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# APPLICATION OF THERMODYNAMIC CALCULATIONS IN THE RESEARCH OF CAST IRONS STRUCTURE

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The contribution summarises the results of application of thermodynamic calculation obtained from oxygen activities measurements in cast irons with various type of graphite microstructure. The results were used to find the relationship between natural logarithm of oxygen activities and reverse value of thermodynamic temperature 1/T. From obtained regression line the calculation of oxygen activities value for significant temperature of molten metal was achieved. Each material has its proper typical oxygen activities range for analysing and controlling graphite quality. Practical implication was successfully tested in a Czech foundry producing centrifugally poured cast iron rolls designed for hot strip mills with spheroidal graphite iron core.

*Key words:* cast, iron, structure, oxygen activity, graphite

## INTRODUCTION

The most useful tools of quality control of the cast iron melts are thermal analysis and measurement of the oxygen activity. Mampaey [1,2] has published several papers on this topic. In the first one of them Mampaey [1] on the basis of thermodynamic analysis elaborated measurement of the oxygen activity in the induction furnace at various temperatures. Thermodynamic access to the study of cast iron solidification was systematically used in the works of Lekakh, Robertson, Loper Jr. [3] and Pirnat, Mrvar, Medved [4]. Thermodynamic considerations used in measurement of the oxygen activity and in evaluation of the results of this study have been analyzed in many other studies in the monographs by Myslivec [5] and Katz [6].

The premise is the fact that the role of oxygen for obtaining of the required graphite structure in cast irons is undisputed. The oxygen activity is changing with the reversed value of thermodynamic temperature (1/T) according to linear relation:

$$\ln K_0 = -\frac{\Delta G^0}{R \cdot T} \tag{1}$$

In relation (1) $\Delta G^0$ is a change of the Gibbs free energy in standard state / J·mol$^{-1}$, T thermodynamic temperature / K and R stands for the universal gas constant 8 314 /J·mol$^{-1}$·K$^{-1}$

$$\Delta G = x \cdot RT \cdot \ln a_0^n \tag{2}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{3}$$

in which T stands for the thermodynamic temperature / K

$$RT \cdot \ln a_0^n = \Delta H^0 - T\Delta S^0 \tag{4}$$

$$\ln a_0 = \frac{A}{T} + B \tag{5}$$

Parameters (A is the slope of straight line and the B is the intercept) have thermodynamic meaning according to the equation in (5).

$$A = \Delta H^0 / R \tag{6}$$

$$B = \Delta S^0 / R \tag{7}$$

## EXPERIMENTAL PROCEDURES

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 melt was cast in two types of casting: cylinders with a diameter 70 mm and height 105 mm for oxygen activities measurement 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 in stream addition of 0,8 % FeSi75. Two modifiers NiMg with 15 % Mg and FeSiMg5 as sandwich process were used. The charge for the preparation of the melt consisted of the pig iron, 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 (GJV) or spheroidal (GJS) graphite. Measurement of oxygen activity was conducted in the mould cavity by laboratory probes placed into thermal axis of cylindrical castings. Oxygen activity was measured continuously from the initial temperature of metal in the mould cavity until

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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.

## RESULTS AND DISCUSSION

Six series of experimental melts with various modifications (nodularization) were made. The measurement of oxygen activities in castings were conducted in castings with various content of residual $Mg_{res.}$ and for compare some castings poured without modification as a cast iron with flake graphite. Resulting exponential dependencies (in the form of exponential curves) of oxygen activity on temperature from 21 castings were then transformed according to the equation (5) to the linear relationship of natural logarithm of oxygen activity ln $a_O$ 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 1. From coefficients of equation (5) A, B, converted into the form y = Ax + B were calculated the oxygen activities for various temperatures. The results of calculated oxygen activities for two temperatures 1 400 °C (1 673,15 K) and 1 300°C (1 573,15 K) were published in our previous work [7].

After categorization of castings according to the microstructure and tensile strength in 5 groups (below mentioned) we can calculated for each of the groups mean values of oxygen activities. Results of the calculation summarises the Table 1.The survey of groups:

– GJL I - castings 80/1, 80/2, 81/1
– GJL II - castings 82 Melt 82 – without inoculation+ application of CO reaction in crucible
– GJV- castings78/1, 78/3, 79/1, 79/3, 81/2
– GJS I - castings 79/4, 79/5, 80/3, 80/4, 81/3

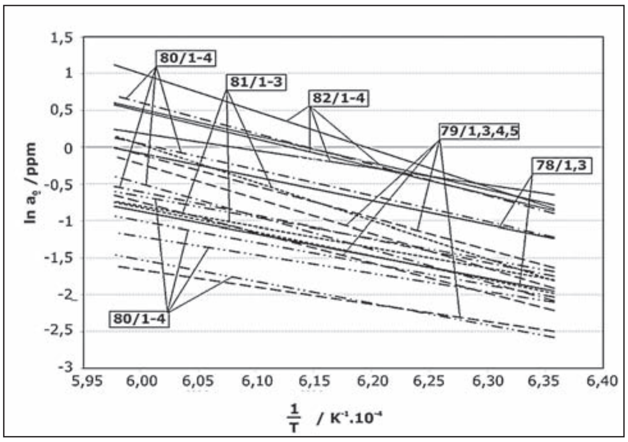


**Figure 1** The transformation of oxygen activity records as the ln $a_O$ function on the reversed value of thermodynamic temperature 1/T

Table 1 **Arithmetic means of oxygen activities in 5 groups of casting with different type of graphite at temperatures of 1 573,15 and 1 673,15 K**

| $a_O$ /ppb at 1 573,15 K | | | | | |
|---|---|---|---|---|---|
| Iron | GJL I | GJL II | GJV | GJS I | GJS II |
| n | 3 | 4 | 5 | 5 | 4 |
| $X_M$ | 250 | 458 | 188,5 | 125,9 | 129 |
| $a_O$ /ppb at 1 673,15 K | | | | | |
| n | 3 | 4 | 5 | 5 | 4 |
| $X_M$ | 909 | 1 276 | 761,2 | 491 | 366,1 |
| $X_M$ the arithmetic mean; n – the number of dates | | | | | |

– GJS II - castings 84 Inoculation 0,8 % FeSi75 + Modification FeSiMg5 and argon injection with refractory armature in the bottom of crucible.

Note: In melts 78, 79 and 80 metal was treated in ladle with different addition of Mg master alloy the casting 80/1 was poured without Mg as reference flake graphite (GJL) piece. Melt 81 Inoculation 0,8 % FeSi75 + modification FeSiMg5 + protection of the bath surface in crucible surface with argon. Although the statistical processing of the results of different sets of cast irons allows a generalization of the oxygen activities values, it does not give any statement about the individual melts, which must be assessed separately. It should be taken in consideration in the following part with industrial application.

Table 2 **The calculated mean values regressions coefficients for cast iron with different graphite shape at the temperatures of 1 573,15 K and 1 673,15 K**

| Casting | Regression coefficients y = Ax + B | |
|---|---|---|
| GJL | A | B |
| $X_M$ GJL I | -43 104 | 26,03 |
| $X_M$ GJL II | -36 853 | 22,95 |
| GJV | A | B |
| $X_M$ | -38 405 | 20,6 |
| GJS | A | B |
| $X_M$ GJS I | -37 948 | 21,97 |
| $X_M$ GJS II | -28 872 | 15,75 |

$X_M$ the arithmetic mean of castings

Coefficients A and B from Table 2 were added to equation (5) and it was thus obtained characteristic relationship for ln aO of both group of castings:

EN GJL I

$$\ln a_O = -43\,104/T + 26{,}03; \quad (8)$$

ENGJL II

$$\ln a_O = -36\,853/T + 22{,}95; \quad (9)$$

EN GJV

$$\ln a_O = -36\,405/T + 20{,}67 \quad (10)$$

EN GJS I

$$\ln a_O = -28\,872/T + 15{,}75;$$

EN GJS II (11)

$$\ln a_O = -37\,948/T + 21{,}97; \quad (12)$$

The oxygen activity depends always on temperature. As we want compare results of different influences on oxygen activity in melts we have to compare various values at same temperature. The equation (8 to 12) makes possible calculation of oxygen activity at the selected temperature e.g. 1 573,15 K or 1 673,15 K like it was above shown.

## APPLICATION OF RESULTS IN A FOUNDRY PLANT

The calculation of the thermodynamic activity of oxygen in cast iron with spheroidal graphite was tested after inoculation and modification at temperatures of 1 400 °C (1 673,15 K) and 1 300 °C (1 573,15 K). The values of the oxygen activities of cast irons recorded in laboratory tests correspond to the calculated activities. The deviations found out between laboratory results and measured values in foundry plant are caused by the difference of used sensors, methods of measurement in castings and in the ladle. Important role plays the difference of chemical composition of materials used in laboratory conditions and in foundry plant too. An accurate measurement of the oxygen activity is implemented in the production of spheroidal graphite cast iron foundry of centrifugally cast rolls in operational melts. For the measurement, the Multi-Lab Celox-III-Foundry from Heraeus Electronite was used with highly sensitive probes developed for the measurement in the cast iron. The device recalculates the oxygen activity of the resulting $a_{O/1\ 420°C}$ (ppb) measured at different temperatures. It is always the same for the reference temperature of 1 420 °C (1 693,15 K). The measurement results are displayed within 20 seconds in the display device, including the data on temperature measurement and electromotive force of measuring probes. The value of assets $a_{O/1420°C}$ obtained in real time allowed to focus on evaluating the quality of metallurgical processing of cast iron during modifications and thus it predicts the quality of the stage before pouring metal into a mould. The oxygen activities were recorded during melting of the charge in the electric induction furnace (EIF), in particular in the course of the modification and of standing after modification of cast iron in the ladle. A brief description of the production of spheroidal graphite cast iron melts No 1-5, and of casting the metal to the mould is recorded in Table 3 When processing GJS were measured oxygen activity (and) from the melting of the EIP and during standing cast iron after the modification and inoculetion. The weight of the processed iron was in the range form 7,6 – 16,8 tons. The GJS modification was performed by two techniques:

a) Core wire injection (CW) filled with pure Mg (melts 1, 2).
b) Sandwich modification (SM) using NiMg master alloy (melts 3, 4, 5).

The metallurgical quality of the ladle treatment of ductile iron was expressed as relationship of oxygen activity value at 1 420 °C on the residual magnesium content ($Mg_{res.}$) before pouring cast iron in the mould (see

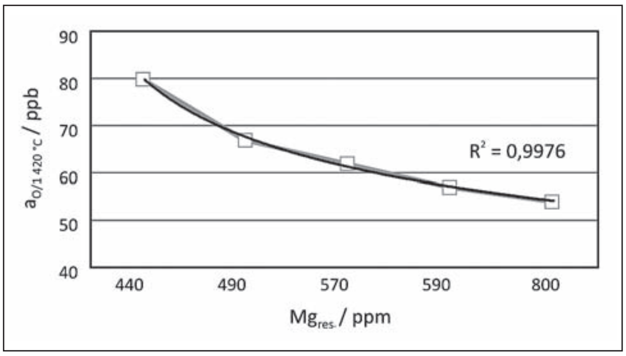


**Figure 2** Relationship between oxygen activity $a_O$ on $Mg_{res}$ for melts 1 – 5

Figure 2). The decrease of the modifying effect of magnesium after the performed modification, measured at five minute intervals is expressed by the growth of oxygen activity aO 1 420 °C during the standing time of the melt in the ladle. In the last measurement of oxygen activity aO/1420 °C the residual Mgres. was evaluated. The correlation of aO and Mgres. (Figure 2) shows a high determination coefficient $R^2 = 0,998$.

The data in Table 3 shows that the highest modifying effect was observed in the melting No 3 with the lowest $a_O$/1 420 °C and the highest one Mgres. = 0,800 ppm.

Table 3 **Results of oxygen activities measurement in melts 1-5, residual Mg content $Mg_{res.}$, weight of melt by different modification method**

| Modification method | Oxygen activities $a_{O/1\ 420}$ °C /ppb | | | | | $Mg_{res.}$ /ppm |
|---|---|---|---|---|---|---|
| | EIF after melting | EIF after alloying | Ladle after modification 5 min | Ladle after 10 min | Ladle after 15 min | |
| 1 CW | 1 412 | 762 | - | - | 62,0 | 570 |
| 2 CW | - | - | 56,3 | 58,5 | 66,9 | 490 |
| 3 CW | - | 1 073 | 51,0 | 53,2 | 54,0 | 800 |
| 4 SM | 1 270 | 764 | 62,3 | 78,6 | 79,5 | 440 |
| 5 SM | 1 220 | 1 037 | 56,9 | 58,8 | 62,9 | 500 |

The GJS produced in this way had the highest metallurgical quality (nodules). Conversely, the lowest melting metallurgical quality was observed in melting No.4, which was characterized by the highest value aO/1420°C = 79,5 ppb at by the lowest Mgres. = 440 ppm.

## CONCLUSIONS

Thermodynamic processing of the results allows the evaluation of stability of metallurgical reactions, which make the decisions of the final cast iron quality. For each of the three types investigated cast irons (EN GJL, GJV and GJS) there are characteristic ranges of values of oxygen activities. In this way we obtain an important instrument for the evaluation of metallurgical quality of cast iron with different shape of graphite, which are created by different metallurgical procedures. In foundries producing complicated and sophisticated production such as parts from centrifugally poured cast iron cylinders designed for rolling mills can extend its tools for estimation of metallurgical quality of molten metal with the measurement of oxygen activity.

On the basis of the evaluation of the operating melts it can be concluded that the measurement of oxygen activity during the metallurgical processing of spheroidal cast iron allows real-time control of the level of the quality of the modification performed after inoculation.

## Acknowledgements

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**Note:** The responsible translator for English language is lecturer from University of Žilina, Slovak Republic.