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GAS EVOLUTION RATES OF GRAPHITE PROTECTIVE COATINGS IN DEPENDENCE ON THE APPLIED SOLVENT AND KIND OF ATMOSPHERE

The results concerning emission of gases from two commercial graphite protective coatings for moulds and cores (water and alcoholic) are given in the hereby paper. Investigations were performed in two systems. One of the systems was corresponding to conditions occurring inside the mould cavity immediately after its pouring with liquid metal (Method 1), while the second was simulating conditions deep inside the mould at a certain distance from the casting (Method 2). Investigations were carried out in the CO_2 atmosphere and in the air. The water protective coating generated 1.5 to 3 times larger volume of gases than the alcoholic coating (in dependence on the measuring method and atmosphere). The smallest differences occurred in the air atmosphere, while the largest in the CO_2 atmosphere.

Keywords: emission of gases, protective coatings, environmental.

1. Introduction

Protective coatings are deposited on surfaces of moulds or cores cavity in order to prevent moulding sands burning-on to castings, to improve casting surface quality and to protect against the liquid metal penetration inside the mould [1- 4]. Coatings can be in a solid state (powders), liquid state or can occur in a form of paste. Liquid coatings, in which alcohol, the most often isopropyl alcohol, is a solvent are mainly applied for iron castings. These coatings are dried by evaporation or burning of a solvent and such operations contribute to the emission of harmful substances, including volatile organic compounds (VOC). The alternative, recommended by the European Union, is the substitution of alcoholic protective coatings by ecological water coatings [5, 6]. Apart from the fact that they are environment friendly, they additionally warrant: an increased work safety (there is not a direct fire hazard as at burning the alcohol based protective coatings), a significant reduction of harmful substances from the VOC group, economical benefits since the price of water is much lower than the price of alcohol. Usually, the natural flake graphite, which should contain maximum 12-15% of ashes, 3% of volatile compounds and 1% of moisture, is applied.

Protective coatings constitute the second, after a binder, source of gases in a mould during its pouring with liquid metal. Liquid protective coatings consist the most often of 3-4 components: refractory grain matrix, binder (dextrin, waste sulphite liquor), density stabilizers (these could be the same substances as binders) and a solvent (water or alcohol). As one of the components of the refractory matrix protective coating for iron castings the graphite - which at high temperatures emits gases - is applied. The graphite which contains volatile substances and ressidual of water of water (especially in case of water coatings) can be a source of gases. In addition, carbon of the graphite causes reduction of water vapour and CO_2 , which generates gases [7-9].

From the point of view of the produced castings quality, not only an amount but also a kinetics of gasses emissions, precisely the time from the moment of pouring the mould with metal and the maximum pressure of gases (in order to not exceed the metalo-static pressure), are important. The fact that the pressure of gases generated from the protective coating will be added to the pressure of gases originated from the thermal decomposition of a binder or lustrous carbon formers, thus increasing the danger of the occurrence of casting defects (penetrations, burn-ons), should be considered. A determination of these gases composition is essential when the health of employees and the environment condition is taken into consideration.

In accordance with the EU recommendations the efforts to develop more and more new ecological materials for foundry practice (including water protective coatings for moulds and cores) are undertaken. These solutions should ensure a work safety and should be environment friendly.

Measurements of gases generated from the protective coating were performed by two methods: the method based on the standard BN-76/4024-05 (however not actual any more) modified in the Laboratory of Environment Protection (Method 1) [10], and the method developed in the Laboratory of Foundry Moulds Technology [11, 12] (Method 2) of the Faculty of Foundry Engineering, AGH. Both methods are comparative methods performed under various conditions, allowing to estimate materials, applied in foundry practice, from the point of view of their gas evolution rates.

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2. Materials applied in investigations

The subject of investigations constituted two commercial protective coatings applied for moulds and cores, marked as follows:

- Sample 1 – water zirconium-graphite coating, applied for castings of grey and white cast iron.
- Sample 3 – alcoholic zirconium-graphite coating, applied for castings of spheroidal, high quality cast iron;

3. Methodology of investigations

3.1. Testing of gas evolution rates of coatings

Tests of gas evolution rates of coatings: water - „Sample 1" and alcoholic – „Sample 3" were performed by two methods. Both methods belong to the group of laboratory methods. Measurements are performed in the CO_2 or air atmosphere. As time goes by, the atmosphere oxidizing potential - in both methods - decreases. Thus, conditions in reactors are coming nearer to conditions which are in the mould cavity, made of moulding sands bound by organic binders or moulding sands with bentonite and lustrous carbon carrier, after its pouring with liquid metal.

3.1.1 Method 1

A ceramic boat with the tested sample (previously dried for 3 hours at a temperature of 110° C) of a mass of app. 1 g (with the accuracy: ±0.01 g) is placed in the tubular furnace (quartz tube), outside the heating zone. Then the furnace is switched on and heated up to a temperature of 1000°C (Fig.1). When this temperature is obtained the reactor is blown through by CO_2 for 5 minutes. After this time the valve introducing CO_2 is closed and the peristaltic pump is switched on to provide the proper negative pressure in the reactor. Then the tested sample is introduced into the reactor, where it very fast achieves the measuring temperature of 950°C. In case of the carbon presence, at not satisfactory oxygen presence, the reduction of CO_2 to CO occurs. This is the so-called Boudouard's reaction, which occurs within the temperature range: 400-950°C:

$$CO_2 + C = 2CO.$$

As the result of this reaction the volume of gases increases two times. Since the pump, carrying away gases from the reaction tube, is continuously operating uphold the constant negative pressure, equal to its initial value, the excess of gases is pumped out and its volume determines the gas evolution rate of the tested sample.

Fig. 1. Research stand for measuring the gas evolution rate of materials (acc. to Method 1), Laboratory of Environmental Protection

3.1.2 Method 2

The tested sample, previously dried at a temperature of 110° C (for 3 hours) of a mass of app. 5 g is placed in the special sampler (Fig. 2) made of heat resistant steel, which has a unilateral lock. On the other side the tester has a tight valve (B4). The closing valve allows to direct the gas emitted from the sample to the measuring system. The same valve, after disconnecting from the sampler, allows to exchange the tested sample (P). In order to decrease the inner volume of the sampler, the insert of heat resistant steel (B3) is placed inside it. Outside the sampler surface, in a pipe, there are thermoelement conduits connected to the temperature recorder. The air filling the sampler due to a temperature increase, increases its volume and together with the emitted gases is directed to the volume measuring system (V_{total}).
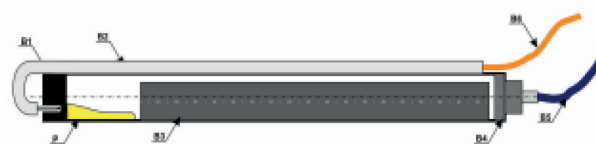

Fig. 2. Sketch of the measurement test probe

In order to determine the real volume of gases emitted from the sample, the calibration of the sampler based on measuring only the air volume being in the sampler - heated to the given temperature (V_p) - should be performed. The real volume of gases emitted from the given sample will be equal to:

$$V_r = V_{total} - V_p$$

4. Results and their discussion

Amounts of gases emitted during the thermal decomposition of protective coatings samples at temperatures 950 - 1000°C in dependence on time, for all tested samples (by both Methods) are given in Table 1, together with the gases emission rates.

Graphical presentation of the results obtained by Method 1 is given in Fig. 3 (emission) and in Fig. 4 (kinetic), while the results obtained by Method 2 in Fig. 5 and Fig. 6.
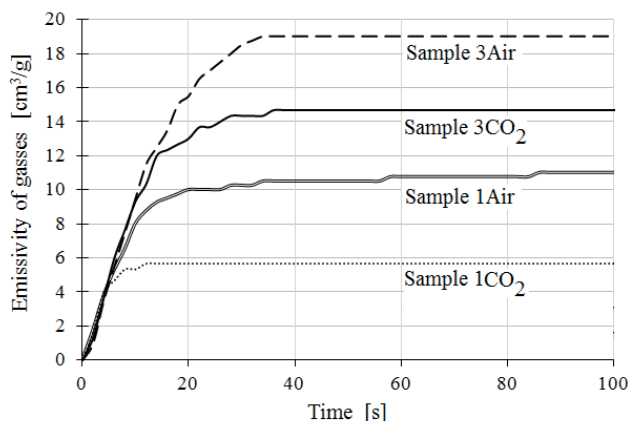
Fig. 3. Volumes of gases emitted from the tested protective coat in dependence on time (test in CO_2 and air atmosphere, Method no 1)
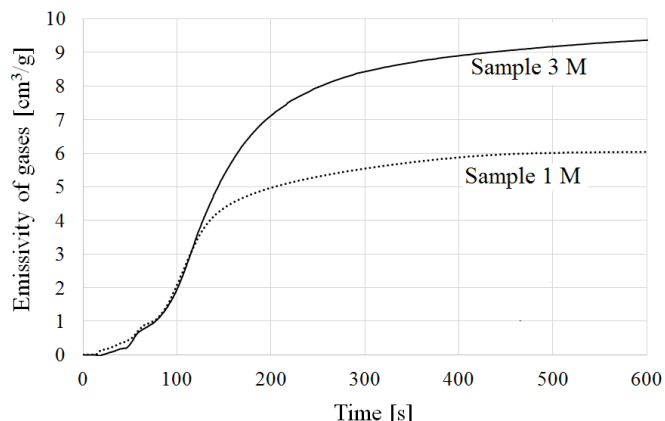

Fig. 5. Volumes of gases emitted from the tested protective coat in dependence on time (test in air atmosphere, Method no. 2)
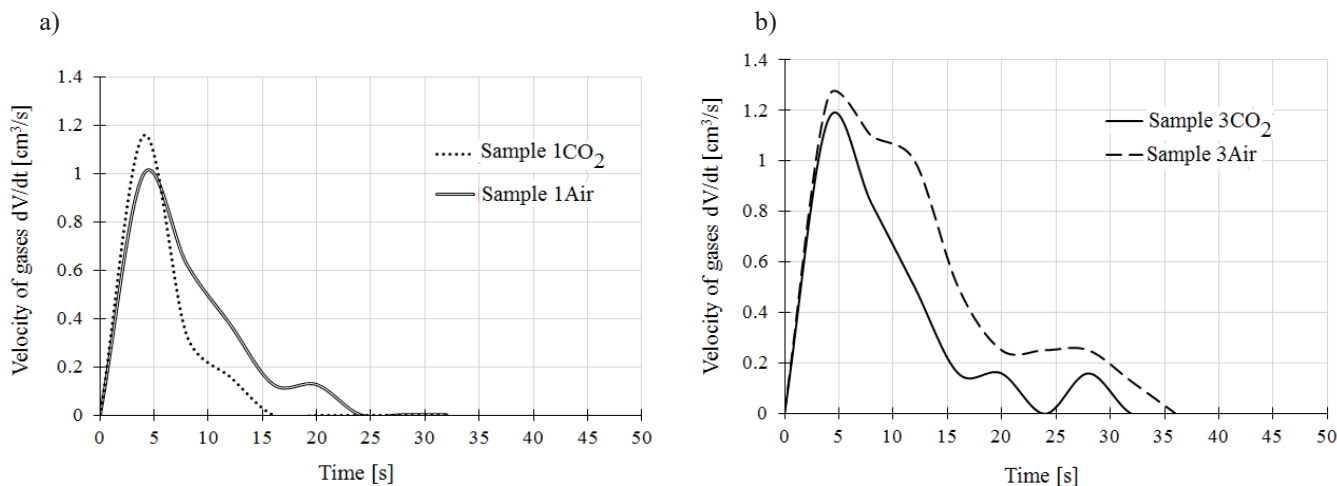
a)

b)

Fig. 4. Velocity of gases emission from the tested protective coat: a) sample 1, b) smaple 3 (test in CO_2 and air atmosphere, Method no. 1)

TABLE 1

Volumes of emitted gases (recalculated for 1 g of a sample) from protective coatings and parameters of the maximum emission rates

Protective coat	Total volume, V [cm³]	Maksimum I		Maksimum II		Maksimum III	
		Time, t [s]	Velocity dV/dt [cm³/s]	Time, t [s]	Velocity dV/dt [cm³/s]	Time, t [s]	Velocity dV/dt [cm³/s]
Sample 1CO_2	5.6	4	1.18				
Sample 1Air	10.75	4	1.0				
Sample 1 M	6.1	15.5	0.025	56	0.035	109	0.065
Sample 3CO_2	14.6	5	1.2				
Sample 3Air	19	4.75	1.28				
Sample 3 M	9.26	-	-	108	0.044	239	0.083

Sign in the table:
CO_2 – the sample tested by the Method 1 in CO_2 atmosphere,
Air – the sample tested by the Method 1 in air atmosphere,
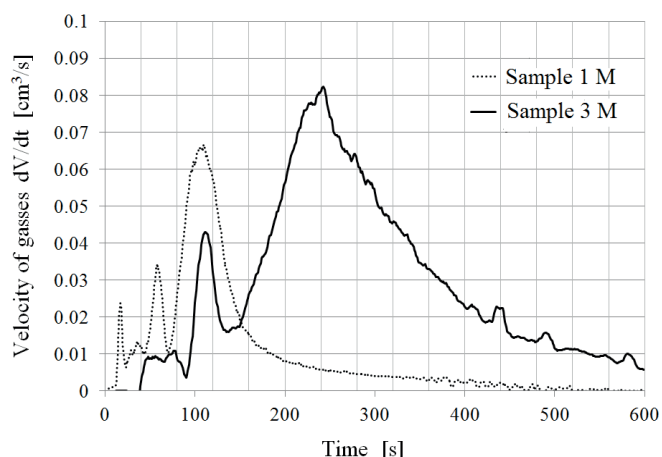M – the sample tested by the Method 2.

Fig. 6. Velocity of gases emission from the tested protective coat (test in air atmosphere, Method no. 2)

4.1. Effect of the atmosphere

Admittedly, both atmospheres (CO_2 and air) applied in the reaction tube (Method 1) are oxidising, but the air containing 21% of oxygen is a stronger oxidiser.

The water coating (Sample 1) as well as the alcoholic (Sample 3) demonstrated significantly higher (nearly twice) emissions of gases in the air atmosphere. On the other hand the maximum emission rate of gases for both atmospheres and both samples was comparable (within the range: 1.0 – 1.28 cm^3/s). Samples were achieving this rate after 4 -5 seconds from the moment of their placement in the heating zone of the reactor. In practice, the gases emission time was from 12 s (for Sample 1 in CO_2) to 38 s (for Sample 3 in the air). Only one maximum occurred in the curve describing the dependence of the gas emission rate on time (Fig. 4).

4.2. Influence of the measurement method

Only in event of the water coating tested in CO_2 atmosphere (Sample 1CO_2) amount of gas emissions measured by Method 1 was comparable to the emissions measured by Method 2.

While in the other tests already obtained significant differences in the amount of the emission of gases measured by Method 1 and Method 2.

The heating process of the sampler containing the sample is much slower in Method 2 and therefore the measurement takes approximately 10 minutes. In the curves of the gases emission rates, for water coating, occurred 3 maxima and for the alcoholic coating are 2 maxima, shifted in time, versus each other. These maxima, for the water coating, occurred much earlier (at a lower temperature) than for the alcoholic coating. Probably the first maximum is the result of evaporation of physically bound water (practically doesn't exist for the alcoholic protective coating), while the second maximum originates from emission of chemically bound water. Maximum III, the highest for both coatings, is the result of the generation of gases in the burning process of the carbon compounds. Since the oxygen amount in the closed sampler is

limited, it can occur that the burning process is not total and the further volume increase of gases is the result of the thermal decomposition of the sample (pyrolysis), when smaller amount of gases is formed than in the case of burning. Probably this is the reason that in Method 2 smaller volumes of gases are generated.

The water protective coating generated 1.5 to 3 times larger volume of gases than the alcoholic coating (in dependence on the measuring method and atmosphere). The smallest differences occurred in the air atmosphere, while the largest in the CO_2 atmosphere. It is difficult to provide - right now - the reason of this effect, since the qualitative and quantitative composition of both coatings is not fully known (e.g. graphite kind and amount).

5. Conclusions

The preliminary measurements of the gases emission from the protective coatings subjected to a high temperature influence in different atmospheres, performed by means of two methods allow to formulate several conclusions;

1. Since both types of measurements are performed under oxidising conditions and in the final phase of the process we are dealing the pyrolysis, the attention should be drawn to finding whether the oxygen amount in the reactor is sufficient for the total burning of the sample. Thus the proper selection of the sample mass is required.
2. Both methods have good and bad points. However, they supplement each other to a considerable degree and when the results of both methods are known, the effects occurring in the mould can be described better.
3. It can be assumed that Method 1 simulates effects occurring at the boundary: liquid metal – moulding sand, it means the boundary where is the coating (shock heating).
4. In case of Method 2, where the heating process is much slower, it can be assumed that it is the simulation of the effect occurring in the mould after its pouring with liquid metal and transportation of heat deep into the mould.
5. Generally the water protective coating generated much less gases than the alcoholic coating.

REFERENCES

[1] A. Baliński, Protective and separating coatings, used for molds and cores sands. Foundry Guide, Krakow, Poland, in polish (2013).

[2] A. Pribulová, P. Futaš, A. Rosová, P. Demeter, D. Baricová, Metalurgija **52**, 51 - 54 (2013).

[3] U.C. Nwaogu, N. S. Tiedje, Material Sciences and Application **2**, 1143 -1160 (2011).

[4] A. Kmita, J. Zych, M. Holtzer, J. Mocek, S. Piasny,

Metalurgija **55**, 589 - 592 (2016).

[5] Reference Document on Best Available Techniques in the Smitheries and Foundries Industry, European Commission, (2005).

[6] J. Campbell, Complete Casting Handbook, Elsevier (2011).

[7] A.M. Abdelwahab, A. Aowal, M. K. Joyce, S. N. Ramrattan, AFS Transactions **11**, 367 - 379 (2009).

[8] A. Ch. Psimenos, S. Wendl, G. Eder, Giessersi **1**, 25 - 29

(2007).

[9] G.L. Di Muoio, N. S. Tiedje, B. B. Johansen, 71st World Foundry Congress, Bilbao, 19 - 21 May (2014).

[10] Polish Standard no. BN-76/4024-05.

[11] Ł. Jamrozowicz, J. Zych, T. Snopkiewicz, Archives of Foundry Engineering **13**, 45 - 50 (2013).

[12] J. Zych, J. Mocek, T. Snopkiewicz, Archives of Foundry Engineering **14**, 105 - 109 (2014).