Kinetics of Gas Emission from Heated Moulding Sands Together with the On-line Assessment of H_2 and O_2 Fractions - New Investigation Method

J. Mocek *, J. Zych

AGH - University of Science and Technology, Faculty of Foundry Engineering,
Reymonta 23 Str., 30-059 Kraków, Poland
*Corresponding author. E-mail address: jmocek@agh.edu.pl

Abstract

The new investigation method of the kinetics of the gas emission from moulding sands used for moulds and cores is presented in this paper. The gas evolution rate is presented not only as a function of heating time but also as a function of instantaneous temperatures. In relation to the time and heating temperature the oxygen and hydrogen contents in evolving gases was also measured. This method was developed in the Laboratory of Foundry Moulds Technology, Faculty of Foundry Engineering, AGH. Gas amounts which are emitted from the moulding sand at the given temperature recalculated to the time unit (kinetics) are obtained in investigations. Results of investigations of moulding sand with furan resin are presented - as an example - in the paper.

1. Introduction

The impact of a high temperature of liquid metal on the casting mould leads to increasing gas (air) volume, which fills the mould cavity and pores of the sand mould. This heating leads to decomposition and gasification of many moulding sand components, mainly binders. In the casting practice, gases generated while filling the moulds and during castings solidification constitute one of major problems which impedes the production of castings without defects.

The source of gases generated and increasing their volume while heating, depends on the mould production technology. Most frequently, in the sand mould technology, these are organic binders, and therefore the measurements for the moulding sand with resin are presented in this paper as an example.

To assess the inclination of the aforementioned materials to generate gases, two groups of methods are applied: one refers to tests performed under laboratory conditions [1, 3], while the second – to tests performed under conditions similar to the ones occurring directly in the mould [4, 6]. In the first case, the sample of the material tested (e.g. moulding sand) is heated in a sealed flask placed in a tubular furnace. The evolving gas volume is measured while heating the moulding sand sample to the selected temperature [1, 3]. According to the second method [4] and its newer variations [6], the sample of the tested moulding sand, forming some sort of a core, is covered with liquid metal in the

mould. During the heating, the volume of gas evolving from the sample is measured. All measurement methods, have their advantages and disadvantages. Neither of them, in the current solution, allows for determining gas evolution kinetics as a function of their temporary temperature. Moreover, there is a justified risk that during the measurements, the volume of gases produced by the heated material is summed up with the volume increase of the air or protecting gas that fills the measurement flask (in the laboratory test), or 'voids' in a porous sample (intergranular voids).

The new method, in which sources of potential measurement errors were eliminated and conditions for studying the gas evolution kinetics as the temperature function were created, is presented in the hereby paper. Volumes of emitted gases are recorded in the real time. In order to identify continuously the atmosphere composition, also in the real time, the oxygen and hydrogen contents were measured in emitted gases.

2. Methodology of investigations

Gas evolution rates were measured in the special laboratory station for testing the gas evolution kinetics and for assessing of gas evolution volumes from moulding and core sands (Fig. 1). The measuring stand consists of the tubular silite furnace PSR-1 (A2) closed at one side (A1) with a temperature control (A3), and the feeder system (A4), in which the flask with the moulding sand sample and built-in thermo-element type S (B) are placed. There is also the pellistor sensor for measuring the hydrogen content (R) and lambda probe (S), differential manometer (C), container with measuring liquid (D1) with the controlled level of liquid outflow (D2), laboratory scale (D3) and multimeter Agilent (E) - recording data. All measurement results are recorded in the computer PC (F) [4]. Due to heating the measuring flask with the moulding sand sample, gases are emitted. These gases are transported via thin hoses of Ø 3mm to the measuring system. The measuring system consists of the connected in series: pellistor bridge measuring the H_2 content and the lambda probe measuring the O_2 content. Gases are then flowing through the connected in parallel differential manometer and are directed to the container above the measuring liquid surface (D1). This increasing gas volume causes liquid pushing out from the container. The pushed out water is continuously weighted and the results recorded in the computer. Knowing the weight of the flown out liquid the volume of gases emitted during the sample heating can be found. The multimeter Agilent records the temperatures of the tested sample, voltages of the: pellistor bridge, lambda probe and manometer. The data are written in the format .xlsx. Sampling frequency is every 0.5 s for a period ~1000 s and the furnace temperature is maintained at the level of 1000 °C.

The measuring flask (tester) seen in Figure 2 was made of heat resistant steel. Outside the flask there is the guiderail (B2) with ceramic insulators. The measured moulding sand portion (P) is poured into the flask. In order to decrease the measuring flask volume a rod is placed inside it (B3). The thermocouple, S type, being inside the flask continuously measures temperatures. The flask is tightly closed by reduction with quick-joint (B4), used for tight joining of hoses enabling flowing of the emitted gases (B5) [7].

Due to the heating of the measuring flask with the moulding sand sample (placed in it) gases are emitted and flowing to the measuring system.
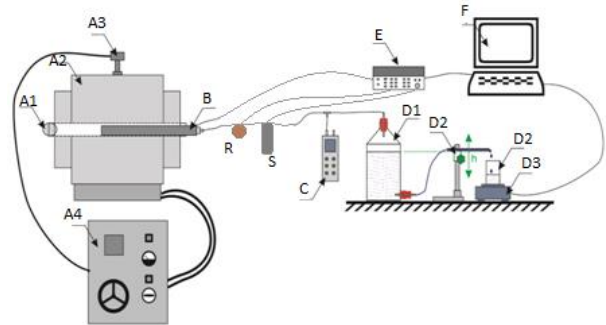

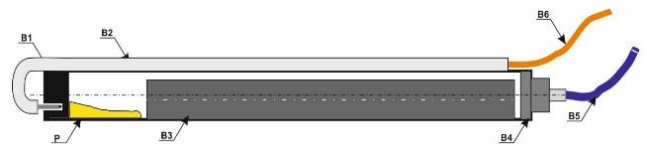Fig. 1. Research stand for investigations the gas evolution kinetics [7]

Fig. 2. Measuring flask (moulding sand tester) [7]

The pellistor gas sensor measures the hydrogen content and provides the answer in Volts. According to the producer Webside [5] the voltage increase in the sensor system equals 0.005 V/1 % of hydrogen (the value described by line 1 in Figure 3) [6].
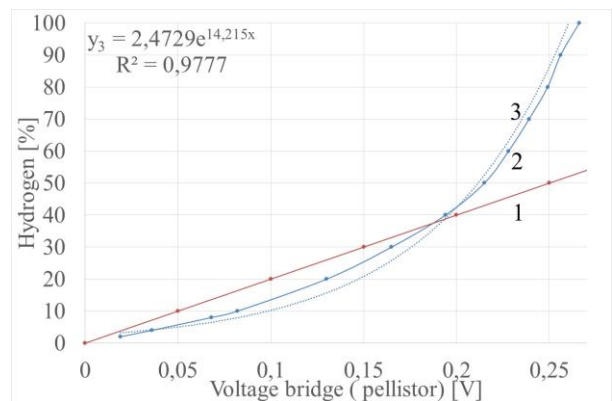

Fig. 3. Variants of the calibration of the pellistor bridge voltage: 1 - Calibration acc. to the producer Website [5], 2 - Calibration performed by the producer, A. Rejowicz, 3 – Acc. to the equation adjusted to the real calibration curve

Previous measurements by the pellistor sensor of the maximum hydrogen content in gases [10], as compared with other methods, were underrated, and therefore the producer - A. Rejowicz, (Sensor Gaz Tychy) experimentally scaled indications, (curve 2, Fig 3). The adjusted exponential equation (curve 3, Fig. 3) much better reproduces the character of the real hydrogen content. The correlation coefficient square: R^2=0.9777. Recalculating of the

hydrogen content acc. to the selected multinomial equation shown in Figure 4 allows to achieve the coefficient R^2=0.9994. Thus, the measurements were recalculated according to this equation.
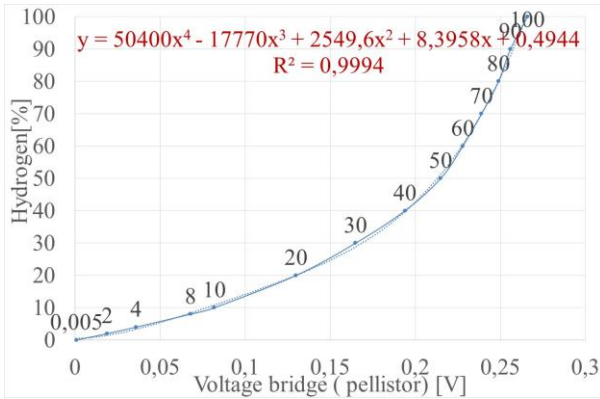

Fig. 4. Characteristic of the pellistor bridge with the multinomial equation adjusted to recalculating the hydrogen content, of the correlation coefficient R^2 = 0.9994

The oxygen content in emitted gases was calculated according to the Nernst equation [9]. The work form of the Nernst equation is presented in equations 1 and 2:

$$log\alpha_O = \log(0,21;10) + \frac{4*V*F}{19,14*T} \qquad (1)$$

$$\alpha_O = Exponentiation(10; log\alpha_O) \qquad (2)$$

where:

α_O – oxygen content in a mixture [atm],
V   – voltage [V],
T   – absolute temperature [K],
F   – Faraday constant F=96500 [C/mol].

3. Investigations results

Results written in calculation sheets allow for the accurate and detailed analyses in various aspects. The measured amounts of the emitted gases are presented either in relation to the time of tests or in relation to the instantaneous temperature.

3.1 Measurements of gas evolution volumes and rates

The optimal amount of the weighted portion equals 5 g. Figure 5 presents the process of gases evolution from the moulding sand with furan resin during heating. Curve 1 Fig. 5 presents the volume of gases flowing out from the flask during its heating (maximum equals 65 cm^3/5g). After cooling the sample in the flask to the ambient temperature the next measurement was performed (curve 2, Fig. 5). The flask without a sample was heated to measure the volume increase of the air present in the

sampler. The volume increase of the air heated to 950°C was equal 15 cm^3/5g. The real gas evolution rate of the moulding sand was calculated from the difference of these two values (curve 3, Fig.5). The total, real gas evolution rate was 50 cm^3/5g.

Increasing volumes of gases during heating, are presented in the real time of the test. During initial 50 s of the measurement gases are not yet emitted but the air is increasing its volume. Figure 6 presents emission of gases from the moulding sand with resin in relation to the instantaneous sample temperature for the chosen procedure.
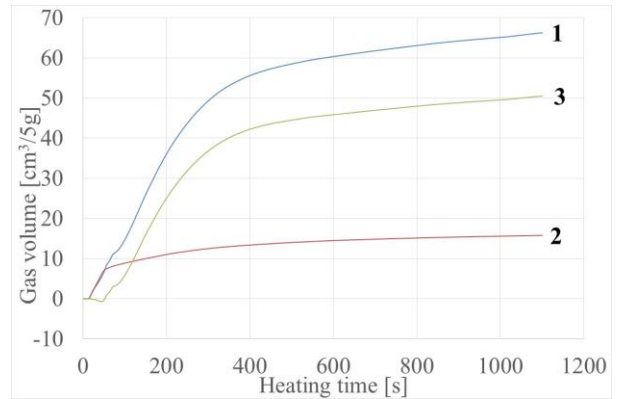

Fig. 5. Gases emissions from the moulding sand with resin: 1 – Total volume of gases flowing out of the flask, 2 – Volume increase of the air heated in the flask, 3 – Volume of gases originated from the moulding sand
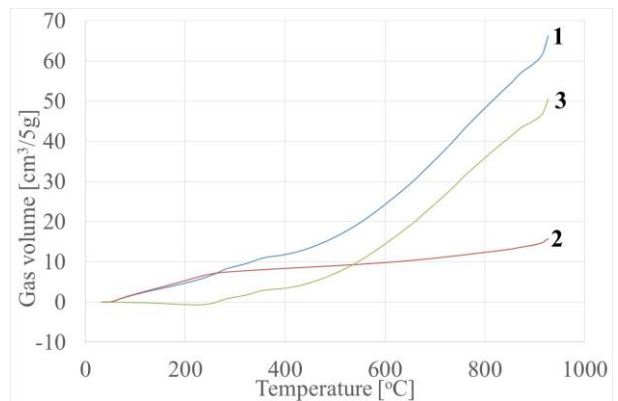

Fig. 6. Emission of gases in relation to the sample temperature: 1 – Total volume of gases flowing out from the flask, 2 – Volume increase of the air heated in the flask, 3 – Volume of gases originated from the moulding sand

The emission of gases from the moulding sand occurs at temperatures above 250 ^{o}C, as seen in curves 1-3, Fig. 6. To determine the specific gas evolution rate for 1g of the moulding sand, the measured values were divided by 5. This specific evolution gas rate is shown in Figure 7, as curve 1. For this particular moulding sand it equals 10 cm^3, which classifies this moulding sand as being a gas emitter [2]. During heating the moulding sand three maximal intensities of gases emissions are seen, from 0.05 to 0.06 cm^3/s, from one gram of the moulding sand (Fig. 7).

More accurate and valuable information are obtained when changes in gas evolution rates are related to the instantaneous temperature, presented in Figure 8. Maximum rates occur at temperatures: 260, 330 and 580 $^{\circ}$C.
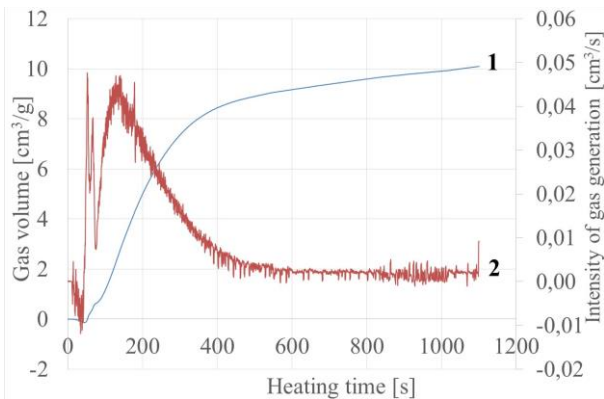

Fig. 7. Kinetics of the gas evolution during heating: 1 – Gases emission from the moulding sand, 2 – Gases evolution rates (kinetics)
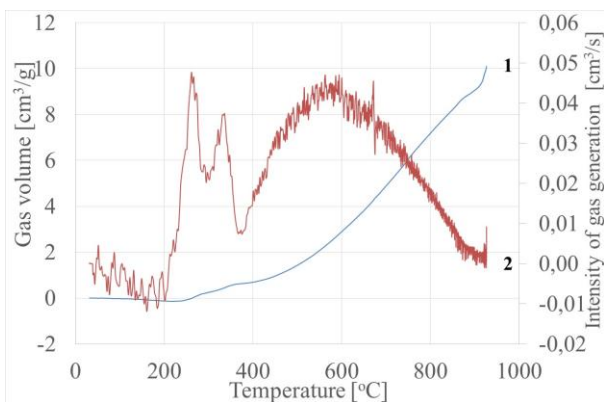

Fig. 8. Kinetics of the gas evolution related to the sample temperature: 1 – Pathways of gases emission from the moulding sand, 2 – Gases evolution rates (kinetics)

In the technological processes at the casting production, not only the total volume of gases emitted from the moulding sand is important. The kinetics of this process, namely, how quickly these gases are emitted and at what temperatures this evolution is the most intensive, is very important. In addition, the composition of the gas atmosphere is important since it decides on the castings surface quality and on various surface defects. On account of surface defects related to reoxidation the knowledge concerning oxygen content in emitted gases is also important. The developed research method allows to determine these values. It is seen that gases are the most intensively emitted in the first minute of heating, after app. 30 seconds. On curves of the emission pathways occurs also another maximum, large and long-term. At a temperature of app. 850 – 900 °C the emission of gases is finished.

3.2 Oxygen and hydrogen content in emitted gases

Effects observed during measuring the gas evolution rates are: burning and organic materials destructions [1]. Burning of organic materials can occur only in the presence of oxygen, which means oxygen contained in the moulding sand intergranular spaces and in the sampler volume. Thus, these amounts are quite small since the sampler work volume equals 40 cm^3, reduced by the volume of 5 g of the investigated moulding sand. An intensive heating rate of the tested sample and scattering of components subjected to destruction cause that the evolution of all gases occurs simultaneously, and the emitted gases are taken outside the sampler and measured there. On account of this, in a similar fashion as in the casting mould, there is a lack of conditions for the total burning and the destruction process occurs. Amounts of oxygen in the moulding sand are small and its diffusion into the mould from the atmosphere can not occur because of a stream of gases flowing out. Endeavours were undertaken to estimate the critical time and temperature, after exceeding of which the destruction of the tested moulding sand occurs. To this aim the oxygen and hydrogen content in emitted gases were continuously measured. Broadening the evolution rates measurements by measuring the oxygen and hydrogen contents in emitted gases allows for more precise identification of reasons of generating the emitted gases. Figure 9 presents the oxygen and hydrogen contents in gases emitted during the measurement. The signal response of the lambda probe is very fast, of a few milliseconds. The signal response of the pellistor from the explosimetric chamber is delayed by a few seconds, which does not require any correction. The oxygen content in emitted gases from the beginning of the measurement is decreasing. During the first seconds of the measurement a small decrease of the oxygen content, as compared to the normal atmosphere, which equals app. 0,21 atmosphere, is seen. After 230 seconds it is at a minimum, i.e. 1×10^{-4} atm. (Fig. 9, curve 1). When the oxygen content is nearing the minimum hydrogen starts intensive emissions. The beginning of the hydrogen emission occurs in the 200-th second of the measurement. The maximal hydrogen content takes 20 % in the emitted gases after 365 s (Fig. 9/2).
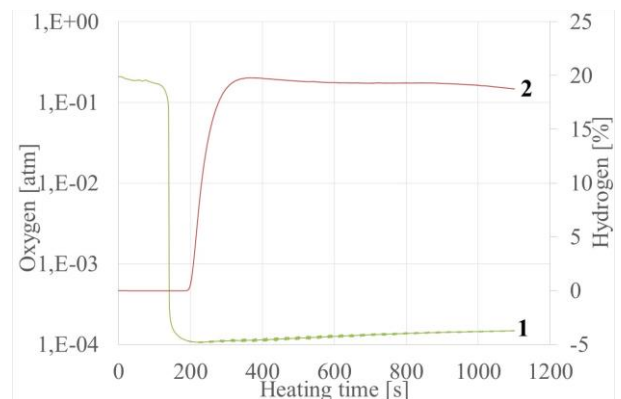

Fig. 9. Hydrogen and oxygen content in emitted gases: 1 - oxygen, 2 – hydrogen

This emission remains at a constant and high level up to the measurement end. The smallest oxygen content in the emitted gases occurs at a temperature of app. 730 °C and remains at this low level at higher temperatures up to the measurement end. The largest amount of hydrogen emits at a temperature of app. 865 °C, which is shown in Figure 10/1.
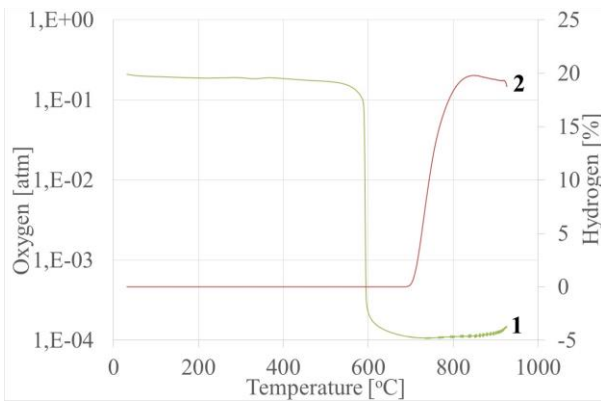

Fig. 10. Hydrogen and oxygen content in emitted gases in relation to a temperature: 1 - oxygen, 2 – hydrogen

Instantaneous rates of emissions of hydrogen and oxygen are presented in Figure 11. Maximum changes of the hydrogen content are equal 0.42 %/s and occur in the 220-th second of the measurement. The highest drops of the oxygen content in the emitted gases are equal $1*10^{-6}$ atm/s and occur after 230 seconds of the measurement (Figure 11/2).
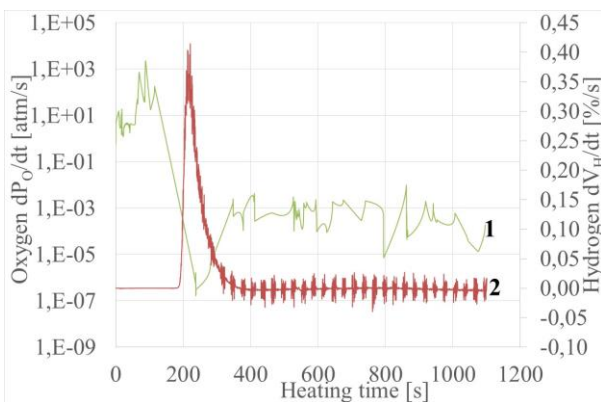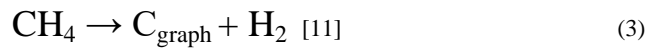

Fig. 11. Changes in the intensity of the hydrogen and oxygen emission: 1 - oxygen, 2 – hydrogen

The measurements results of changes of the hydrogen and oxygen content in relation to the instantaneous temperature of the tested moulding sand is shown in Figure 11.

In the sampler shown in Figure 2 the volume filled with air very limited purpose. The result of this is a small amount of oxygen in the sampler. Disintegration of binders is very quickly carried out in oxygen-free atmosphere. One very likely breakdown process is methane according to the reaction:

$$CH_4 \rightarrow C_{graph} + H_2 \text{ [11]} \tag{3}$$

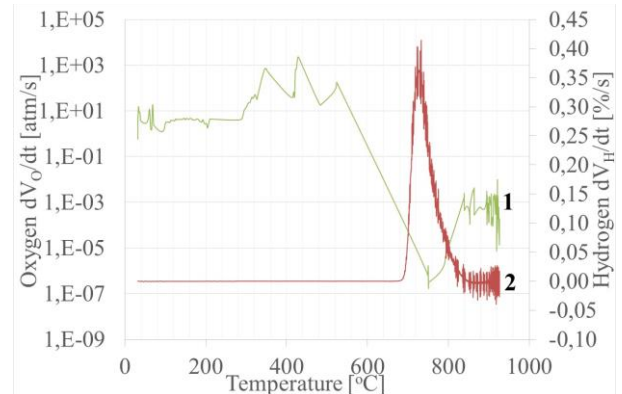The presence of graphite on the element B3 Figure 2 indirectly confirms this thesis.

Fig. 12. Changes in the intensity of the hydrogen and oxygen emission in relation to a temperature: 1 - oxygen, 2 – hydrogen

The smallest amount of oxygen occurs in flowing out gases at a temperature of 750 °C (Fig. 12/1). Maximal hydrogen amount emits at a temperature of app. 730 °C.

4. Conclusions

1. The selected measurement method of the gas evolution rate allows to determine the kinetics of gases emission from heated moulding sands.
2. Measurement results provide detailed data concerning the total gas evolution rate, special gas evolution rate, and the expansion of the heated air contained in empty spaces in the sampler.
3. Measurements of the gas evolution rate are performed under conditions of atmospheric pressure which makes them similar to the conditions under which measurements of the gas evolution rate of the mould poured with liquid alloy, are performed.
4. The furnace heated up to 1000 °C, together with the steel sampler, causes drastic heating of the tested moulding sand, in a similar fashion as in the vicinity of the metal-mould boundary.
5. Results of measurements can be presented in the real time and in relation to the instantaneous temperature of the heated moulding sand.
6. The Lambda probe and pellistor sensor measure in the on-line mode fractions of H_2 and O_2 in gases emitted from the moulding sand.
7. The continuous measurement assigned to the measuring time and temperature of the tested sample allows to observe a complex process of the gas evolution from moulding sands.
8. The measurement of the oxygen and hydrogen contents illustrates directly the time and temperature of the burning

process as well as the beginning of the destruction of the tested moulding sand.

9. The research stand has a high potential of the investigation possibilities concerning gas evolutions from moulding materials.

Acknowledgments

References

[1] Lewandowski, J.L. (1997). *Materials for molds.* Kraków: Akapit. (in Polish).

[2] Lewandowski, J.L, Solarski, W. & Pawłowski Z. (1993). Classification of molding and core terms of gassing. *Przegląd Odlewnictwa*. 5. (in Polish).

[3] Urbanik, E. (1964). *Kinetics of gases from the dried core sand binders for organic.* Unpublished doctoral dissertation, AGH, Department of Foundry, Kraków. (in Polish).

[4] Holtzer, M., Dańko, J., Lewandowski, J.L., i inni. *Station for research of the volume and harmfulness of gases compounds from the materials used in foundry and metallurgical processes.* AGH. Polska.; PL 398709 A1. Zgłosz. 2012-04-02; Biuletyn Urzędu Patentowego ; ISSN: 0137-8015 ; 2013 nr 21, s. 26.

[5] http://www.sensorgaz.com.pl, 2016

[6] Holtzer, M., Waśniewska-Królikowska, D., Bobrowski, A., Dańko, R., Grabowska B., Żymankowska-Kumon, S. & Solarski, W. (2012). Research emissions of hazardous compounds from mass media bentonite and lustrous carbon in contact with the liquid metal. *Przegląd Odlewnictwa*. 62(3-4), 124-132. (in Polish).

[7] Mocek, J., Zych, J., Krubnik, Ł. (2014). Selected issues casting of Al - Si technology in full form, XVII International Scientific - Technical Conference Foundry Non-Ferrous Metals, Kraków – Starachowice. (in Polish).

[8] Żółkiewicz, Z. *The kinetics of thermal decomposition foamed polystyrene pattern and the resulting gases influence on the content of hydrogen, nitrogen and oxygen in gray cast iron, in the "full mold process".* Unpublished doctoral dissertation, AGH, Department of Foundry, Kraków. (in Polish).

[9] Staronka, A., Holtzer, M., Piekarska, M. (1997). *Fundamentals of Physical Chemistry of Metallurgical and Foundry Processes.* Kraków: Wydawnictwo AGH. (in Polish).

[10] Zgondek, A.P. (2013). *Zawartość wodoru w gazach wydzielających się w strefie przesuszonej piaskowej formy zalewanej żeliwem.* Unpublished master thesis, AGH, Department of Foundry, Kraków. (in Polish).

[11] Baller, J., Köppen, M. (1994). *Manual casting defects. Disadvantages associated with the masses of the flasks and prevention.* IKO-Erbslöh Industriemineralien und Kohlenstoffe.