Gaseous Atmosphere During Gas Forming Tendency Measurements of the Selected Protective Coatings for Sand Moulds

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Abstract

Protective coatings have direct contacts with hot and liquid alloys. As the result of such contacts gases are emitted from coatings. Gas forming is a tendency of the tested material to emit gases under a temperature influence. In order to assess the gas forming tendency either direct or indirect methods are applied. In the hereby work, the measurements of the gas forming tendency were performed under laboratory conditions, by means of the developed indirect method. The research material constituted samples of six selected protective coatings dissolved either in alcohol or in water. These coatings are applied in sand moulds and cores for making cast iron castings. The assessment of their gas forming tendency was presented in relation to temperatures and heating times. The occurrence and changes of oxygen and hydrogen contents in gases outflowing from the measuring flask during tests, were measured by means of gas sensors. The process of the carbon monoxide (CO) emission during tests was also assessed. The following gas sensors were installed in flow-through micro chambers: for oxygen - lambda probe, for hydrogen – pellistor, for carbon monoxide - sensor (dedicated for CO) FIGARO TGS 822 TF. The results of direct CO measurements were recalculated according to the algorithm supplied by the producer of this sensor.

Keywords: Gas forming tendency, Oxygen, Hydrogen, Carbon monoxide, Protective coatings

1. Introduction

Such technological property as the gas forming tendency of coatings is essential due to the casting defects formation: gas bubbles, skinholes, pitted skin, pinholes, porosity [1,2,3]. More strict environment standards do not allow harmful substances emissions by foundry processes. Changes of coatings soluble in alcohol into water soluble ones causes changes of the characteristic and composition of gases emitted during the castings production. The gaseous atmosphere inside the mould cavity, its oxidizing or reducing character, influences directly the quality of casting surfaces and kind of defects. It also provides

changes of the harmful influences for foundry plants employees and for surroundings. Producers of coatings, in order to limit applications of easily vaporizing substances, are changing coatings diluted in alcohol to water coatings. However, it often causes 'technological harmfulness'.

2. Tested protective coatings

Liquid protective coatings contain three or four components:

- refractory grain matrix (of one or a few components), it means the material, which should not react with liquid alloys and with components of moulding and core sands,
- binder,
- stabilizers aimed at preventing the sedimentation of the refractory grain matrix and binder in diluents.

Stabilizers should maintain a density and viscosity of liquid coatings at the determined level, due to which they prevent the protective coating from per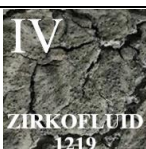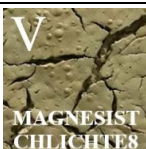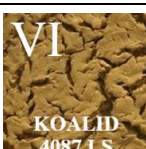meating too deep into the mould cavity or core. As stabilizers in water coatings are applied: bentonite, moulder's clay, cellulose derivatives, and also alginates.

- diluents (water, alcohol or other liquid).

Table 1 presents selectively chosen coatings subjected to tests and their characteristic features [7]. Matrix compositions and diluents caused that these coatings were dried at a temperature of 130 °C, before the measurements. For this work aims the tested coatings got numbers I-VI.

Table 1.
Characteristic features of protective coatings subjected to gas evolution tests [7]

Sample and trade number of a dried coating	Matrix, diluent and color after drying	Application
I ARKOFIX 1220	Aluminosilicates Graphite; Alcohol; Grey	The most often applied for resin moulding sands, self-hardening, especially for the cold-box process. For all grades of cast irons and non-ferrous metals alloys.
II KOALID 2290	Magnesium silicate, graphite; Alcohol; Light grey	For all processes of forming moulds and cores. For all grades of cast iron and non-ferrous metals.
III ARKOPAL 8720	Silicates, graphite iron oxide; Water, Red-brown	For the cold-box process. For all grades of cast iron.
IV ZIRKOFLUID 1219	Zircon ($ZeSiO_4$); Alcohol; Light grey	For all castings and foundry materials
V MAGNESIST CHLICHTE8	Sintered magnezite; Alcohol; Light green	For all binders and grain matrices, especially for olivine. For casting of manganese cast steel
VI KOALID 4087 LS	Aluminosilicates; Alcohol; Yellow	For cold-box processes and for producing shell moulds. For all grades of cast iron.

3. Measurements of gas evolution rates

Measurements of gas evolution rates, for the aims of the hereby paper, were performed by the indirect method (under laboratory conditions). The set-up for measurements is shown in figure 1 [4,8,9,10]. The essence of measurements, according to the applied method, is based on placement of the flask containing a coating sample in a furnace heated to app. 1000°C and on measuring – in the real time – second after second, the volume of gases originated from decomposition and burning of the tested sample. In addition, the sample temperature is measured, which singles-out this method [4] from similar methods developed and applied earlier [15, 16, 17]. The set-up presented in earlier works

of the authors [9] was additionally equipped with the flow-through micro-chamber with CO (TGS822TF) sensor. Measurement signals were recorded by the agillent 34970A recorder. Sampling frequency was $2s^{-1}$ for more than 1000s.
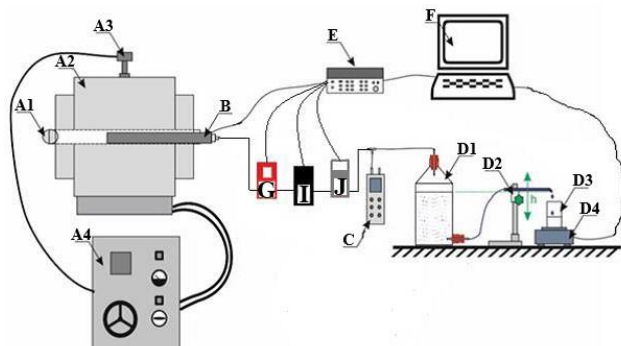

Fig. 1. Set-up for measuring gas evolution rates and gaseous atmosphere [8] :a) pipe furnace A1-A4, b) measuring flask with a thermocouple and conductor B , c) differential manometer C, d) measurement of gas volume D1-D4, e) multi-channel recorder agillent E, f) PC for data recording F, g) flow-through micro-chamber with lambda probe G, i) flow-through micro-chamber with pellistor [5] I, j) flow-through micro-chamber with Figaro sensor J [6]

4. Measurement results

Successive figures present results recorded during tests and then recalculated according to the assumed algorithms. Figure 2 shows pathways of gases evolution from the tested protective coatings during the gases evolution rate test. The evolution of gases is intensive in a few first minutes (app. 200s) and then this intensity decreases.

Figure 3 presents pathways of gases evolution in relation to the temperature value. Protective coatings II and III started intensive evolutions of gases at a temperature of app. 400°C, while the remaining coatings at app. 500°C. On account of amounts of evolved gases the tested coatings were divided into groups, according to the classification proposed by J. L. Lewandowski [11, 12]. A very high gas forming tendency has coating III, a high gas forming tendency have coatings VI and I, an average gas forming tendency have coatings II and V, and a low gas forming tendency characterises coating IV.

Figures 4 and 5 show the intensity of gases evolution rates (process kinetics) determined for tested protective coatings during the test.
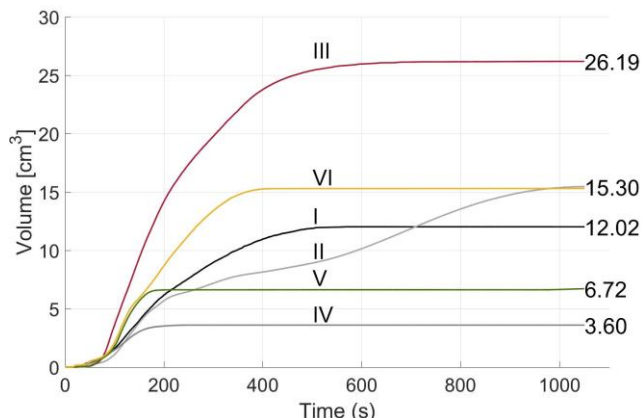

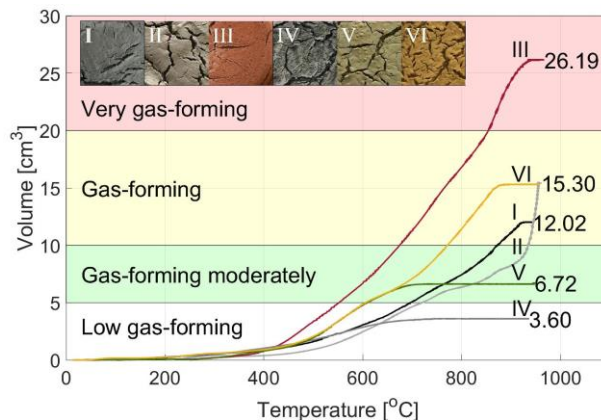Fig. 2. Pathways of gases evolution during tests of coatings: I, II, III, IV,V and VI

Fig. 3. Classification of gas evolution rates during heating of coatings: I, II, III, IV, V and VI

The evolution rate of gases from coating III reaches its maximum (0.3 cm^3/s) after 40s, while from coatings I and II the maximum rate (0.06 cm^3/s) is seen after 120s.

Gas evolution rates (kinetics of the process) of coatings IV, V and VI, during their sintering tests, are shown in figure 5. Maximum value of the gas forming rate of coating IV occurs after 120s and reaches the level of 0.03 cm^3/s, while for coatings V and VI the maximal value equals 0.1 cm^3/s and occurs after 110s. It can be concluded, on this base, that the best – for practical reasons – is coating IV since it emits gases with the lowest intensity and their amount is the smallest one. Thus, the gas forming tendency of this coating is the lowest.

Generally, coatings are characterised by various intensities of gases emission, which occurs at different temperature.

Intensity of gases emission from protective coatings I, II and III at a temperature range from app. 100 °C, is shown in figure 6.

In case of coating, I the maximum intensity (0.05 cm^3/s) occurs at a temperature of 610°C. For coating II the similar maximum (0.06 cm^3/s) is seen at T = 525°C. The highest rates of gases emission for coating III (0.3 cm^3/s) occur near a temperature of 230 °C.
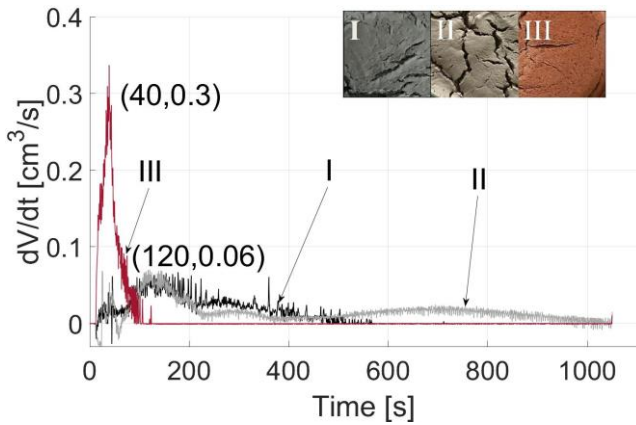
Fig. 4. Kinetics of gas evolution rates determined for coatings: I, II and III during the test
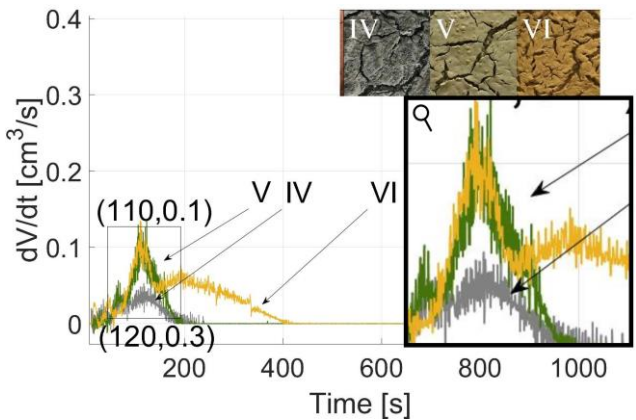

Fig. 5. Kinetics of the gas evolution for coatings IV, V and VI during the test
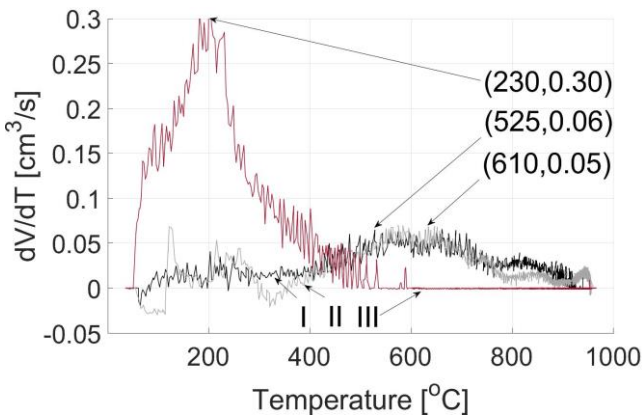

Fig. 6. Pathways of the intensity of gases emission from coatings I, II and III during heating – as a temperature function

Pathways of changes of the intensity of gases emission as a temperature function for protective coatings IV, V and VI, are shown in figure 7. Coating IV reaches the maximum intensity of gases emission (0.03 cm³/s) at a temperature of 552 C. This intensity is the lowest one, as compared with the remaining

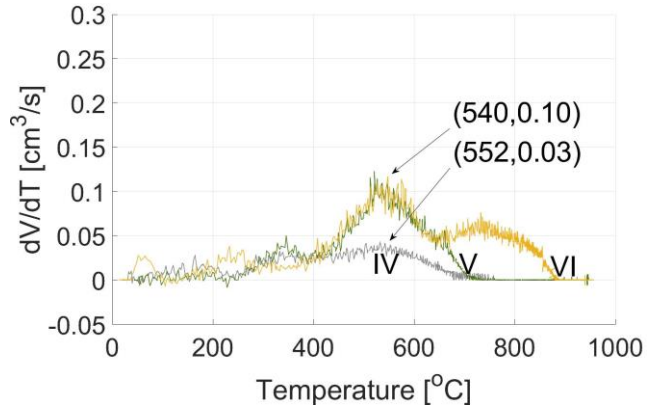coatings. Coatings V and VI reach maximum rates (0.1 cm³/s) at a temperature of 540 °C.

Fig. 7. Pathways of the intensity of gases emission from coatings IV, V and VI during heating

The smallest value of the peak of the gases emission intensity characterises coating IV and this peak occurs at a temperature of 550 °C.

4.1. Hydrogen in a gaseous atmosphere

Hydrogen dissolves in the liquid ferrous alloy within a wide range, its solubility increases along with the alloy temperature increase [14].
Hydrogen content in gases emitted from the test flask during investigations of the gas forming tendency of coatings, are presented in figures 8 and 9.
Maximum hydrogen content in gases emitted from protective coatings equals 39% for coating I, 43% for coating II and 37 % for coating III.
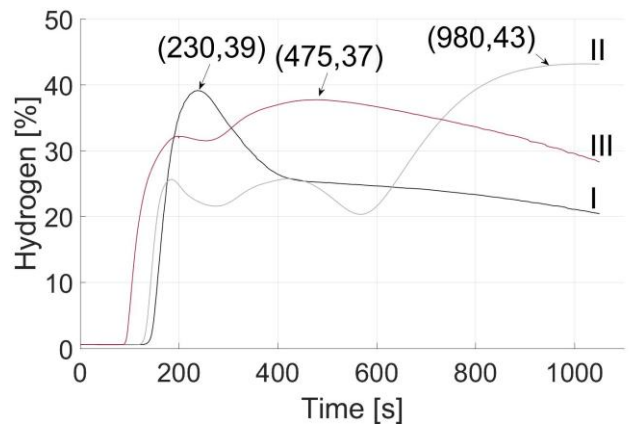

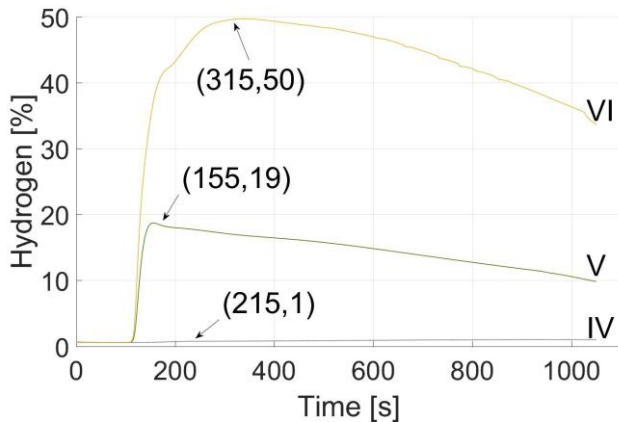Fig. 8. Hydrogen content for coatings I, II and III during the test

Fig. 9. Hydrogen content in the gaseous atmosphere, during the test, for coatings IV, V and VI

Maximum hydrogen content in gases emitted from coatings IV, V and VI equals, respectively: 1%, 19% and 50 %. In case of coating VI the highest peak value of the hydrogen content – out of six tested coatings – is seen.
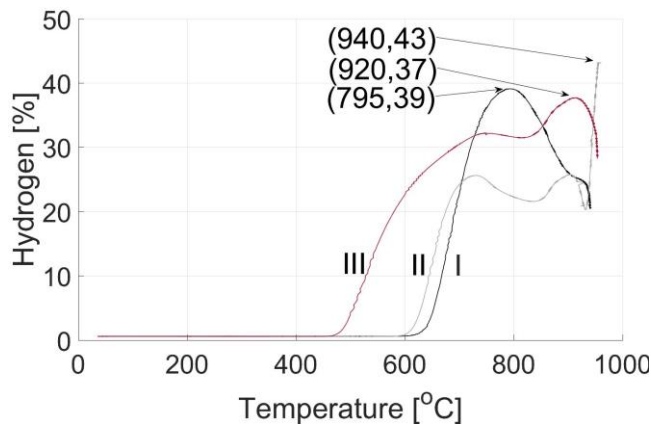

Fig. 10. Hydrogen content in gases emitted from coatings I, II and III, at a temperature increase.

4.2. Percentage hydrogen content in emitted gases during heating samples of coatings I, II and III

In case of coating, I the maximum value occurs at a temperature of 795 °C and equals 39%, for coating II – at a temperature of 940°C and equals 43%, while for coating III – the maximal peak occurs at a temperature of 920°C and equals 37%.
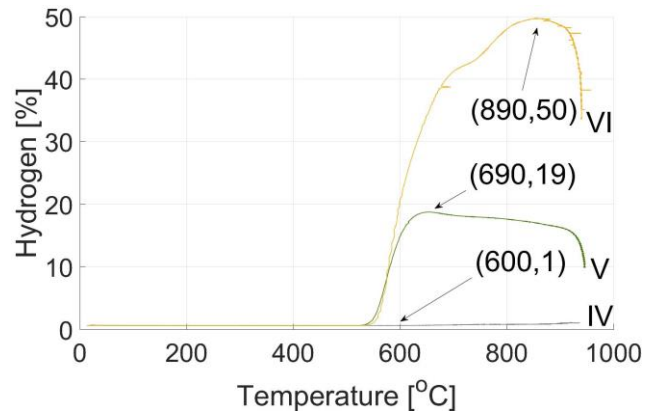

Fig. 11. Hydrogen content in gases emitted from coatings IV, V and VI

4.3. Percentage hydrogen content in emitted gases during heating samples of coatings IV, V and VI

The maximal hydrogen content (50%) in emitted gases characterises coating VI, its peak occurs at a temperature of 890 °C, the lowest hydrogen content (1 %) – characterises coating IV, while at a temperature of 690 °C coating V emits maximum 19% of hydrogen.

Pathways of the hydrogen emission from tested coatings are presented in figures 12 and 13.
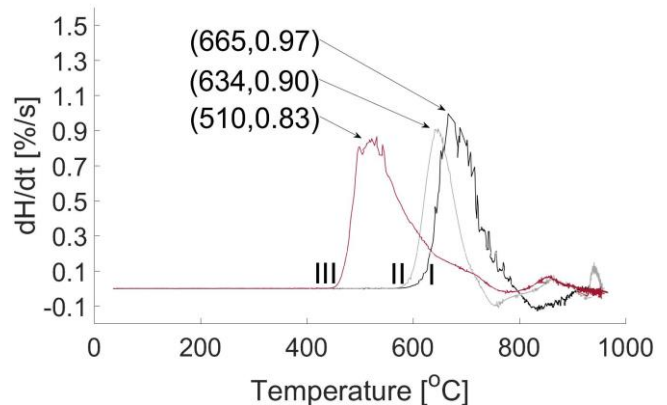

Fig. 12. Intensity of the hydrogen emission from coatings I, II and III, heated during the test of their gas forming tendency.
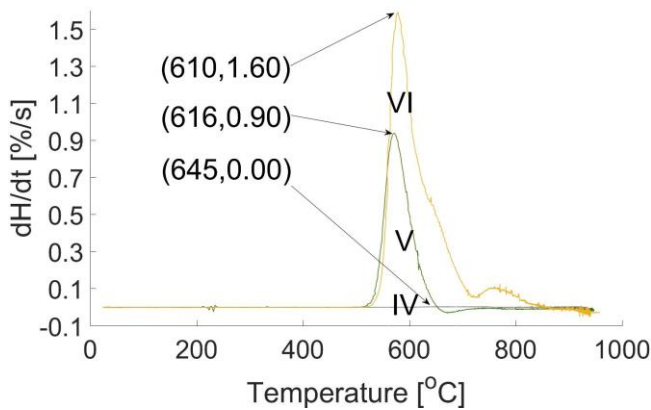
Fig. 13. Intensity of the hydrogen emission from coatings IV, V and VII, heated during the test of their gas forming tendency.

Maximal rates equal from 0[%/s] for coating IV to 1.6 [%/s] for coating VI. These values, for the remaining coatings, do not exceed 1[%/s]. Maximal increases of the hydrogen content occur at temperatures above 600 °C. The only exception constitutes water-soluble coating, for which this characteristic temperature is above 500 °C.

4.4. Oxygen in emitted gases

Characteristic pathways of oxygen content changes in gases during the gas forming tendency tests, are presented in figure 14.
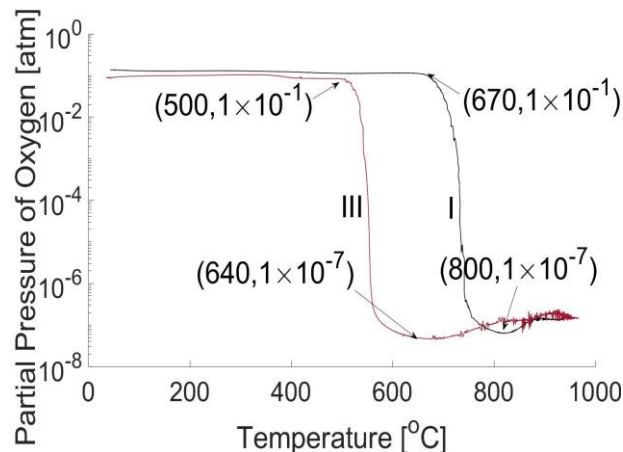

Fig. 14. Partial pressure of oxygen in relation to the temperature of coatings I and III subjected to tests.

The diagram presents measurements of oxygen content for coating I diluted by alcohol and coating III diluted by water. Out of 6 tested coatings these results were selected as examples. In both cases oxygen stabilises its content at the level of $1 \cdot 10^{-7}$ [atm.]. This stabilization occurs for coating I at a temperature of 800°C, while for coating III already at a temperature of 640°C. This indicates a probability that at the boundary of the foundry alloy and mould the atmosphere will be without oxygen originated from coatings. At a temperature above 800°C a small increase of oxygen content occurs for coating I.

4.5. Carbon oxide content

Changes of the oxygen content in gases during the tests of the gas forming tendency are logically confirmed by the measured carbon monoxide content, shown in figures 15 and 16 and presented directly in a voltage signal form during the measurement.

Results of measurements with using the Figaro sensor were recorded as voltage signals, and than calculated according to the producer's instruction [6]. The signal from the FIGARO sensor in the flow-through micro-chamber was recorded in a form of voltage U_o of measuring bridge. CO content was calculated according to equation (1):

$$CO = ((U-U_0)/U_0)^{-2} \text{ [ppm]} \qquad (1)$$

where: U=5[V]

U_o – recorded voltage of measuring bridge.

During each test of the gas forming tendency carbon monoxide was evolving. The calculated results are shown in figure 17.
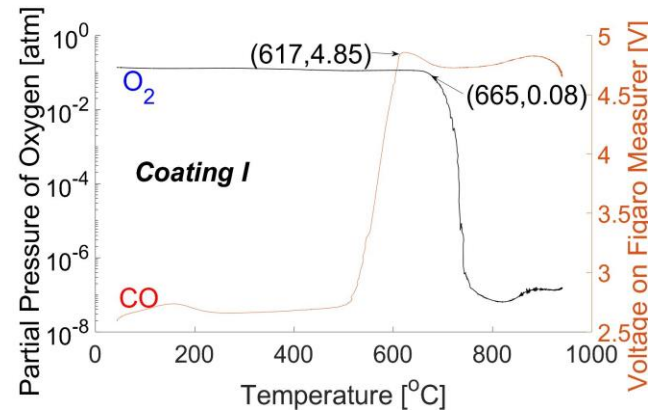

Fig. 15. Pathways of CO content changes during heating – in relation to a parallel decreasing oxygen content, for coating I
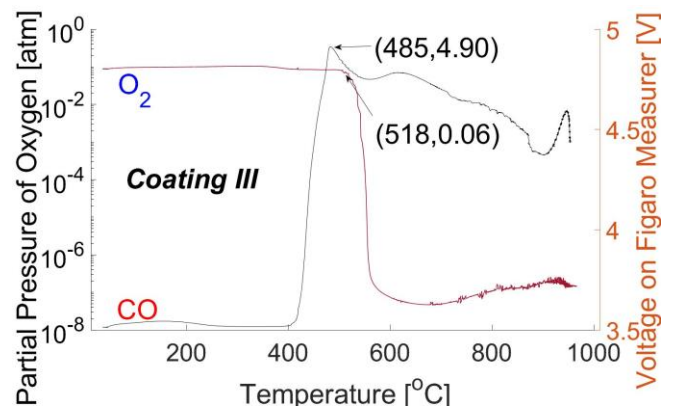

Fig. 16. Pathways of CO content changes during heating – in relation to a parallel decreasing oxygen content, for coating III

The analysis of results allows to conclude that the highest amount of carbon monoxide is evolving from coating III at a

temperature of approximately 485 °C; (3165ppm). Significant amounts of carbon monoxide are also evolving from coating II, but at a higher temperature – app. 600 °C; (2718ppm). For some coatings a secondary increase of carbon monoxide content occurs at a higher temperature. The second increase in carbon monoxide release requires further research.
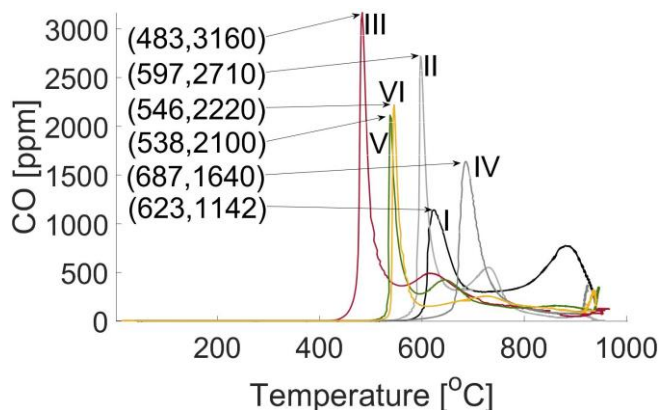

Fig. 17. Calculated CO content emitted from coatings during their heating (coatings I-VI)

5. Conclusions

1. Investigated protective coatings are foundry materials of a wide range of gases emission tendency during heating. They can be classified as having the gas forming tendency from a very low to a very high. Measured values of gas volumes are within a range: 3.60 - 26.19 cm^3/g. The smallest gas volume was emitted from coating IV, while the highest from coating III.

2. An important parameter characterising coatings is the rate (intensity) of gases emission. Too high rate, even at smaller volumes of gases, can cause casting defects of a gaseous origin.

3. The hydrogen content in gases emitted during the tests of the gas forming tendency varies within the range from 1% (coating IV) to 50% (coating VI) atmosphere. Hydrogen is emitted at a temperature significantly above 600 °C. The coating with a water solvent is an exception since it is emitting hydrogen at above 500 °C.

4. Minimal oxygen contents are stabilizing at a very similar level ($1 \cdot 10^{-7}$), but at different temperatures. Alcohol coating I stabilizes its decrease at 800 °C, while water coating III at 640 °C.

5. During each test carbon monoxide was evolving from heated coatings. The results indicate that the highest tendency to evolving carbon monoxide characterizes coating number III, and the intensity peak occurs at a temperature of app. 485°C, (3165 ppm). A significant amount of carbon monoxide emits also from coating number II, but at a higher temperature - app. 600°C, (2718ppm). For some coatings a secondary peak of carbon monoxide increase is seen at high temperatures.

Acknowledgment

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