

# Thermodynamic Analysis of Cast Irons Solidification With Various Types of Graphite

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## Abstract

The contribution summarises the results of oxygen activity determinations, which were measured and registered continuously in castings from cast irons with various types of graphite. The results were used to find the relationship between two variables: natural logarithm of oxygen activities and reverse value of thermodynamic temperature  $1/T$ . Obtained regression lines were used to calculate oxygen activity at different temperatures, to calculate Gibbs free energy  $\Delta G$  at the different temperatures and to calculate the single  $\Delta G$  value for significant temperature of the graphite solidification. The results were processed by a statistical analysis of data files for the different types of graphite with flake, vermicular and spheroidal graphite. Each material has its proper typical oxygen activities range and individual temperature function of Gibbs free energy for analysing and governing casting quality.

**Keywords:** Continuous oxygen activity measurement, Calculation of Gibbs free energy, Cast iron solidification

## 1. Introduction

In a recent paper [1], J.G. Sturm and G. Busch have shown that cast iron is a predictable material and they have stated that melting and used metallurgical procedures have a decisive impact on the integrity of the properties of castings. This is especially true for the cast parts with which metallurgical processing is important for the final structure and properties of castings. Except for the graphite, the microstructure of a cast-iron casting contains other components, each of which depends on a different content of carbon, silicon, oxygen, and other present elements. After finishing of solidification, we can encounter the following types of the shape of graphite in castings: flake (lamellar) graphite, vermicular (compacted) graphite and spheroidal (nodular) graphite. There can also come into existence metastable white

structure with eutectic cementite (ledeburite) too. The way of solidification is thus closely connected with chemical composition of the basic cast iron melting, the cooling rate and the way of inoculation and modification.

Inoculation is a typical procedure for the grain refinement and it involves on the introduction of nucleating agents (inoculants) into the melt. The inoculation effect on graphite nucleation in cast irons is based upon the formation of complex non-metallic micro inclusions. The inoculants chemistry usually includes active elements which have high affinity toward oxygen, prospective to sulphur and nitrogen. The necessity of inoculation of different types of irons is determined by the thermodynamic nature of the transfer from liquid to solid state iron - carbon equilibrium diagram which has stable or metastable liquid-solid types of transformations [2].

Modification is in the present paper preferred equivalent for English formulations “graphite spheroidization” or “nodulizing,” (nodulizing treatment, Mg treatment). Modification practice supports the transformation from flake to nodule (spheroidal) shape graphite and in the same time undercools the melt. That is a reason why effective inoculation have to promote the stable austenite-graphite solidification and minimizes any austenite-carbide solidification.

The most useful tools of quality control of the melt are thermal analysis and measurement of the oxygen activity. As stated by [3] and many other authors, a considerable role is played in both processes by oxygen. F. Mampaey [4,5,6] has published recently several papers on this topic. In the first one of them Mampaey [4], on the basis of thermodynamic analysis elaborated measurement of the oxygen activity in the induction furnace at various temperatures. He continued with papers on the utilization of the measurement of oxygen activity for the determination of optimal properties of ductile iron [5] and with cast iron with vermicular graphite [6]. In several previous studies, the authors of the contribution have also dealt with the behavior of oxygen in cast irons and the present contribution utilizes and verifies the results of a continuous measurement of oxygen activities in castings [7,8] into thermodynamic relationships using the thermodynamic equilibrium with the strongest deoxidizing element

## 2. Thermodynamic considerations

Thermodynamic relationships used in measurement of the oxygen activity and in evaluation of the results of this study have been analyzed in detail in many other studies and will be briefly mentioned. These are the above mentioned studies by Mampaey [4,5], T.Elbel and J.Hampl [8,9], the monographs by A.Zadera [10], J.Senberger [11], T.Myslivec [12] and S.Katz [13].

We depart from the fact that the role of oxygen for obtaining of the required graphite structure in cast irons is undisputed. The relation between oxygen in solution and oxygen bound in oxides in the melt can be described by the Nernst ratio for the equilibrium constant  $K_0$  expressed with the help of activities [11].

$$K_0 = \frac{a_o}{a_{MeO}} \quad (1)$$

The relation (1) constitutes the equilibrium between the oxygen in the melt  $a_o$  and the oxygen in oxides  $a_{MeO}$  at constant temperature. The value of the equilibrium activity in the melt according to the reaction (1) is strongly influenced by temperature. The oxygen activity is changing with the reversed value of thermodynamic temperature ( $1/T$ ) according to linear relation:

$$\ln K_0 = -\frac{\Delta G^0}{R \cdot T} \quad (2)$$

In relation (2)  $\Delta G^0$  is a change of the Gibbs free energy in standard state [ $\text{J}\cdot\text{mol}^{-1}$ ],  $T$  – thermodynamic temperature [K] and

$R$  stands for the universal gas constant  $8.314 [\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$ . The equilibrium state is an extreme case where the metallurgical procedures can occur in practice. In real conditions the composition of melts more or less approaches the equilibrium. In a non-equilibrium state, oxygen from the melt can pass into oxide or conversely, oxides can “dissolve” in the melt. With regards to the oxide of the base metal  $\text{MeO}$ , the process of these reactions can be predicted according to the value of the Gibbs free energy between equilibrium and unbalanced state which is given by the equation:

$$\Delta G = -x \cdot RT (\ln a_o^r - \ln a_o^n) \quad (3)$$

Where  $a_o^r$  is an oxygen activity in an equilibrium state and  $a_o^n$  is in unbalanced (real) state. The  $x$  symbol stands for the number of moles of the Me element that enter into the reaction with 1 mole of oxygen. In the case that only one element enters the reaction with the oxygen and the product of the reaction is an oxide, its activity can be considered unit :

$$\Delta G = -x \cdot RT (\ln 1 - \ln a_o^n) = x \cdot RT \cdot \ln a_o^n \quad (4)$$

the content of deoxidizing element in an equilibrium and unbalanced state can be considered identical. For cast irons in a furnace and in a ladle, in the interval of temperature from 1350 to 1400 C, the values of  $\Delta G$  range before inoculation and modification from - 65000 to - 45000  $\text{J}\cdot\text{mol}^{-1}$  [9]. If  $\Delta G$  has a negative value, the reaction will run between oxygen and silicon that will be dissolved in a cast iron. The reaction  $(\text{SiO}_2) = [\text{Si}] + 2 [\text{O}]$ . Then proceeds from the right to the left and the volume of silicon oxide increases in the melt or new crystallization nuclei may appear based on  $\text{SiO}_2$ . With higher temperatures, the deoxidation effect of carbon begins to show and the value of  $\Delta G$  between  $[\text{Si}]$  and  $[\text{O}]$  increases.

As the change of the standard free energy  $\Delta G [\text{J}\cdot\text{mol}^{-1}]$  is dependent on temperature, thermodynamic properties are usually expressed with the help of standard enthalpy  $\Delta H^0 [\text{J}\cdot\text{mol}^{-1}]$  and the entropy  $\Delta S^0 [\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}]$  of formation, according Van 't Hoff equation :

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

in which  $T$  stands for the thermodynamic temperature [K]. To express the free energy according to equation (4) the equation (2) takes the shape:

$$RT \cdot \ln a_o^n = \Delta H^0 - T\Delta S^0 \quad (6)$$

In conclusion, it can be said that measurement of the oxygen activity that controls chemical reactions in the melt can be used for monitoring of changes that these reactions activate. The equation of linear temperature dependency obtained by experimental measurement is often used to do that. It is in the following shape:

$$\ln a_0 = \frac{A}{T} + B \quad (7)$$

Parameters A is the slope of straight line and the B is the intercept have thermodynamic meaning according to the equation in (6). The B constant presents the changes of content of deoxidizing elements (Al, Si, Mg) and activities of the corresponding oxide. Mampaey [6] explains the physical nature of the A coefficient as being proportional to the standard change of enthalpy  $\Delta H^0$ . For the reaction at the constant pressure  $\Delta H^0$  is equal to the heat evolved by the reaction. With the exothermic reaction the value  $\Delta H^0$  is negative. By modification of equations (6) and (7) we obtain the relationship:

$$\Delta G = R(A + B \cdot T) = 8.314(A + BT); [J \cdot mol^{-1}] \quad (8)$$

If we find out the course of the  $\ln a_0$  dependency on the temperature according to equation (6), we can calculate the values of standard enthalpy and entropy from the following equations (9) and (10).

$$A = \Delta H^0 / R \quad (9)$$

$$B = \Delta S^0 / R \quad (10)$$

### 3. Experimental procedures and results

For the study of graphite nucleation in cast irons, several samples of melts of the chemical composition near eutectic were melted in a middle frequency induction crucible with the capacity of 100 kg. The melts was cast in two types of casting: cylinders with a diameter 70 mm and height 105 mm for oxygen activities measurement that is schematically shown in Figure 1 and Y blocks for the tensile strength testing and metallographic analyse. The melt was taped into a small ladle with capacity 20 kg. Inoculation was made with in stream addition of 0.8 % FeSi75. Two modifiers NiMg with 15% Mg and FeSiMg5 as sandwich process were used.

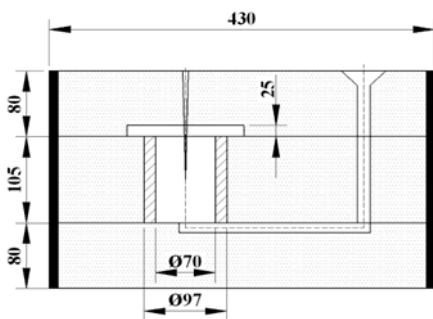


Fig. 1. Test mould for continual determination of oxygen activity in a cylinder casting

The charge for the preparation of the melt consisted of the pig iron with low content of S, return material and steel scrap. From each 100 kg melting, three to five ladles with various level of modification were cast at the same chemical composition in order

to achieve different content of Mg for obtaining cast iron with vermicular or spheroidal graphite. Measurement of oxygen activity was conducted in the mould cavity by laboratory probes placed into thermal axis of cylindrical castings according to Figure 1. The mould was made from bentonite molding mixture. The working surface of the mould cavity itself was made of insulating lining. Oxygen activity was measured continuously from the initial temperature of metal in the mould cavity until the end of solidification, which lasted approximately for 18 minutes. The probe is a sensor composed of solid electrolyte and a reference mixture fixed in a tube from silica glass. The probes were produced by Termosondy Kladno from commercial immersion probes TSO 6 for a single measurement of oxygen activities in furnaces. The contact with the melt was ensured by molybdenum wire. Electromotive force from the sensor was registered with 1 Hz frequency.

Fifteen castings (melts 77 to 79) were cast by using the master alloy NiMg noduliser and there was conducted measurement of oxygen activities in six castings with various content of residual Mg. Another series of ten casts (melts 80 and 81) was cast using the FeSiMg5 noduliser and there were registered oxygen activities in seven castings. One ladle was poured without modification as a cast iron with flake graphite for comparison. The chemical composition of cast iron (main elements) is illustrated in Table 1 and Table 2. In the melt No. 81, the melting was conducted under an Ar protective atmosphere. In the course of the melt, Argon was continually transported on the surface of the melt with the help of a refractory armature placed at crucible of the electric induction furnace.

Out of experimental castings, there were first evaluated records of measurements of oxygen activities depending on time and temperature. The resulting exponential curves were published in our previous study [7] and we assume that it is not necessary to repeat them again. Out of these curved lines, we subtracted values of oxygen activities at various temperatures. For specification of these values and for obtaining of equations that will enable further thermodynamic considerations, these dependencies were transformed according to the equation (6) as the natural logarithm oxygen activity  $\ln a_0$  linear relationship on the reversed value of thermodynamic temperature  $1/T$ . There were obtained very strength relationship with a high coefficient of correlation for all 21 castings. The summary of all regression lines is illustrated in Figure 2.

Coefficients of equation (7) A, B, converted into the form  $y = Ax + B$  are summarized in Table 4. In the first column of Table 4 the determination coefficient is stated. According the ultimate tensile strength and verifying microstructure to individual samples of castings EU standards were appropriated. They are indicated with abbreviations in last column of the same table.

From the data in Table 4 we can calculate the oxygen activities for various temperatures. In Table 5 there are stated the values of calculated oxygen activities for the temperatures of 1400 °C (1673.15 K) and 1300 °C (1573.15 K). Oxygen activities calculated for these two temperatures were put into Table 5 together with the data about the content of the residual Mg in a cast iron, the mean value of ultimate tensile strength, total oxygen content  $O_{OX}$  with the note about the method of preparation of cast iron.

Table 1.  
Chemical composition of the melts 78 and 79

Element (wt.%)		Melting on air – modification by NiMg				
Casting Nr	78/1	78/3	79/1	79/3	79/4	79/5
C	3.63	3.72	3.57	3.6	3.64	3.59
Si	2.67	2.66	2.58	2.51	2.5	2.47
Mn	0.554	0.661	0.516	0.514	0.512	0.515
P	0.105	0.101	0.103	0.102	0.106	0.102
S	0.0111	0.0125	0.0125	0.0119	0.0114	0.0122
Mg	0.016	0.0260	0.0234	0.0265	0.0435	0.031
O <sub>OX</sub> (ppm)	51	28	67	49	16	39

O<sub>ox</sub> total oxygen content

Table 2.  
Chemical composition of the melts 80 and 81

Element (wt.%)		Melting on air				Melting with Ar protection		
Casting Nr.	80/1	80/2	80/3	80/4	81/1	81/2	81/3	
FeSiMg5 (%)	0	0.5	1.0	1.5	0	0.5	1.0	
C	3.57	3.45	3.51	3.66	3.55	3.56	3.65	
Si	1.94	2.19	2.4	2.76	1.4	2.32	2.33	
Mn	0.215	0.219	0.223	0.223	0.187	0.191	0.194	
P	0.0307	0.0324	0.0324	0.0339	0.033	0.0349	0.0343	
S	0.011	0.01	0.01	0.011	0.012	0.011	0.013	
Mg	0	0.009	0.017	0.0382	0	0.0123	0.0181	
O <sub>OX</sub> (ppm)	103	56	42	66	174	84	96	

O<sub>ox</sub> total oxygen content

Table 3.  
Chemical composition of melts 82 and 84

Element (wt.%)		Deoxidation with CO reaction				Argon injection			
Casting Nr	82/1	8/2	82/3	82/4	84/1	84/2	84/3	84/4	
FeSiMg (%)	0	0	0	0	1.0	1.5	1.0	1.5	
C	3.71	3.57	3,34	3,10	3,4	3.37	3.48	3.31	
Si	1.67	1.67	1.66	1.68	2.69	2.72	2.8	2.42	
Mn	0.43	0.436	0.433	0.439	0.347	0.349	0.346	0.346	
P	0.121	0.121	0.119	0.121	0.0672	0.0557	0.0686	0.0658	
S	0.02	0.0198	0.0205	0.0201	0.0169	0.017	0.016	0.016	
Mg	0	0	0	0	0.0209	0.0265	0.0223	0.0227	
O <sub>OX</sub> (ppm)	-	-	-	-	7.6	12.1	6.4	70.3	

O<sub>ox</sub> total oxygen content

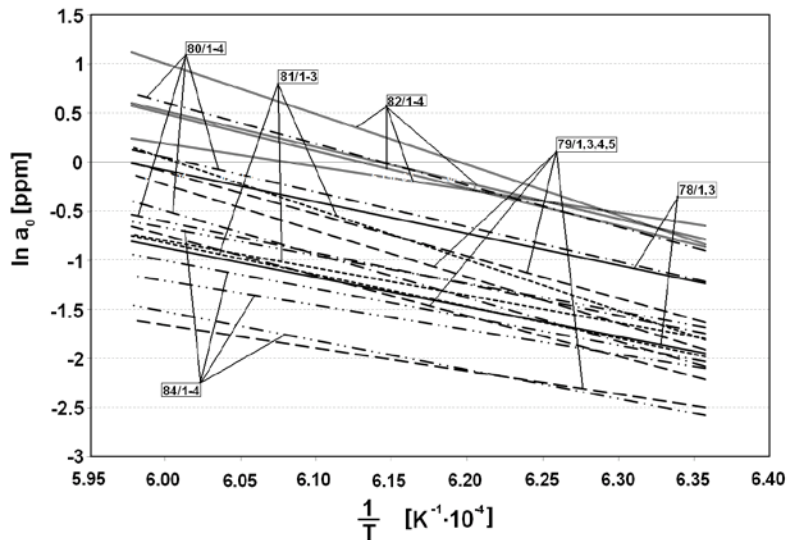


Fig. 2. The transformation of oxygen activity records as the  $\ln a_o$  function on the reversed value of thermodynamic temperature  $1/T$

As the modifying effect does not express only residual content of Mg, but also the content of sulfur and metals of rare earth, the calculated rates of the sulfur surplus indicator according to J.P. Hrusovsky and F. Wallace [14] were added to the table.

$$\Delta S = \% S - 0.34 (\% RE) - 1.34 (\% Mg) \quad (11)$$

In which  $\Delta S$  (%) stands for sulfur surplus in cast iron, % RE stands for the content of rare earth in cast iron and % Mg stands for the residual content of magnesium. The  $\Delta S$  parameter presents mainly the sulfur content minus stoichiometric amount for the production of the  $MgS$  sulphide. This parameter  $\Delta S$  defines the areas of cast irons with flake, vermicular and spheroidal graphite and the authors successfully made use of it in the previous studies [15].

From the Table 5 a regression analysis was conducted between the oxygen activity at the temperatures of 1573.15 and 1673.15 K on the sulfur surplus in ppm. It has been found out that there exists a moderate dependence with the determination coefficient  $R^2 = 0.5175$  and  $0.4475$  which was expected, with regards to the previous study [7]. The results are stated in Figure 3. It has been confirmed that the production of graphite in cast irons is connected to the oxygen activity. Thanks to the dominant reaction of Mg with oxygen, modified cast irons have low oxygen activity, in contrast with cast irons with flake graphite.

For the confirmation of the above mentioned relation, the results of the calculation of oxygen activity have been divided into three groups for particular types of the GJL cast irons – 7 rates, GJV - 5 rates, and GJS 9 rates. In each file, an arithmetic mean and a standard deviation have been calculated. The results are summarized in Table 6 for the oxygen activity at the temperature of 1573.15 K and Table 7 at the temperature of 1673.15 K.

Table 4.

The coefficients of the equation  $y = Ax + B$  ( $y = \ln a_o$ ,  $x = 1/T$ )

Casting	Regression coef. $y = Ax + B$			Cast iron
	A	B	$R^2$	
78/1	-30 055	17.158	0.947	GJV
78/3	-32 160	16,211	0.966	GJV
79/1	-42 953	25.669	0.991	GJV
79/3	-47 089	28.021	0.998	GJV
79/4	-41 025	23,867	0.998	GJS
79/5	-23 331	12,336	0.984	GJS
80/1	-35 265	21,204	0,964	GJL
80/2	-42 276	25.972	0,996	GJL
80/3	-44 293	-26.077	0,996	GJS
80/4	-32 014	18.602	0.934	GJS
81/1	-51 573	30.974	0,923	GJL
81/2	-27 966	15.978	0.985	GJV
81/3	-32 459	18.653	0.980	GJS
82/1	-51 615	31.97	0.928	GJL
82/2	-37 868	23.206	0.990	GJL
82/3	-36 536	22.419	0.995	GJL
82/4	-21 393	14.229	0.984	GJL
84/1	-29 535	16.197	0.993	GJS
84/2	-28 964	13.768	0.991	GJS
84/3	-28 676	16.701	0.983	GJS
84/4	-28 315	16.318	0.928	GJS

Table 5.  
The survey of the principal measured and calculated results

Number of casting	Mg <sub>REZ</sub> content	ΔS ppm	a <sub>0</sub> 1673 K ppb	a <sub>0</sub> 1573 K ppb	ΔG [J·mol <sup>-1</sup> ]	Tensile strength [MPa]	O <sub>OX</sub> [ppm]	Note
78/1	160	-95.15	447	142.7	-11 200	214	51	Modification by NiMg
78/3	260	-216.8	989.8	291.7	-41 870	273	28	
79/1	230	-186.2	997.1	195	-40	260	67	
79/3	270	-233.45	884.3	147.8	-1 700	292	49	
79/4	440	-464.55	520.7	109.6	-9 080	638	16	
79/5	310	-290.3	200.2	82,5	-22 370	504	39	
80/1	0	108.7	1135.4	297.4	1 770	134	103	Modification FeSiMg
80/2	90	-15.7	2023.2	406	1 090	289	56	
80/3	170	-126,1	673.1	125.1	-5 510	404	42	
80/4	382	-497,1	587.4	174.1	-7 400	509	66	
81/1	0	118,7	1162	163.8	2090	180	174	FeSiMg protection with Ar
81/2	123	-53.6	487,7	165.5	-10 280	363	84	
81.3	181	-110.7	473,8	138.1	-6980	417	96	
82/1	0	200	3067,9	431.7	15 590	158	no tests	CO reaction without modification
82/2	0	198	1774	420.9	7 970	181		
82/3	0	205	1826,4	455.8	8100	207		
82/4	0	201	1276,3	524.7	20 170	194		inoculation
84/1	209	-111	231,5	76.4	-20 240	595	7.6	Argon injection
84/2	265	-185.1	305,7	122.4	-49 290	651	7.1	
84/3	203	-138.8	381,6	132	-6090	588	6.1	FeSiMg
84/4	227	-207.2	545,6	185.4	-8 420	460	70.3	

0 – means that Mg was not added

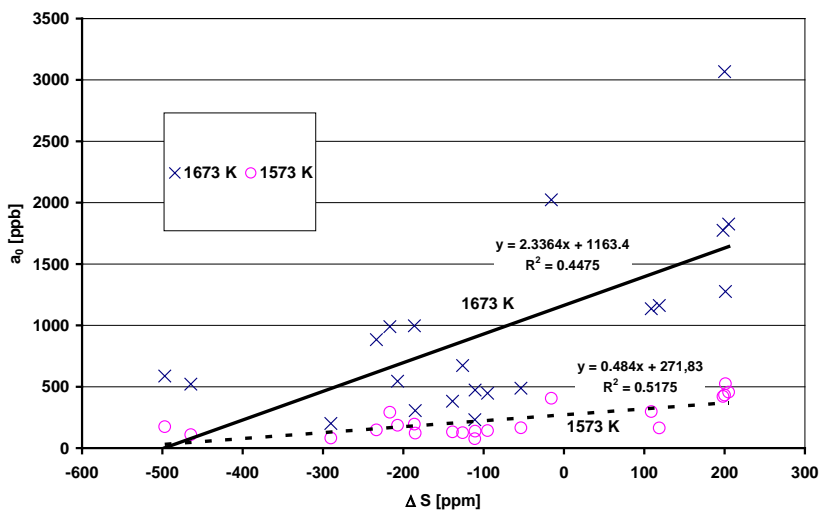


Fig. 3. The oxygen activity (ppb) dependence on the sulfur surplus in ppm

Result of the Table 6 for a summary of the calculated oxygen activities at 1573.15 K were subjected to tests of significance of mean values and variances. With regards to the normality of the distribution, the test was conducted only for the files GJL and GJS. There has been found a significant difference of both sets on the significance level of  $p = 0.05$ . The mean oxygen activity of the

GJV file is located between the two sets tested, however, it is considerably smaller than with GJL and it nears the GJS. The same result of statistically significant difference of oxygen activity was obtained for files of mean values from Table 7, set at the temperature of 1673.15 K.

Table 6.  
Arithmetic means and standard deviations of oxygen activities at 1573.15 K

Oxygen activity at the temperature of 1573.15 K			
Iron	GJL	GJV	GJS
n	7	5	9
$x_M$ [ppb]	385.5	188.5	126.19
s [ppb]	119.6	61.18	36.49

$x_M$  – the arithmetic mean ; s – the standard deviation

Table 7.  
Arithmetic means and standard deviations of oxygen activities at 1673.15 K

Oxygen activity at the temperature of 1673.15 K			
Iron	GJL	GJV	GJS
n	7	5	9
$x_M$ [ppb]	1782.37	761.18	437.97
s [ppb]	661.38	272.3	163.13

$x_M$  – the arithmetic mean; s – the standard deviation

Also from the found out coefficients of A, B regression equation (7) listed in the Table 4 there was conducted a division into three files for each type of cast iron. From the specific values for each of the castings, there could be made calculations of the change of the Gibbs free energy  $\Delta G$  for two temperatures 1573.15 and 1673.15 K, i.e. in the range of metallurgical reactions in cast iron. These data are listed in Tables 8, 9 and 10. The example of calculation for the casting 80/1 at 1573.15 K :

$$\Delta G = R ( A + B.T) = 8.314 ( - 35\,265 + 21.204 \cdot 1573.15) = 15\,862.5 \approx 15\,860 \text{ [J}\cdot\text{mol}^{-1}\text{]}$$

Table 8.  
The calculated values of the free energy change for cast iron with flake graphite at the temperatures of 1573.15 K and 1673,15 K

Casting	Regression coefficients		$\Delta G$	$\Delta G$
	y = Ax + B		1573.15 K	1673.15 K
GJL	A	B	[J·mol <sup>-1</sup> ]	[J·mol <sup>-1</sup> ]
80/1	-35 265	21,204	-15 860	1 770
80/2	-42 276	25.972	-11 790	1 090
81/1	-51 573	30.974	-23 660	2 090
82/1	-51 615	31.97	-10 150	15 590
82/2	-37 868	23.206	-11 320	7 970
82/3	-36 536	22.419	-10 540	8100
82/4	-21 393	14.229	8 240	20 170
$X_{MI}$	-43104	26.03	-17 100	1 650
$X_{PMII}$	-36853	22.95	- 5 942	12 957

$X_{MI}$  the arithmetic mean of castings 80/1, 80/2, 81/1  
 $X_{PMII}$  arithmetic mean of castings 82

Table 9.  
The calculated values of the free energy change for cast iron with vermicular graphite at the temperatures of 1573.15 K and 1673.15 K

Casting	Regression coefficients		$\Delta G$	$\Delta G$
	A	B	1573.15 K	1673.15 K
GJV			[J·mol <sup>-1</sup> ]	[J·mol <sup>-1</sup> ]
78/1	-30 055	17.158	-25 460	-11 200
78/3	-32 160	16.211	-55 350	-41 870
79/1	-42 953	25.669	-21 380	-40
79/3	-47 089	28.021	-25 000	-1 710
81/2	-27 966	15.978	-23 530	-10 280
$X_M$	-38 405	20.6	-30 144	-13 020

$X_M$  the arithmetic mean

For further analysis, let us go back to the coefficient A (the slope) from the equation (7) and break down some of the previously mentioned castings that deviate outside the mean value of the given group of cast irons. The values of coefficients A and B of the Table 8 to 10 were arranged according to the procedures of melting and off furnace treatment.

Table 10.  
The calculated values of the free energy change for cast iron with spheroidal graphite at the temperatures of 1573.15 K and 1673.15 K

Casting	Regression coefficients		$\Delta G$ 1573.15 K	$\Delta G$ 1673.15 K
	y = Ax + B		[J·mol <sup>-1</sup> ]	[J·mol <sup>-1</sup> ]
GJS	A	B	[J·mol <sup>-1</sup> ]	[J·mol <sup>-1</sup> ]
79/4	-41 025	23.867	-28 530	-9 080
79/5	-23 331	12.336	-32 630	-22 370
80/3	-44 293	-26.077	-27 110	-5 506
80/4	-32 014	18.602	-22 870	-7 400
81/3	-32 459	18.653	-25 900	-6 980
84/1	-29 535	16.197	-33 710	-20 240
84/2	-28 964	13.768	-58 490	-49 290
84/3	-28 676	16.701	- 19 980	-6 090
84/4	-28 315	16.318	-21 990	-8 420
$X_{PRI}$	-37 948	21.97	-27 448	-10 267
$X_{PRII}$	- 28 872	15.75	-33 350	-21 118

$X_{MI}$  the arithmetic mean of castings 79/4, 79/5, 80/3, 80/4, 81/3  
 $X_{MII}$  the arithmetic mean of castings 84

Cast iron with flake graphite  
The set was divided into 2 groups 3 castings of 80/1, 80/2, 81/1 prepared by the inoculation of FeSi and castings 82 without inoculation. For the coefficients A and B were added to equation (7) substituted arithmetic mean from these melts. The relationship was thus obtained from the equation (9) calculated relationship :

$\ln a_O = -43\,104/T + 26.03$  ; (castings of 80/1, 80/2, 81/1)  
 $\ln a_O = -36\,853/T + 22.95$  ; (castings 82/1, 82/2, 82/3, 82/4 were not inoculated)

#### Cast iron with vermicular graphite

All 5 castings from Table 9 were evaluated by the same procedure:

$$\ln a_O = -36\,405/T + 20.67$$

#### Cast irons with spheroidal graphite

This set was divided into two groups: four castings from the melt 82 and second set forms 4 remaining castings (without the casting 79/5 was excepted from the evaluation).

$$\ln a_O = -28\,872/T + 15.75$$
 ; 4 castings 84/1,2,3,4  

$$\ln a_O = -37\,948/T + 21.97$$
 . 4 castings 79/4, 80/3, 80/4, 81/3,

It can be said that the slope of the line (7) is the more steeper the more magnesium is added into the melt. This corresponds to the value of  $A = -28\,872$  for the castings processed by injection of the melt by argon, where there was obtained even at the relatively low Mg content the cast iron with spheroidal graphite.

The second set of castings from cast iron with spheroidal graphite processed without Ar injection and with the NiMg modification (two castings) and FeSiMg (one casting) has  $A = -37\,948$  which approaches the mean value of the A coefficient for GJV and even to castings from GJL from the melt processed by a CO reaction and melted under the protective atmosphere of Ar, without inoculation and modification.

A set of three castings of the cast iron with flake graphite had the smallest slope whose melt was processed by the FeSi inoculation. The sample 79/5  $A = -23\,331$  had the lowest slope at all.

The coefficients A were compared with values by Mampaey [5] which were given for common logarithm of oxygen activities. For the comparison with the results presented, the coefficients have been restated for the natural logarithm. Mampaey comments this by the claim that at low temperatures of oxygen activities, equation based on the mean value of  $A = -59\,150$ , which corresponds to heat associated with the formation of MgO. This means that under these conditions all the dissolved oxygen present in the melt, which reacts to formation of the oxide, is the one with the Mg.

On the other hand, when there is dissolved no Mg in the melt  $A = -29\,900$ . This value may be compared with the reaction of formation of  $\text{SiO}_2$ , for which it is stated  $A = -35\,400$ , then reactions for FeO  $A = -17\,250$  and  $A = -35\,400$  for the formation of MnO. Thus, as soon as more FeO is created instead of  $\text{SiO}_2$  less heat is released. This conclusion is in according to Mampaey [6] of important practical implications. The activity of oxygen in the basic melt (without the presence of Mg and other elements with high activity to oxygen) can vary, because the oxygen in solution is different but also because silica activity can vary. The last option is quite likely because the ratio of  $\text{FeO}/\text{SiO}_2$  can vary in the melt within wide limits. Arithmetic mean of  $\Delta G$  from Tables 8 to 10 were plotted into the Table 11 for both temperatures considered yet. From Table 11 we can read that cast irons with flake graphite have the lowest value of  $\Delta G$  as opposed to modified cast irons.

At the temperature of 1573.15 K the change of Gibbs free-energy has the lowest value at GJS II processed by modification of FeSiMg followed by GJV, GJS I, GJL I and GJL II. At higher temperature of 1673.15 K the mean value of the GJS II set is about  $8000\text{ J}\cdot\text{mol}^{-1}$  lesser than the GJV, followed by GJS I, and finally GJL I and GJL II with positive values of  $\Delta G$ . Thus, we can formulate another partial conclusion of the thermodynamic analysis.

We depart from the general thermodynamic condition that the reaction product with the lowest free energy will be the most stable. In our case, it is cast irons modified by Mg i.e., by spheroidal graphite and vermicular graphite. The set of all experimental data, however, contains some anomalies and there is a need to further analyse individual cases, where in the melt, where in addition to changes in the oxygen activity different amounts of oxides are formed. The activity of a dissolved substance [O] in a solvent (cast iron) will be affected by the presence of other solutes.

Table 11.

The calculated  $\Delta G$  values for the three types of cast irons at the temperature of 1573.15 a 1673.15 K

Grade of cast iron	$\Delta G$ [ $\text{J}\cdot\text{mol}^{-1}$ ]		Castings Number
	1573.15 K	1673.15 K	
GJL I	-17 100	1 650	80/1;80/2;83/1
GJL II	-5 942	12 957	82/1,2,3,4
GJV	-30 144	-13 020	78/1,3;79/1,3;81/2
GJS I	-27 448	-10 267	79/4;80/3,4;81/3
GJS II	-33 350	-21 118	84/1,2,3,4

With the help of the calculated values in Table 11, we can express the change in Gibbs free energy  $\Delta G$  as a temperature dependence for particular groups of cast irons and compare them with the equations for the pure components. For the coefficients A and B from equation (7) we will substitute the arithmetic means from the stated melts and castings. From the obtained values, then, according to equation (8) we will calculate the relationship:

#### Cast iron with flake graphite

$$\text{GJL I: } \Delta G = -358\,400 + 216.4 T ; [\text{J}\cdot\text{mol}^{-1}]$$

$$\text{GJL II: } \Delta G = -306\,400 + 190.1 T ; [\text{J}\cdot\text{mol}^{-1}]$$

#### Cast iron with vermicular graphite GJV:

$$\Delta G = -319\,300 + 171.8 T ; [\text{J}\cdot\text{mol}^{-1}]$$

#### Cast iron with spheroidal graphite

$$\text{GJS I: } \Delta G = -315\,500 + 180.9 T ; [\text{J}\cdot\text{mol}^{-1}]$$

$$\text{GJS II: } \Delta G = -240\,000 + 131 T ; [\text{J}\cdot\text{mol}^{-1}]$$

Although the statistical processing of the results of different sets of cast irons allows a generalization of the thermodynamic analysis, it does not give any statement about the individual melts, which must be assessed individually. This approach is beyond the scope of this paper and will be presented in the publications to come.



## 4. Conclusions

This paper summarizes the results of measurements of oxygen activities, which were determined by continuous measurement in castings in cast irons with different graphite type. The results were recorded as the exponential dependence of oxygen activity on the temperature measured from the highest metal temperature in the mould to the solidus temperature.

The exponential relationship were then transformed into the straight line ones in semi-logarithmic scale for the dependent variable of the natural logarithm of the activity of oxygen to the inverted value of the thermodynamic temperature  $1 / T$  (independent variable).

The obtained regression lines with high correlation coefficient were then used to calculate the oxygen activities at different temperatures that confirmed the findings from the literature and the authors' earlier works. Activities of oxygen for sets with flake and spheroidal graphite were statistically significant in the observed heats, while the values of oxygen activity in a group of heats of cast iron with vermicular graphite lie between these two extreme values.

From the obtained regression relationships it was then possible to evaluate the lines from the equation (7), for which, the slope of the line (7) is the more steeper, the more magnesium is added into the melt. From the relation (8) it could then be calculated the Gibbs free energy dependence on temperature and also the specific values of  $\Delta G$  for temperatures  $1300^{\circ}$  and  $1400^{\circ}$  C. In this way we obtained a tool for the evaluation of metallurgical quality of melts in foundries producing complicated sophisticated production such as e.g. centrifugally poured cast iron cylinders designed for rolling mills.

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