

# Evolution of the gas atmosphere during filing the sand moulds with iron alloys

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Received 30.06.2009; accepted in revised form 06.07.2009

## Abstract

Evolution of atmosphere of the mould cavity when pouring the cast iron has been analyzed. It was found that in dry sand mold the cavity is filled by air throughout the casting time. In green sand the air is removed by the water vapor the hydrogen or carbon oxides formed in contact with the liquid metal. The theoretical results have been confirmed experimentally.

**Keywords:** Reoxidation, Mould atmosphere; Thermo chemical analysis.

## 1. Introduction

In the numerous papers it was stated that during casting of iron in the green sand mould the surface of metal is oxidized [1, 2, 3, 4] forming the defects like surface porosity, pinholes etc. Experimental evaluation of reoxidation effects is rather difficult. The rise of the oxygen activity in alloy is negligible [4, 5]. The oxygen from the mould atmosphere forms rather the liquid or solid oxides that doesn't influence the activity in solution. The reoxidation is limited to the surface layer when the oxides forms and the time of the mould filling is too short for the diffusion to the bulk metal. In experimental studies large inclusions was found in the surface zone [1,5]. Also the measure of the total oxygen in castings by extraction in vacuum gives a doubtful results [4]. Results are averaged for a large volume. For this reason authors decided to study the probability of the oxidation and reduction reactions between the gases formed in the mould, by the analysis of the mould atmosphere when pouring and by the thermo chemical analysis of probability of different reaction between the sand components, evolution of gas atmosphere, and reaction of this atmosphere with the liquid iron alloys. Previous studies of authors proved that when the cast iron fills the mould cavity the partial pressure of oxygen decreases especially quickly

when the sand is prepared with the addition of the coal dust [3,4]. In general opinion, when pouring the cast iron in presence of coal dust, the mould atmosphere becomes reducing. When the steel is cast in the green sand mould drop of partial pressure of oxygen is independent of the presence of coal dust in the moulding sand. Authors tested the evolution of the composition of gas atmosphere during filling the moulds. Testing device is presented in the Figure 1. The metal was cast to the inclined sand mould by the runner with small section. Time of filling was about 10 seconds. The partial pressure of oxygen was measured in gas phase flowing out from the cavity, through large flow-off. For this aim the zirconia cell was used as the sensor. For the hydrogen a special type of pellistor was prepared by the Sensor Gas Society in Tychy. The sensor measures the heat conduction of the gas, influenced mainly by the content of hydrogen. Figure 2 presents as an example the results obtained during filling the mould with the carbon steel for oxygen

## 2. Thermo chemical analysis of the reoxidation

### 2.1 Dry sand mould

At the initial moment of pouring the mould cavity is filled by air and partial pressure of the oxygen  $P_{O_2} = 0.21 \text{ atm}$ . The rest is nitrogen. Short time of pouring eliminates the possibility of its transfer to the metal. The character of the atmosphere is determined by reaction:



It's free Gibb's energy is equal to [6]:

$$\Delta G^0 = -123720 - 0.503 T \text{ J/mol}$$

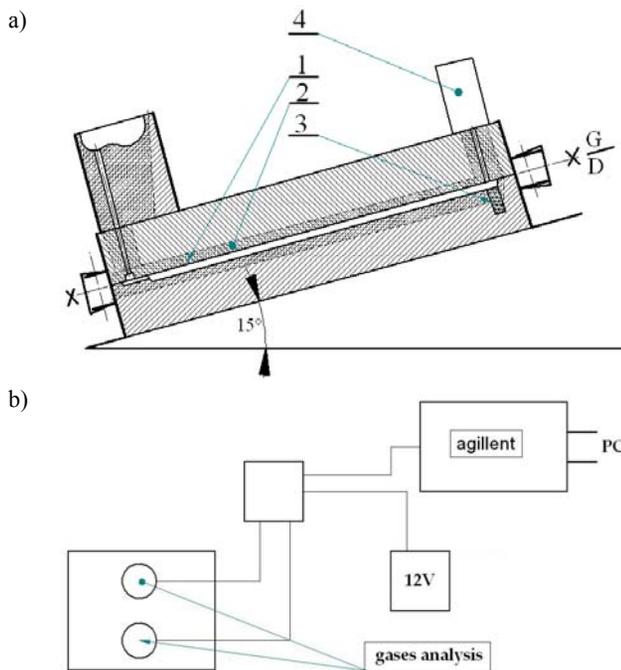


Fig.1. Test mould: a) sand mould; 1 upper surface of the mould cavity, 2 moulding sand, 3 sample for the chemical analysis, 4 gases analyzers b) registration of data

Figure 3 presents calculated oxygen activity for the equilibrium with iron saturated with oxygen. Results of calculation are much lower than experimentally measured in green sand mould (Fig.2). It indicates that forming of reducing atmosphere is improbable. The reoxidation can be only impended by limiting the time of reaction or partial pressure of oxygen.

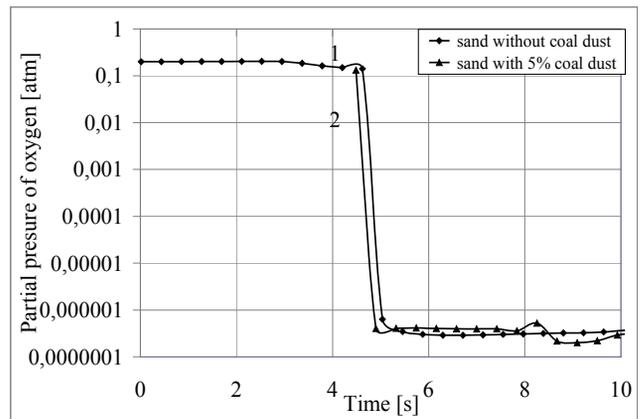


Fig.2. Evolution of the partial pressure of oxygen in the gas removed from the green sand mould filled with cast steel

Figure 4 presents the evolution of  $P_{O_2}$  during filling the dry sand mould with cast iron. It rests on the constant level. A little drop may be observed because a part of oxygen is consumed for oxidations of iron or more probably oxidation of other cast iron elements: aluminum, silicon or even carbon.

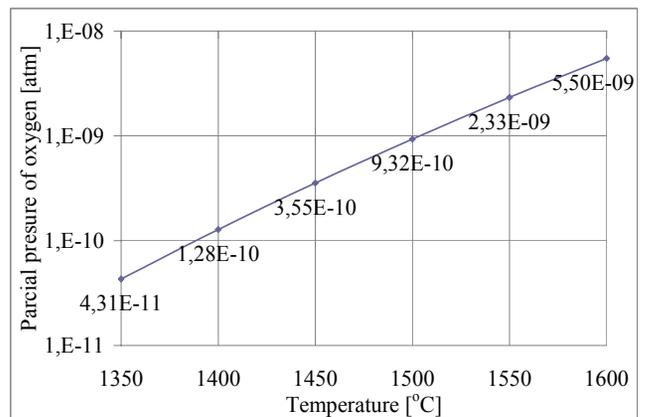


Fig.3. Oxygen activity for the equilibrium for iron saturated with oxygen

Addition of the coal dust or other reducing elements to the dry sand can ameliorated the casting surface quality, rising the interfacial energy mould-metal. The lack of oxygen excludes the possibility of carbon oxidation in the bulk sand. For the reaction:



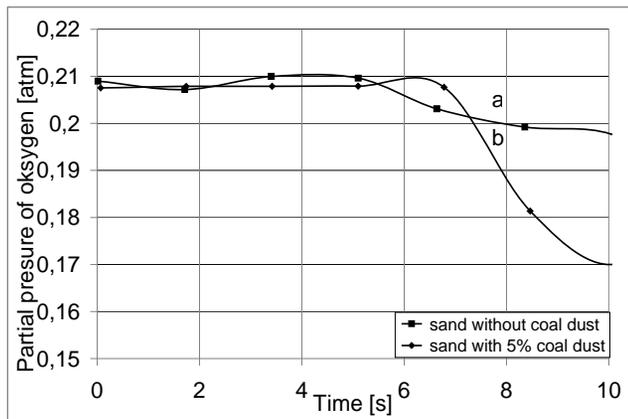
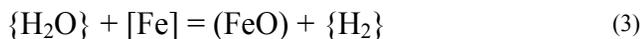


Fig.4. Evolution of the partial pressure of oxygen during casting the iron in dry sand mould

the nucleation of gas bubbles and then the high supersaturation is necessary the oxidation is possible mainly at the surface of cavity. The quantity of carbon dioxide formed is too limited to considerably influence the mould atmosphere. It is confirmed experimentally. Results are presented in the Figure 4 during filling the mould the partial pressure of oxygen decreases to about 0.17atm.

## 2.2. Green sand mould without the coal dust addition

In the green sand mould the water steam forms the condensation zone. For nucleation of the water steam bubbles the pressure must attain 100kPa. Transport through the dried layer is isobaric and the raise of temperature increases the volume of steam. In the green sand mould with 5% humidity from 1G of the sand is evacuated 0.05G of water. After evaporating and heating to 1000°C it's volume attains  $3.61 \cdot 10^{-4} \text{m}^3$ . During filling the mould with cast iron or steel the steam fulfils practically all free volume of the mould. It causes the drop of partial pressure of oxygen. In the gas leaving the mould it rests only 0.12 atm. Evolution of the partial pressure of oxygen is presented in the Figure 5 The water steam oxidizes the liquid iron because for the reaction:



the Gibbs free energy is very negative and equals [7]:

$$\Delta G^0 = 58616 - 51.51 T \text{ J/mol} \quad (4)$$

The oxidation causes the sudden rise of the partial pressure of hydrogen especially at the temperature of liquid steel. This pressure is nearly in equilibrium with iron saturated with hydrogen. It is presented in the table 1

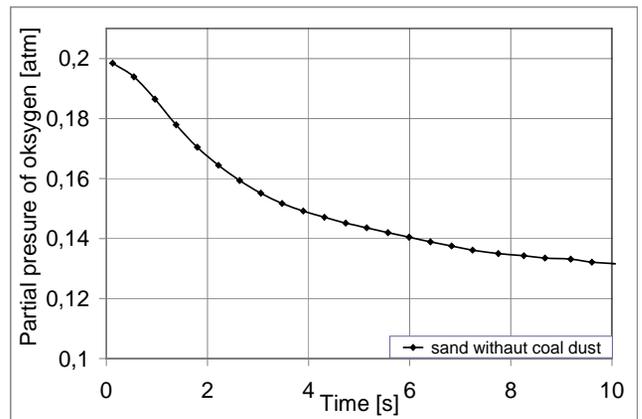


Fig.5. Evolution of the partial pressure of oxygen during pouring the cast iron in the green sand mould

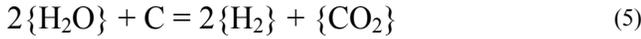
Hydrogen is partly absorbed by metal; the rest is evacuated from mould, burning outside in contact with atmosphere. The oxygen from reduction of the water steam forms the iron oxide. The pieces cast in green sand are particularly endangered by reoxidation. The oxidizing however results from contact with water steam and not the free oxygen because it's evacuated from the mould just at the beginning of pouring. The calculated pressure of hydrogen can be much more dangerous for casting surface, particularly for the long pouring time. This opinion is confirmed by foundry practice. Frequently the pinholes appear in castings produced in green sand moulds, especially for alloys with high concentration of strong deoxidizers like aluminum or magnesium. They react with steam much easier than iron and the absorption of hydrogen is quicker.

Table 1.  
Partial pressure of hydrogen in equilibrium with water steam and liquid iron

Temperature [C]	Partial pressure of hydrogen [atm]	Concentration of hydrogen in iron [ppm].
1350	0.971	19.00
1400	0.976	20.49
1450	0.980	21.98
1500	0.983	23.48
1550	0.985	24.98
1600	0.987	26.48

### 2.3. Green sand mould with the coal dust

The water steam formed in condensation zone flows throughout the dry sand rich in coal dust and oxidizes the carbon:



Gibbs free energy is equal to [7]:

$$\Delta G^0 = 84935 - 37.49 T \log T + 18.49 T \quad J/mol$$

The pressure of steam equals 1atm and the equilibrium pressure of the formed carbon dioxide can be calculated as:

$$P_{CO_2} = \frac{Kp_{\{H_2O\}}^2}{P_{\{H_2\}}^2} \quad (6)$$

Even for the initial pressure of hydrogen equal to 1atm, for the temperature 100°C pressure of CO<sub>2</sub> attains 0.97atm. In reality in the layer of dry sand only the traces of hydrogen can appear because at the temperature of the sand the dissociation of water steam rests negligible. The Figure 6 presents the values of Gibb's free energy and equilibrium constant calculated for the reaction (4). Equilibrium values are never obtained because short time of process and limited carbon content. The true concentration depends on the kinetic factors and have to be verified experimentally. It can be supposed that the mixture CO<sub>2</sub>-H<sub>2</sub>O-H<sub>2</sub> penetrates the mould cavity, replacing former air atmosphere. The partial pressure of oxygen drops to traces. It was confirmed experimentally as well for cast iron as for steel.

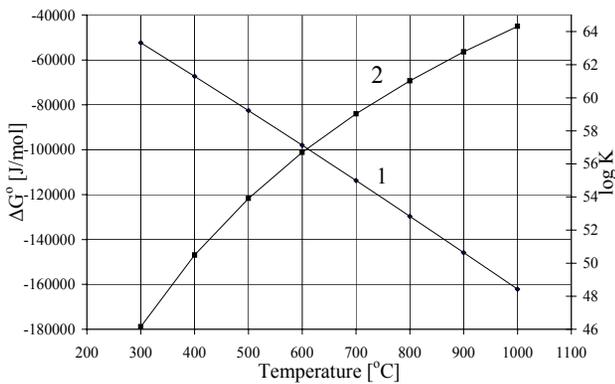


Fig.6. Gibb's free energy (1) and equilibrium constant (2)for the reaction of reduction of water steam by carbon

The result of the experiment is presented in the figure 7. In spite of heating the gas the reduction of carbon dioxide to monoxide is improbable. Reduction appears at the surface of liquid alloy:

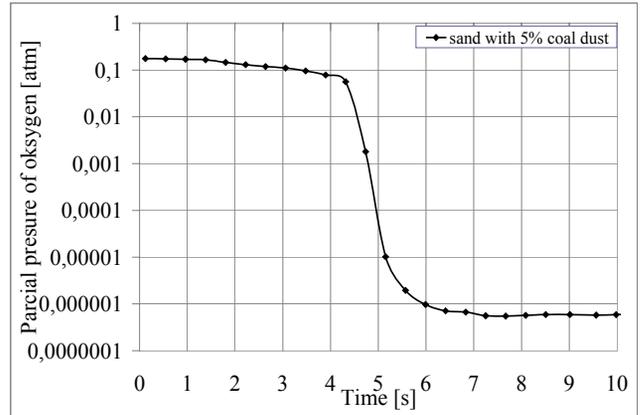


Fig.7. Evolution of the partial pressure of oxygen during pouring the cast iron in the green sand mould with 5% of coal dust

Hydrogen formed as a product of the reduction of water steam can react with the coal dust, forming the hydrocarbones, mainly methane:



For this reaction the change of Gibbs free energy has been calculated as [9]:

$$\Delta G^0 = -16720 + 12.1 T \ln T - 14.2 T \quad J/mol \quad (8)$$

Figure 8 presents the values of the Gibbs energy calculated for different temperature. It can be concluded that the formation of methane is probable up to 1100 K.

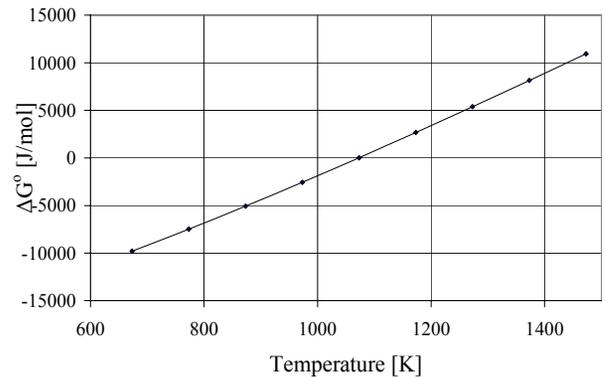
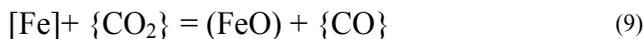


Fig.8. The Gibbs free energy of methane formation vs. temperature

It means that methane can appear in the layer of the dehydrated sand, between the condensation zone and the surface of mould cavity. It is very probable that also the other more complex hydrocarbones can form as the products of reaction of coal dust with the water steam. W. Solarski and E. Zieliński [11] analyzed the gas formed in the sand core, immersed in liquid iron. Besides of methane they have found also the traces of C<sub>2</sub>H<sub>6</sub>. When the gas hydro carbides penetrate the mould cavity they becomes instable because of too high temperature. It confirms the

mechanism proposed by P. Jelinek, that the different forms of carbon on the surface of cavity are the products of the decomposition of gas phase. For heterogeneous nucleation it is the lustrous carbon, homogeneous nucleation produces the soot [10]. In effect the gas phase in the mould cavity is composed mainly by hydrogen, water steam and carbon oxides. Iron and other components of alloy reduce carbon dioxide:



$$\Delta G^0 = 23012 - 24.27 T \quad \text{J/mol} [7]$$

Supposing that the activity of condensed phase: Fe and FeO equals 1:

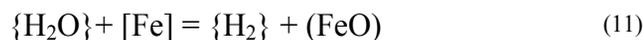
$$\ln K = \ln \frac{P_{\{\text{CO}\}}}{P_{\{\text{CO}_2\}}} = \exp\left(-\frac{\Delta G^0}{RT}\right) \quad (10)$$

Pressure of carbon oxide, calculated from eq (9) is presented in the Table 2. It raises with the raise of temperature.

Table 2.  
Partial pressure of CO in equilibrium with carbon dioxide

Temperature °C	Partial pressure of CO <sub>2</sub> [atm]			
	0.2	0.4	0.6	1
1300	0.390	0.561	0.657	0.762
1400	0.410	0.587	0.691	0.780
1500	0.440	0.610	0.701	0.796
1600	0.460	0.629	0.718	0.801

More intensive is the reduction of water steam:



and [7]:

$$\Delta G^0 = 20083 - 18.74 T \log T + 73.64 T \quad \text{J/mol}$$

Even for the initial pressure of H<sub>2</sub>O equals to 0.1atm, at 1200°C calculated partial pressure of hydrogen attains 0.75 atm.

In foundry practice the absorption of hydrogen by the liquid metal is limited by the short time of mould filling. J. Orlenius and al [8] measured the rise of hydrogen content in the cast iron. Special test mould with a long runners and large feeder has been constructed. They found that the content of hydrogen measured in riser is 50 to 80% higher than in the ladle. Unfortunately the tests have been executed only for the sands bounded with different synthetic resins.

Authors observed the change of hydrogen partial pressure in gas flowed out from green sand mould with 5% of coal dust.. Figure 9 presents the results of experiment.

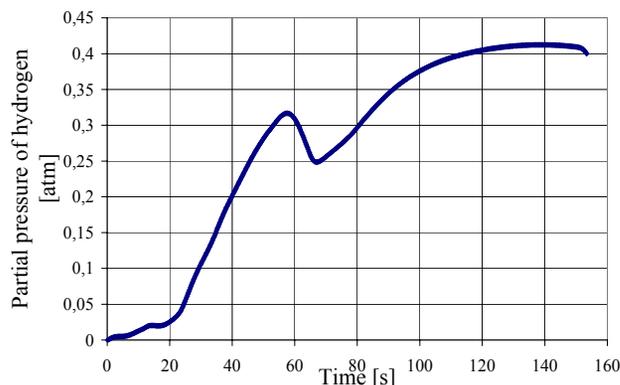


Fig.9. Evolution of the partial pressure of the hydrogen in the gas evacuated from green sand mould with addition of 5% of coal dust

Pressure of hydrogen raises to about 0.4atm. The maximum value is observed after 125s while the pouring time is about 10s. Probably it's caused by the delayed reaction of pellistor, but it cannot be excluded that the reduction of water steam is possible also after pouring or even when the alloy is in solid state. Besides of hydrogen in the gas phase are probably water steam and oxides of carbon.

### 3. Results

During casting the oxidation of ferrous alloys through oxygen is possible only in dried sand moulds. The addition of coal dust decreases the initial partial pressure of oxygen to about 0.17atm and the atmosphere in the mould is strongly oxidizing. The formation of carbon oxide is possible only at the surface of mould cavity. In the green sand mould the water steam formed in condensation zone is transported to mould cavity and heated, but even at 700°C the dissociation is impossible. The steam fills the cavity eliminating former air atmosphere. Partial pressure of oxygen drops to 0.12-0.14atm. Water steam reacts with liquid metal particularly with steel, because of high temperature of alloy. In the zone of contact calculated pressure of hydrogen is nearby the equilibrium with saturated alloy. Its transfer to the bulk metal is limited only by the short time of contact. Therefore the prolongation of the time of pouring as well as the development of the surface of contact raises the final concentration of hydrogen in alloys. When the coal dust is added to the green sand the steam promotes the nucleation of the CO<sub>2</sub> and hydrogen in the dried layer. In equilibrium state nearly all steam is reduced, but the process of reduction depends on kinetic factors and the results cannot be provided from thermo chemical considerations. Hydrogen reacts with coal dust producing the different gaseous hydrocarbons mainly methane. As the nature of these hydrocarbons except methane is not known, the probability of formation cannot be evaluated. The hydrocarbons become

instable at the temperature of metal cavity and decomposes producing the pyrolytic carbon: lustrous or soot. The morphology of pyrolytic carbon confirms [10] that it crystallizes from gaseous phase.

In effect the cavity of the mould is filled by the mixture of H<sub>2</sub>O, CO<sub>2</sub> and CO. Rise of the fraction of carbon oxides in the gas phase lowers the reduction of the water steam and probably the absorption of hydrogen in liquid metal. The partial oxygen pressure in the gas carried away from mould filled with cast iron is much lower than for sand mould without coal dust but for iron alloys it rests oxidizing. In case of steel casting, because of much higher temperature, process of the formation of new mould atmosphere is so quick that no difference is observed.

## Acknowledgements

Studies was sponsored by the polish Ministry of Sciences and Informatics in the project no 11.11.170.318 z.4.

Authors want to thank the direction and personnel of Gas Sensor Soc. in Tychy for elaboration for us the sensors of hydrogen.

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