Archives
of Materials Science
and Engineering

Volume 33
Issue 2
October 2008
Pages 111-116

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

Behaviour of oxygen in cast irons

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Received 16.06.2008; published in revised form 01.10.2008

ABSTRACT

Purpose: Cast irons are the basic structural material and they form 75% of the world production of castings. The crystallization of cast iron and the formation of graphite are a complex process influencing by oxygen. The aim of our study is to identify the role of oxygen in Fe-C-Si melts.

Design/methodology/approach: Continuous comparison of changes in metal composition and oxygen activity during melting, pouring, and solidification of experimental castings, using metallographic methods and microanalysis. Determination of total oxygen content in cast iron by the high temperature extraction method.

Findings: Oxygen activity in graphitic cast irons is determined during manufacture of liquid metal and its pouring mainly by carbon and silicon activities. Silicon deoxidates cast irons at lower temperatures, at higher temperatures this function is taken over by carbon. Logarithmic dependences of oxygen activity on temperature for individual graphite forms (lamellar, vermicular, and spheroidal ones) have been obtained. Determination of total oxygen content in cast iron on the other hand gives valuable information for controlling surface and internal quality of cast irons.

Practical implications: Possibility of control the cast iron structure and graphitization during crystallization by monitoring the oxygen content with an indirect method of oxygen activity measurement in the melt before metal pouring the mould.

Originality/value: The used method gives reproducible results which are comparable under different conditions of metal melting and pouring. Obtained knowledge extends the understanding in the field of cast irons crystallization by less known influence of oxygen.

Keywords: Casting; Oxygen; Cast iron; Graphite morphology

MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Alloys of Fe with carbon, silicon and other elements, in the course of whose solidification and crystallization graphite precipitates from the melt are called cast irons. Cast irons are the basic structural material and they form 75% of the world production of cast raw products of all metals and alloys. Graphite is the crystalline form of carbon and it crystallizes in the hexagonal system with lattice parameters of 0.246 and 0.070 nm. Depending on the shape of graphite precipitated from the melt during crystallization we distinguish three basic kinds of cast iron (marked with abbreviation in accordance with the European standard [1]):

- cast irons with lamellar graphite (GJL for short),
- cast irons with vermicular graphite (GJV for short),
- cast irons with spheroidal graphite (GJS for short).

The crystallization of cast iron and the formation of graphite are a complex process made up of the primary phase crystallization and the eutectic phase crystallization. Eutectic crystallization is not a continuation of primary crystallization: it is a separate process which is however influenced by primary crystallization. According to M. Lampic [2] in melts containing Fe-C-Si-O-X and other elements the crystallization of graphite proceeds at different rates. The highest rate is for lamellar graphite and the lowest for spheroidal graphite. Under otherwise identical conditions GJS will thus crystallize much more slowly than GJL. In lamellar graphite irons the crystallization nucleus of graphite is based on silicon dioxide as the product of the deoxidation reaction:

$$\left(\mathrm{SiO_2}\right) \leftrightarrow \left[\mathrm{Si}\right] + 2\left[\mathrm{O}\right] \tag{1}$$

Reaction (1) is probably the most important reaction in cast iron metallurgy [3, 4]. In GIS, however, in which the melt is treated with magnesium, which deoxidizes the melt with an initial oxygen content of 5 to 10 ppm, the role of a silicate-based nucleus is a bit disputable. But since cast irons with lamellar and spheroidal graphite yield similar results if treated with identical inoculants, a similar inoculation process was formerly assumed for both types of cast iron.

The role of oxygen in the processing of cast irons and in obtaining the required structure, i.e. deoxidation and possible re-oxidation of the melt, is indisputable. In the formation of GJS and GJV two successive steps are important, which are characterized by the reactions given below. First it is the addition of Mg to the melt, according to the strong deoxidation equation (2) and then desulphurization (3):

$$\left[\mathrm{FeO}\right] + \left\{\mathrm{Mg}\right\} \rightarrow \left(\mathrm{MgO}\right) + \left[\mathrm{Fe}\right] \tag{2}$$

$$\left[\mathrm{FeS}\right] + \left\{\mathrm{Mg}\right\} \rightarrow \left(\mathrm{MgS}\right) + \left[\mathrm{Fe}\right] \tag{3}$$

$$\left\{\mathrm{Mg}\right\} \rightarrow \left[\mathrm{Mg}\right] \tag{4}$$

Reaction (4) represents the dissolution of a certain amount of metallic magnesium in the metal affecting the shape of graphite (it is called modification). To ensure a sufficient amount of crystallization nuclei, the inoculation agent, mostly based on FeSi, is then added, which may contain some of the elements Ca, Ce, Al, Ba, and Sr or their combination. Some experts also attach importance to the desulphurization and deoxidation effects of these elements, and they recommend adding them to the melt prior to the modification.

Oxygen can be present in the melt in two forms – either as an element dissolved in the matrix or in the form of a chemical compound. In addition to the assumed effect on graphite morphology as given above, oxygen in solution also affects the surface tension and running property of the metal. Up to now, these relations have not been exactly described mathematically. It is not possible to establish directly the content of oxygen dissolved in cast iron but using special probes it is possible to establish the activity of oxygen [7, 8]. In the melt are oxides that are directly related to heterogeneous nucleation centres and metal re-oxidation when the melt is flowing while being poured into the mould [9, 10]. Oxidic scum is formed in microvolumes of graphite particles. They can be identified using a scanning electron microscope . Oxidic inclusions can also occur on a macroscopic scale and thus affect both the surface quality and inner quality of semi-finished cast products [9].

The authors of the contribution have worked out a methodology of continuous measurement of oxygen activity during metal cooling and thus they have gained information about oxygen behaviour in carbon saturated iron alloys under temperature of eutectic transformation unpublished in literature up to now. Measurement results give a new view on oxygen behaviour at the beginning of cast iron crystallization [8]. Oxygen activity is also strongly dependent on temperature. Equilibrium values of oxygen activity calculated from available data for solidification temperatures of carbon-saturated Fe alloys are in the order of 10^{-7} to 10^{-8}. Such low oxygen activities are not taken into consideration in the theories about the role of oxygen in eutectic reactions. However, in our experiments [8, 9] low oxygen activities corresponding to the equilibrium values were confirmed. Differences between oxygen activities were recorded for three kinds of cast iron at a temperature of 1350ºC: 0.97ppm[6] for GJLI, 0.30 ppm for GJV, and 0.16 ppm for GJS. This fact is due to the equilibrium of chemical reaction (1), which changes with the temperature. These results are in agreement with the findings of Lekaly [5], Mampaey [6, 10] and Hummer [7, 11].

2. Experimental methodology

The research was aimed at determination of both total chemically bonded oxygen, and oxygen activity too. For determination of total oxygen content the method of high temperature extraction on the LECO apparatus was used. Samples for analysis were prepared by turning from melting samples taken from the ladle or from casting cut-outs after passing the melt through the foundry sand mould.

Oxygen activity was measured on the one hand with TSO probes made by the firm Termosondy Kladno, and on the other with so called oxygen sensors (gauges) developed from the TSO probes. The measurement principle and the used probes were published in previous contributions [8, 9] and they will not be described here again. The sensor is formed by solid ZrO_2 electrolyte stabilized with MgO with Cr_2O_3+Cr reference mixture. Molybdenum wire formed the contact with the bath and the line from the reference mixture. Temperature was measured with a Pt-PtRh10 thermocouple. Oxygen activity was calculated from the measured voltage on the concentration cell and from temperature. Oxygen activity was measured on the one hand in induction furnace and on the other in moulds after casting. All cast iron types were measured in inoculated and non-inoculated state. Most of measurements were done on test castings of cylindrical form weighing 15 kg. In all cases the mould was made from green bentonite moulding mixture. Cast iron for preparation of GJV and GJS was modified in mould or in ladle with Bjomet 5 modifier. For inoculation in a gating system a filter was placed on which inoculation particles based on Si with addition of 1 up to 2 % Ca, Al, Ba, Ce were put as required (inoculants of the trade name OPTIGRAN were used). Measurement started from the contact of the sensor with the melt after filling the mould and it lasted till achieving the eutectic temperature. Inductance voltage scanning of the sensor and the thermocouple lasted about 30 minutes.

3. Results

3.1. Determination of total oxygen content

Total oxygen content was determined in conditions of melts on furnaces in foundries and in a laboratory shop.

First set of melts was studied on a cupola furnace supplying liquid metal for casting of engine blocks. Besides total oxygen content the hydrogen and nitrogen contents were determined too in studied melts. Samples were taken from the cupola forehearth, from the ladle after inoculation, and from the ladle after cast iron alloying with Cu. Results are given in Tab. 1. The Table gives calculation of arithmetic average and of standard deviation. Oxygen content after melting in the cupola doesn't differ too much from values determined after inoculation and in next operation after alloying with Cu. Values of 50 up to 60 ppm are lower than that ones given by Mampaey (70 up to 150 ppm) [6]. Nevertheless in castings in which gas cavities combined with shrinkage cavities occurred, the oxygen values of 140 up to 160 ppm were measured.

Nitrogen contents are higher than oxygen ones but they correspond to literary data. Hydrogen contents in some cases were above 5 ppm what is considered a critical value for the formation of blow holes and shrinkage cavities in castings and in such cases the casting were also refused for the reason of those defects.

Next set relates to melting of spheroidal graphite cast iron for crankshafts in an electric arc furnace. Hydrogen, oxygen, and nitrogen contents were determined again. Results are given in Tab. 2. It can be seen that after melting there is high total oxygen content that decreased in next phases after decarburization and after modification with Mg it increased again almost double what confirms the well known fact of oxides formation during that out-of furnace treatment of cast iron.

Cast iron with vermicular graphite melted in a 40 kg electric induction furnace was further on studied. The matter was two sets of melts for which the pinholes formation in castings cast after cast iron modification with magnesium in ladle and in mould was examined [12]. In that case the oxygen and nitrogen analyses were done on samples cut out from castings. Results are summarized in Table 3.

Very low nitrogen contents were determined here but oxygen content was higher than expected from the melt treated in induction furnace (30 up to 80 ppm according to Mampaey [6]). Arithmetic average is influenced by high values found out in melts with higher titanium content of 140 up to 200 ppm [12]. If those values would be excluded from the set the arithmetic averages will range about 40 ppm. It is interesting that the arithmetic average of total oxygen content for the set of melts treated with Mg in ladle is higher than in case of in mould modification what confirms to a certain extent the differences in pinholes occurrence in castings that is higher one just in castings from cast iron modified in ladle.

Use of data from determination of total oxygen suggests certain anomalies in metallurgy of cast iron melting and treatment but it doesn't cover the physical and chemical basis of studied phenomena. Oxygen not bonded on oxides but solved in the melt is only involved in reactions with deoxidation elements. In cast irons it is necessary to take into account the oxygen activity. For that reason in chosen melts the oxygen activity was measured with parallel determination of total oxygen content in castings. That checking is given in Table 4.

From analyses made on several samples from three cast iron kinds no coherence between total content of fixed oxygen and oxygen activity measured in the temperature zone of cast iron liquidus can be found out.

Nevertheless it is turning out that the determination of total oxygen content in cast irons, similarly as in steel, has its importance for quality control of castings because the deviations from standard values specified in operating schedules indicate a possibility of gas defects formation in castings and of shrinkage cavities or shrinkage porosity too. Present modern spectrometric apparatuses [13] enable to determine total oxygen content during operation on line and in such a way it is possible to take quick measures for changes in technological process.

Table 1.
Content of gases in cast iron from cupola and after consequent out-of furnace treatment

Statistics	Drawing from cupola forehearth			Drawing from ladle after inoculation			Drawing from ladle after alloying		
	H_2	O_2	N_2	H_2	O_2	N_2	H_2	O_2	N_2
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
N	8	8	8	7	8	8	8	5	5
x	3.047	43.5	62.25	3.33	45	48.37	4.432	45.6	58.6
s_x	0.636	6.144	3.67	1.3	10.87	17	3.17	8.357	3.411

N – number of values, x – arithmetic average, s_x – standard deviation

Table 2.
Content of gases in GJS melted in an electric arc furnace

Sample No	Content of gases [ppm]			Note
	H_2	O_2	N_2	
TL1	-	377	43	After melting
TL2	4.3	51	71	After carburization
TL3	5.6	35	31	Before tapping
TL4	3.1	69	34	After modification

Table 3.
Content of gases in castings from GJV melted in an induction furnace

Statistics	Modification in ladle		Modification in mould	
	O_2 ppm	N_2 ppm	O_2 ppm	N_2 ppm
N	5	5	9	9
X	114.8	26.4	86.22	18.66
s_x	66.1	9.05	11.78	13.515

N – number of values, x – arithmetic average, s_x – standard deviation

Table 4.
Comparison of total oxygen content with oxygen activity in cast iron samples

Melt	Total O_2 content	O_2 activity	Temperature
No	ppm	ppm	
22	P	O	1200°C
GJL	1500	0.505	
25	P	O	1320°C
GJS	78.6	0.325	
61	O	O	1200°C
GJV	30	0.0257	
62	O	O	1200°C
GJV	55	0.144	
63	O	O	1200°C
GJV	35	0.1155	

Explanatory notes: P – sample drawing from ladle. O – drawing (measurement) in casting

3.2. Oxygen activity determination

Oxygen activity in cast irons is most frequently measured within the range of 1350 up to 1450°C. Measured values are hardly comparable in this temperature range as the influence of temperature on the measured value of oxygen activity is considerable. Basic statistical characteristics of measured oxygen activities during cooling in moulds have been obtained from melts done in our previous works [8, 9]. Those characteristics of oxygen activity for chosen temperatures of 1180 and 1200°C and then always for each 50 °C up to temperature of 1400°C are given in Table 5.

Fig. 1. graphs mean values of oxygen activities taken from Tab. 5. in dependence on inverse value of temperature. Regression lines based on the van´t Hoff reaction isotherm can be drawn through those points. Thus it is possible to obtain logarithmic dependences of oxygen activity on temperature for individual graphite forms. Figures of structures (unetched, magnification 100x) are attached to it with corresponding graphite morphology.

Based on measured data the regression functions were calculated in the form (5)

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

Table 5.
Oxygen activity values /x/ in cast irons (ppm) in dependence on temperature and graphite form

Temperature	Lamellar graphite			Compact graphite			Spheroidal graphite		
[°C]	N	x	s_x	N	x	s_x	N	x	s_x
1400	7	1.480	0.181	-	-	-	-	-	-
1350	9	0.966	0.151	7	0.304	0.117	5	0.156	0.037
1300	9	0.621	0.159	8	0.164	0.056	3	0.081	0.009
1250	12	0.254	0.139	10	0.075	0.023	12	0.038	0.024
1200	9	0.090	0.056	10	0.042	0.021	16	0.024	0.023
1180	7	0.096	0.084	5	0.033	0.017	16	0.021	0.020

N – number of values, x – arithmetic average, s_x – standard deviation

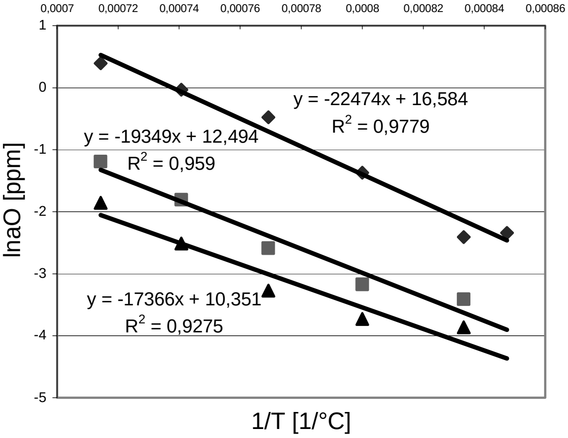

Fig. 1. Dependence of oxygen activity on inverse temperature value

For lamellar graphite cast iron for expressing the oxygen activity a function has been obtained in a form as follows (Fig. 2):

$$\ln a_O = -\frac{22474}{T} + 16.584 \tag{6}$$

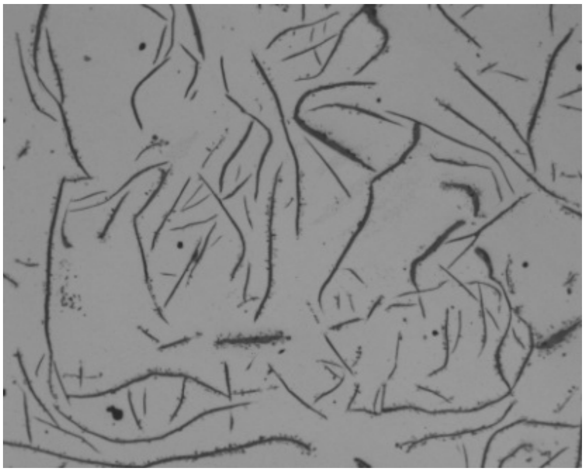

Fig. 2. Lamellar graphite cast iron

For vermicular graphite cast iron it is valid as follows (Fig. 3):

$$\ln a_O = -\frac{19349}{T} + 12.494 \tag{7}$$

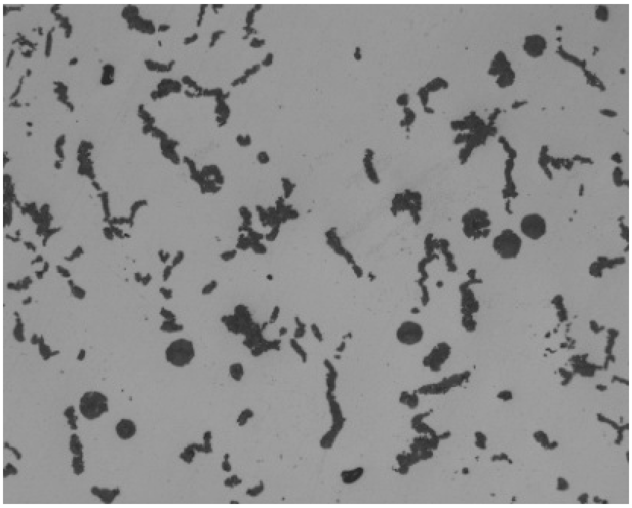

Fig. 3. Vermicular graphite cast iron

For spheroidal graphite cast iron it is valid as follows (Fig. 4):

$$\ln a_O = -\frac{17366}{T} + 10.351 \tag{8}$$

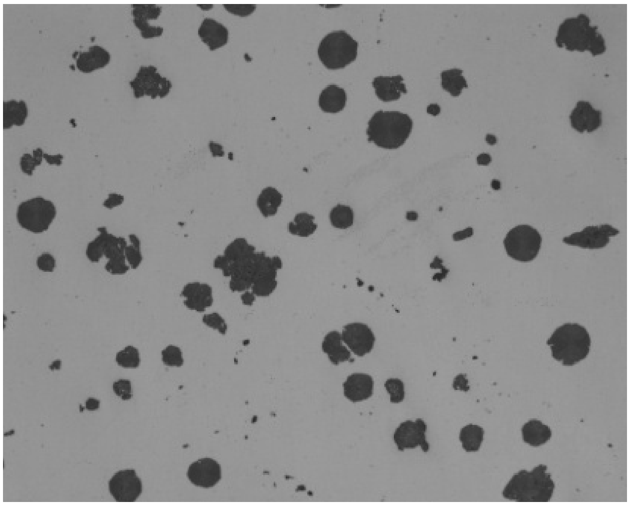

Fig. 4. Spheroidal graphite cast iron

Obtained equations of temperature dependence of oxygen activity (6) up to (8) are derived for temperature in degrees of Celsius with resulting oxygen activity in ppm values.

The A coefficient in the equation (5) has the meaning of a thermodynamic function (9) and the B coefficient has the meaning of a function (10):

$$A = \frac{\Delta H^\circ}{R} \tag{9}$$

$$B = \frac{\Delta S^\circ}{R} \tag{10}$$

in which ΔH° is a standard enthalpy change, ΔS° is a standard entropy change and R is a universal gas constant (R=8.314 J.mol^{-1}.K^{-1}).

Thus the oxygen activity and graphite morphology relations have been indirectly obtained. Based on them it is possible to add Mg in the basic melt for the formation of spheroidal or vermicular graphite and at the same time to purposely control and influence oxygen activity in the melt.

4. Conclusions

Oxygen activities measured under liquidus temperature are unusually extrapolated with the aid of equations (5) and (7) for temperatures of 1400 up to 1500°C and very good coincidence with oxygen activity measurement in the work [14] has been obtained. All values of oxygen activity measurement from the mentioned work for cast irons after modification with magnesium were within the range determined with equations (7) and (8). With oxygen activities given by Mampaey [6] the coincidence for lamellar graphite cast iron has been obtained in the temperature zone of 1450°C. For spheroidal graphite cast irons Mampaey [14] gives higher oxygen activity values than the authors and the work [15] too. Measurements made by this work's authors show the highest coincidence with equilibrium oxygen activities for given chemical composition.

Use of sensors for continuous measurement of oxygen activity in melting units and in moulds is an original method by this work's authors and it will continue to be used for study of oxygen influence on graphite morphology.

Determination of total oxygen content in cast irons can suitably complete the oxygen activity measurement and in operating conditions it can give data for control of surface and internal quality of castings.

Acknowledgements

The work was realized with financial support of the Grant Agency of the Czech Republic in the framework of the project of the registration number 106/08/0789.

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