30 °C/min from the temperature of 20 to 1 200 °C, then from 1 200 to 1 600 °C at 10 °C/min. Due to the higher sensitivity of the sensor, this method (DTA) can also determine solidus temperature for analysed steel grade.

Table 1 **Chemical composition of analysed bearing steel. Content of elements / wt. %**

C	Si	Mn	P	S
0,93-1,05	0,15-0,35	0,25-0,45	max. 0,025	max. 0,015
Cr	Mo	Cu	Al	
1,65-1,95	0,15-0,30	max. 0,30	max. 0,050	

In the context of this paper, attention was focused on the study of T_L and T_S for 100CrMo7 bearing steel grade. Its chemical composition according to the specifications is listed in Table 1.

In addition to the above methods of thermal analysis, T_L and T_S determined on the basis of computational relationships used in the steel plant (industrial partner, IND) were used for result's discussion. These values were further complemented by own calculations carried out when including of complex chemical composition available in specialized programs (IDS Solidification Analysis Package) and ThermoCalc (database TCFE7).

RESULTS AND DISCUSION

Before a determination of T_S and T_L by above described thermo-analytical methods, a number of methodological experiments were realised. For both used methods and devices, a calibration experiments on standard samples from nickel (purity 4N5) with the known melting point (1 455 °C) had been made. Deviations obtained in experiments with "pure" nickel then allow us to quantify the value of temperature correction expressing the effect of experimental conditions on the value of the T_S and T_L of real steel grades. Corrected T_S and T_L for each valid experiments incl. basic statistical analysis (mean, standard deviation and coefficient of variation) are then given in Table 2.

As mentioned above, the DTA method was applied on small samples (120 - 210 mg) during heating mode. For each sample, DTA curve was analysed and T_S and T_L were read and corrected. Corrected values gained during the heating of individual samples were then averaged (1 280 °C), average value is considered the actual T_S of analysed steel grade. T_S detected using methods DTA show higher standard deviation (10 °C) and also higher coefficient of variation (0,78 %). However, this variability is from the generally accepted point of view negligible. Therefore, the variability at T_L is even lower and average value (1 440 °C) can also be considered as relevant.

Unfortunately, it was not possible to determine T_S by DirTA method on large samples. It was possible to read only T_L from the cooling curves when mentioned DirTA method was applied. The variability of measured values is again very low (0,20 %). Acquired and to experimental conditions corrected values can be considered as relevant. Final T_L identified using this methodology (1

Table 2 **Corrected T_S and T_L obtained based on used thermo-analytical methods**

Device	Method	Experimental conditions			Results					
		Sample	Mode	Heating/ cooling speed	T_S			T_L		
				°C/min	/ °C	Statistics		/ °C	Statistics	
SETSYS	DTA	V1C9	H	10	1 296	Mean	1 280 °C	1 443	Mean	1 440 °C
		V1C10			1 275			1 438		
		V1C11			1 271	St. deviation	10 °C	1 435	St. deviation	3 °C
		V1C2			1 277	Var. coef.	0,78 %	1 442	Var. coef.	0,20 %
Jupiter	DirTA	V1.1	C1	5	-			1 442		
			C2		-			1 441		
		V1.3	C1	10	-			1 439	Mean	1 441 °C
			C2		-			1 435		
		V1.4	C1		-			1 440	St. deviation	3 °C
			C2		-			1 441	Var. coef.	0,20 %
		V1.5	C1		-			1 446		
			C2		-			1 440		

Note: H – heating, C1 – 1st cycle of cooling, C2 – 2nd cycle of cooling

Table 3 **Comparison of measured and calculated T_L and T_S**

Source	T_S / °C	T_L / °C	ΔT_S / °C	ΔT_L / °C
Thermal analysis	1 280	1 441	X	X
IND	1 125	1 469	-155	28
IDS	1 319	1 451	39	10
ThermoCalc	1 318	1 453	38	12

441 °C) was imputed as an average of the values obtained in a series of relevant experiments performed by DirTA method.

For practical reasons it is preferable for the T_L as a result of high temperature thermal analysis appropriate to consider higher value, i.e. T_L = 1 441 °C.

When comparing T_S and T_L refined by correctly set methodology of high thermal analysis with computationally specified values, it is possible to state that the real experimentally determined T_S and T_L vary significantly from theoretically computed ones in the case of 100CrMo7 steel grade. The difference between the theoretically calculated values and measured ones is summarized in Table 3.

The most noticeable difference was achieved for studied two temperatures (T_S and T_L) when compared the experimentally determined values with those used in conditions of industrial partner, wherein the difference between the T_S is 155 °C, and T_L is 28 °C. Theoretically calculated temperature (IDS, respectively ThermoCalc) are very close to each other. They varies less than the values given industrial partner from the experimentally determined T_S and T_L, but the differences are not completely negligible (39; 38; resp. 10 and 12 °C). In all cases, significant difference between the T_S than the T_L is reflected.

CONCLUSIONS

The methods of comprehensive verification of solidus and liquidus temperatures of selected 100CrMo7 steel grade were presented in this paper. Acquired knowledge can be summarized as follows:

The two methods used thermal analysis showed a high degree of reproducibility of the results, indicating correct setting of experimental methodology.

The accuracy of the measured T_L highlights their almost identical average value obtained using different methods for very different masses of samples where the difference between them was 1 °C.

For this particular steel grade (100CrMo7), the T_S on the cooling curve of a large sample cannot be identified if a direct thermal analysis is applied. It is underlining the approach taken when multiple methods for determining the T_S and T_L of real steel grades are used.

Utilisation of above described methods of thermal analysis led to determination of solidus (1280 °C) and liquidus (1441 °C) temperatures for 100CrMo7 steel grade.

Measured temperatures differ from the theoretically specified tens to more than 100 °C. Theoretically calculated (IND) T_S is about 155 °C lower than the measured. T_L was then calculated by industrial partner of 28 °C higher than it really is.

The findings suggest that the issue of determining the T_L and T_S requires a comprehensive approach using multiple methods of solution. Larger differences against calculations can be expected especially in the case of special steel with high carbon or alloy elements content. In the final stage, it should be resorted to operational experiments that would allow adjusting its own casting technology, so as to considerable savings, not only in a possible lower temperature of superheating of individual heats. Furthermore, it is appropriate to implement the results to numerical simulations aimed at optimizing the casting process and solidification of the steel, leading to more accurate results corresponding to real conditions.

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