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State of the art of metal reoxidation study of iron castings

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ABSTRACT

Purpose: Metal reoxidation causes a number of iron castings defects, particularly when pouring them in green-sand moulds. One of them is pinholes the occurrence of which is explained by several hypotheses. One of possible causes is reoxidation processes in the foundry mould cavity. During its flowing in the gating system and in the mould cavity the liquid metal gets into contact with oxygen from air and water vapour. Secondary oxidation of elements takes place in sequence of their affinity to oxygen.

Design/methodology/approach: Therefore the authors were aimed at cast irons. Besides indirect methods the reoxidation was researched mainly by direct measurement of oxygen activity during filling of a mould up to solidus temperature.

Findings: The use of oxygen activity measurement for direct study of changes caused by reoxidation processes is limited and that it is more suitable for study of the influence of different factors on cast iron crystallization and graphite morphology.

Practical implications: Obtained results have confirmed that oxygen activity measurement can serve to the casting quality control. But it is little sensitive for explanation of processes running in a cavity during metal casting.

Originality/value: Continuous monitoring of oxygen activity changes in a foundry mould is an original solution since other authors have done their measurements only in a furnace with disposable sensors.

Keywords: Metallic alloys; Metal reoxidation; Oxygen activity measurement; Iron casting

MATERIALS

1. Introduction

Reoxidation is a concomitant effect of metal and alloy casting processes when thin oxide layers of basic metal or its alloyed and accompanying elements are formed on surface of flowing metal in sequence of their affinity to oxygen. Formation of surface films and oxidic skins in flowing metal and diffuse processes have a great import for reoxidation processes. J. Campbell [1] has explained those effects in an excellent way. Oxygen can be present in iron alloys in two forms: either as a dissolved element or bound to oxide. Besides formation of different defects in steel or iron castings the oxygen in solution influences also graphite morphology in cast irons. Direct determination of oxygen content solved in metal is not possible but with the aid of special probes the oxygen activity can be determined [2, 3]. Oxygen activity is strongly dependent on temperature and it decreases with falling temperature. The cause of that fact can be found in probably the most important chemical reaction in cast iron metallurgy (1) the equilibrium of which changes with temperature.

$$(SiO_2) + [C] \leftrightarrow [Si] + 2\ \{CO\} \tag{1}$$

Under higher temperature it shifts to left, silicon and oxygen are less compounded and thus more active oxygen is formed in cast iron melt.

Metal reoxidation can be studied in 4 ways:

- Study of changes of metal chemical composition
- Monitoring the occurrence and composition of inclusions in metal
- Analysis of casting defects
- Monitoring the changes of oxygen activity in metal

First three methods can be considered the indirect ones because they study the reoxidation consequences after casting solidification and cooling. The fourth method enables direct study of metal changes running particularly during its secondary oxidation, and namely by means of the oxygen activity changes. Monitoring the changes of metal chemical composition was used by authors of the above mentioned work [2] for the research of reoxidation in steel castings, but for iron castings it is not suitable. Another method of searching the inclusions in metal and mould, as well as the analysis of pinholes in castings was used by many authors when solving the nonconforming products in foundries [4, 5, 6].

Oxygen activity measurement was originally developed for steel quality control and it became a current checking method in steel plants. In foundry industry the research was aimed at utilization of this method for iron castings and in particular for the grades with compacted and spheroidal graphite.

Hummer [7], Hecht [8], Mampaey [3, 9] and Ghorpade [10] studied the oxygen activity in a furnace before casting and they have stated that the measured values can be used for prediction of graphite morphology in cast iron and/or in its metallurgical grade too. Results of oxygen activity measurements by Hummer, Hecht, and Mampaey were obtained with the use of commercial foundry sensors and equipment of the firm Heraeus Electro-Nite and the measurements were done in a furnace without the influence of foundry mould atmosphere. The greatest susceptibility to reoxidation has a green-sand mould. It is confirmed by above mentioned Campbell [1] who presupposes that the majority of secondary oxidation results from metal reaction with water vapour from a mould but not from air that is ejected from the mould already in first casting phases and that the addition of carbonaceous additives in moulding mixture helps to eliminate this problem.

2. Experimental

Experiments to the study of metal reoxidation in a foundry mould were based on continuous oxygen activity measurements during filling the mould and metal solidification. A comparative experiment was used when under otherwise the same conditions (the same cast metal composition, the same measurement temperature a_O) the kind of moulding mixture and the way of filling the mould were changed. Two types of stepped castings weighing 19.2 kg and 21 kg were used for the research.

The mould was made from green bentonite mixture. Sodium bentonite was used as a binder. The mixture did not contain any carbonaceous additive, for higher plasticity the dextrin was added in it in amount of 0.75 wt %. Loss by ignition was 1.75 %. Used quartz sand has its granularity d_{50} = 0.27 mm. Mixtures differed with their water content. The test casting metal was melted in an electric mid frequency furnace of the 100 kg volume. A shank ladle was used for casting. The metal was inoculated (FeSi 75) in a casting ladle and modified in-mould for preparation of GJV and GJS with the aid of the nodulariser Bjomet 3.

Oxygen activity in castings was measured with probes TSO 6 of the firm Termosondy Kladno s.r.o. (Ltd.) and with sensors derived from those probes. The probe consists of a measuring element sealed with refractory material in a quartz tube. The measuring element is formed by solid electrolyte ZrO_2 stabilized with CaO with reference mixture Cr_2O_3+Cr. Contact with bath and the line from the reference mixture was from molybdenum wire. Temperature was measured with thermocouples Pt-PtRh10 of diameter 0.3 mm placed in a corundum capillary tube of diameter 3 mm. The thermocouple measuring end was placed in a corundum protective casing of diameter 6 mm. Fig. 1. shows sensors for continuous measurement in comparison with the commercial probe TSO 6.

Measurements of electromotive voltage (EMV) of sensors for determination of oxygen activity and of thermocouples were recorded during the all time of casting up to the total casting solidification. A measuring card connected to PC or an independent logger quite divided from supply mains were used for recording. Shielding was attached to the contact with metal bath. The contact was formed by Mo wire of diameter 1 mm in a ceramic protective casing. From the casing always juts its very short part only. The line of Mo contact was connected to the „+“ pole of the measuring card or the logger and the probe line to the „–“ pole.

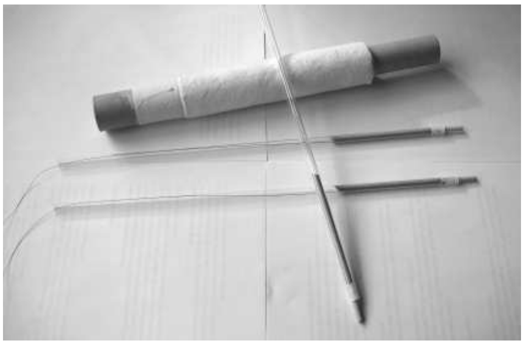

Fig. 1. Measuring probe TSO 6 and sensors for continuous measurement of oxygen activity

Oxygen activities in metal were calculated according to the equation (2) CSAV Ostrava, [ppm]:

$$\log a_O = 8,516 - (13272 - 10,08*E)/ (T + 273) \qquad (2)$$

where: a_O – oxygen activity [ppm]
T – melt temperature [°C]
E – electromotive voltage of the probe [mV].

3. Results

Influence of moisture on change of oxygen activity in metal during filling the mould and casting solidification was checked for lamellar graphite cast iron – GJL, compacted graphite cast iron – GJV, and spheroidal graphite cast iron – GJS. Metal was cast in green bentonite moulds with low, mean, and high moisture. Tapping temperature of cast iron ranged between 1460 and 1480 °C. A comparative experiment was done during measurements and the metal of the same chemical composition and the same temperature was cast from one ladle in three moulds with changing moisture of moulding mixture.

During those measurements the differences in oxygen activity for GJL were found out under temperature of 1300 °C. With increasing moisture the growing oxygen activity values can be found here:
Moisture 2.4 %; a_O = 0.30 ppm
Moisture 3.5 %; a_O = 0.35 ppm
Moisture 4.9 %; a_O = 0.50 ppm

Oxygen activities equalize under solidification temperature and they form 0.05 ppm only. In case of spheroidal graphite cast iron the oxygen activity measurements under temperature of 1290 °C were successful for two moulds only. Under the moisture 2.1 % the measured value was a_O = 0.38 ppm and under the moisture 3.6 % it was a_O = 0.31 ppm. When temperature dropped to the solidification temperature the oxygen activity for both moulds decreased to 0.12 ppm. In case of compacted graphite cast iron the measurement under temperature of 1300 °C was successful only for a mould with moisture of 2.1 % where oxygen activity was measured a_O = 0.11 ppm and under solidification temperature it decreased to 0.07 ppm.

Further experiments were aimed at oxygen activity measurements in compacted graphite cast irons GJV where pinholes occurrence was found out in test castings [6]. On the basis of simplified plan of the experiment 5 melts were prepared in which following items were chosen as constant parameters: composition of metal charge in induction furnace, basic chemical composition of metal, basic composition of moulding mixture, amount of nodulariser, and casting temperature. Dominant factors were the Al content in cast iron (3 levels from 0.012 up to 0.25 %), moulding mixture moisture (3 levels from 2 up to 5.2 %), and a degree of metal flow rate in mould cavity (2 ways of runner gating in the mould cavity ε = 0.3 and 0.6). As dependently variables were the oxygen activity and the occurrence of pinholes in castings. Sensors for continuous oxygen activity measurements were put in a mould cavity with different moisture. Metal was melt in a 100 kg furnace by remelting the uniform charge of return material. Metal was inoculated in a ladle and modified Bjomet 3 in a reaction chamber in a mould. EMV [mV] was taken off in dependence on temperature and calculated values of oxygen activity related to the highest common recorded temperature and it was 1200 ± 1 °C. Table 1 shows chemical composition of studied melts.

Table 1.
Chemical composition of experimental melts

Element	Chemical composition of melts [%]				
	Number of melt				
	61	62	63	64	65
C	3.45	3.49	3.51	3.47	3.60
Mn	0.38	0.39	0.18	0.18	0.18
Si	2.91	2.62	2.78	2.75	2.61
P	0.020	0.020	0.020	0.020	0.020
S	0.009	0.009	0.008	0.008	0.007
Cr	0.029	0.027	0.027	0.029	0.032
Cu	0.146	0.147	0.148	0.150	0.152
Al	0.012	0.015	0.050	0.251	0.190
Mg	0.031	0.0235	0.0255	0,023	0.0230

In one melt 4 bars were cast; 2 bars from a common sprue: A casting and B casting.

Results of measurements of three melts are given in Table 2.

Table 2.
Results of oxygen activity measurements at bar castings with different moistures and different methods of mould filling (1 – sensor position farther from the ingate ε = 0.6, 2 – sensor position nearer to the ingate ε = 0.3)

Castings 61	Moisture /%/	O_2 activity	Temperature [°C]
A1	3.0	0.0539 ppm	1201
A2	2,06	0.0153 ppm	1201
B1	4,68	0.008 ppm	1201
B2	3.0	0.0259 ppm	1201
A1	1,93	0.175 ppm	1201
A2	3.08	0.304 ppm	1201
B1	3.08	0.012 ppm	1201
B2	5,23	0.153 ppm	1201
Casting 63			
A1	2,8	0.273 ppm	1199
A2	4,94	0.008 ppm	1199
B1	1,99	1.130 ppm	1199
B2	4,94	0.003 ppm	1136

It could be expected that similarly as in case of the above mentioned results of GJL the a_O will be lower at low moisture of moulding mixture and on the contrary it will be higher at high moisture. But the given extreme values were measured in case of one melt just contrariwise. If the extreme values (1,13 ppm) are even excluded from the evaluation, no dependence between the mould moisture content and oxygen activity issues. No relation can be also found between aluminium content in cast iron and oxygen activity. In castings with high aluminium content of 0.19 and 0,25 % the pinholes occurred in high numbers, and namely under low and also high moistures (> 4 %). Thus the conclusions known from literature about the influence of Al on pinholes occurrence in cast irons were confirmed [11,12]. Neither high moisture of moulding mixture nor the fact that the mixture did not contain carbonaceous additives has led to pinholes formation. Literature too places accent on those causes of pinholes formation. Our another previous work contradicted that conclusion too [6]. In case of castings with pinholes occurrence unfortunately failed the measuring apparatus and it was not possible to determine oxygen activity in them.

Differences in measured values of oxygen activity can be caused by a fact that the sensors take off the EMV inside the casting and no in surface layers which are relevant for reoxidation processes occurrence. The influence of mould moisture in the wall centre will be probably not shown in such a way as e.g. in-mould modification conditions and the formation of possible reaction products.

As it was noted by Hummer, Hecht, and Mampaey in the above mentioned works the oxygen activity influences the graphite morphology. That fact was shown in our previous research works too.

From melts measured for cast irons during last two years a statistical data set has been set up. Oxygen activities in lamellar graphite cast iron under temperatures above 1300°C are considerably higher. With temperature drop the oxygen activity differences between lamellar graphite cast iron and other cast iron grades decrease, the measured oxygen activity values are on a distinctiveness limit of used sensors and under temperature beneath 1200 °C the activity zone of lamellar graphite cast irons permeate the other ones.

Those results are work out in a graphical form in Fig. 2. Higher values in the zone are valid for non-inoculated cast irons, the lower ones for inoculated ones. Zones for spheroidal graphite cast iron and for compacted graphite cast iron touch one another.

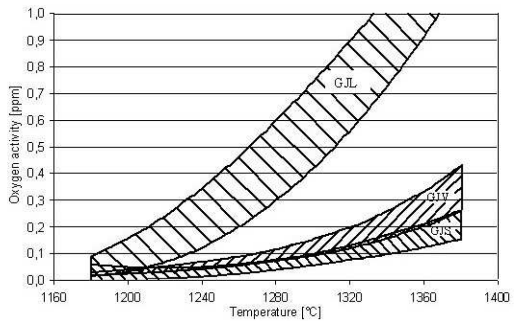

Fig. 2. Dependence of oxygen activity on temperature for 3 basic cast iron grades (GJL, GJV, GJS)

4. Discussion of results and conclusion

Presented results show that the use of oxygen activity measurement for direct study of changes caused by reoxidation processes is limited and that it is more suitable for study of the influence of different factors on cast iron crystallization and graphite morphology. During those processes the secondary and tertiary metal oxidations also occur. It is also supported by similarity of very low values of oxygen activity values when compared our results with that ones by other authors. The increase of oxygen activity in cast iron during reoxidation processes is obstructed by high content of the deoxidation element (Si). In contradistinction to steels the oxygen activity in cast irons under solidification temperatures is controlled by silicon content. Deoxidation element content in steels deoxidized with aluminium is 0.03 up to 0.05 % (Al). During reoxidation processes in some casting places the all aluminium able to react with oxygen can be spent. Then the oxygen activity is not controlled by aluminium content and defects can occur in castings. Thus it is important to hold strictly the deoxidation conditions and at the same time the uniform mould filling with the aim of not forming the places in castings with lack of deoxidation elements. The similar conclusions has also published by Chojecki and Telejko [13].
In addition to it the reoxidation processes run in casting surface layers where sensitivity of probes and their durability are very low particularly in case of steels. Then other methods must be used, as e.g. the study of surface defects of castings and of changes of metal chemical composition.

Analysis of casting surface defects as an indirect method of reoxidation study was used by us in several previous works for the research of pinholes in castings [6] and recently for the expertise of defects in steel castings [14]. Secondary slag inclusions were the studied defects and slag and oxidic inclusions in immediate vicinity of defects were analysed. Elements with lower deoxidation ability (Si, Mn, and Fe) partook in those inclusions. Slag taken from the metal level in a mould during casting was analysed too. That slag also contained high Mn and Fe contents confirming the secondary oxidation of steel when after consuming the deoxidizing aluminium the other elements are oxidized according to the affinity series to oxygen. Analysis of even small slag samples and inclusions with the aid of X-ray diffraction analysis or in combination with the research on an electron microscope (SEM) gives reliable evidences of causes of defects in castings and it also confirms the occurrence of reoxidation processes but it is not able to evaluate the kinetics of those processes and the influence of different technological casting parameters. In spite of this the mentioned work by Zadera et al. [14] has discovered that to the defect occurrence also the mould coating containing zirconium oxide contributes which was found out in slag floating in metal and also in slag occurred in the defect.

Acknowledgements

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