ARCHIVES
of
FOUNDRY ENGINEERING

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

ISSN (1897-3310)
Volume 19
Issue 2/2019

41 – 48

8/2

Multiparameter Assessment of the Gas Forming Tendency of Foundry Sands with Alkyd Resins

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Received 25.03.2019; accepted in revised form 23.04.2019

Abstract

Gas atmosphere at the sand mould/cast alloy interface determines the quality of the casting obtained.
Therefore the aim of this study was to measure and evaluate the gas forming tendency of selected moulding sands with alkyd resins. During direct and indirect gas measurements, the kinetics of gas evolution was recorded as a function of the temperature of the sand mixture undergoing the process of thermal destruction. The content of hydrogen and oxygen was continuously monitored to establish the type of the atmosphere created by the evolved gases (oxidizing/reducing). The existing research methodology [1, 7, 8] has been extended to include pressure-assisted technique of indirect measurement of the gas evolution rate. For this part of the studies, a new concept of the measurement was designed and tested.
This article presents the results of measurements and compares gas emissions from two sand mixtures containing alkyd resins known under the trade name SL and SL2002, in which the polymerization process is initiated with isocyanate. Studies of the gas forming tendency were carried out by three methods on three test stands to record the gas evolution kinetics and evaluate the risk of gas formation in a moulding or core sand.
Proprietary methods for indirect evaluation of the gas forming tendency have demonstrated a number of beneficial aspects, mainly due to the ability to record the quantity and composition of the evolved gases in real time and under stable and reproducible measurement conditions. Direct measurement of gas evolution rate from the tested sands during cast iron pouring process enables a comparison of the results with the results obtained by indirect methods.

Keywords: Gases, Moulding sand, Casting defects, Pressure, Cast iron

1. Introduction

Various processes occurring at the molten alloy–sand mould interface, including gas evolution from moulding and core sands, are the main factors that determine the casting surface quality. Due to the fact that castings are not always subjected to machining, it is necessary to ensure high surface quality in the raw product.

2. Sands with alkyd resins

Sands with alkyd resin binder belong to the group of urethane processes. The binder contains an alkyd resin modified with a drying oil, while the crosslinking compound is polyisocyanate. Alkyd resin sands have an extremely beneficial feature useful under workshop conditions. This advantage is their low sensitivity to the presence of impurities and process disturbances. They are

almost odourless, easy to compact ("self-compacting" of the sand is often sufficient), while additional sand compaction with e.g. hand-operated rammer is necessary only in the facing layer. These sands can be used not only as a backing sand but often also as a facing sand.
In spite of a number of advantages, alkyd resin sands also have some drawbacks resulting mainly from the high viscosity of binder and isocyanate, which makes accurate dosing and correct mixing of ingredients very difficult. The affinity of the drying oil to oxygen present in the air causes the formation of an oxidized layer on the surface of the binder in the container. The interaction between isocyanate and moisture contained in the air creates products of the binding reaction on the surface of the mixed sand [1].

3. Gas forming ability

Under the influence of the high temperature of molten alloy, the components of moulding sands, mainly binder, undergo the process of thermal destruction. One of the consequences of this destruction is the high rate of gas emissions. This in turn significantly affects the casting quality as well as the working conditions in a foundry shop [3, 15]. Therefore our knowledge of the moulding sand behaviour, and particularly of the kinetics and the amount of gases generated, allows us to avoid harmful effects of the sand mould tendency to form gases.

Table 1.
Classification of the gas-forming ability of moulding sands [3]

Type of sand	Value of V_g, cm^3/g
Low rate of gas formation	up to 5.0
Medium rate of gas formation	above 5.0 to 10.0
High rate of gas formation	above 10.0 do 20.0
Very high rate of gas formation	above 20.0

The term *gas forming tendency* means the ability of the sand to produce and release gases under the influence of the temperature of the molten alloy being cast. When the cast molten alloy enters into contact with the moulding sand, the gasified sand components have two ways of escape, i.e. either through the sand layer or through the molten alloy. The composition of the gases emitted depends on the composition of the sand mixture. The main gases include CO, CO_2, N_2, H_2 as well as other compounds in gaseous, liquid and solid form. An indicator of the sand mould ability to form gases is the volume of gas produced by 1 gram of the sand (cm^3/g) or the volume of gas emitted by 1 gram of the sand containing 1 part by weight of the gas-forming material expressed in cm^3/(gram part by weight), otherwise known as a specific gas forming ability [4]. A classification of the moulding sand ability to evolve gases is presented in Table 1.
The escaping gases are one of the main sources of the formation of numerous surface defects in castings, which include internal and external blowholes, pitted skin, pinholes, porosity, orange peel, etc. [2].

4. Hydrogen in cast iron

Hydrogen effect on the properties of cast iron is closely related to its effect on the casting structure. With the increasing content of hydrogen, the hardness and brittleness of cast iron also increase, while the bending and tensile strengths show slight decrease. An important technological property of cast iron is its castability, and it tends to decrease with the increase in hydrogen content. In grey cast iron, hydrogen increases the linear shrinkage [6]. The most unfavourable effect of hydrogen is increasing the tendency to the formation of gas porosity in castings, which occurs along with the drop in metal temperature after pouring of the casting mould [14]. Hydrogen in cast iron is generated not only by the casting mould material but also by the charge materials, very fine ferroalloys, inoculants, humid air as well as refractory lining of furnaces and ladles. The solubility of hydrogen in cast iron decreases in the presence of elements such as carbon, silicon, chromium, oxygen, and increases with the increasing content of manganese [6]. In ductile iron, the source of hydrogen is the reaction occurring between magnesium contained in the metal and water contained in the moulding sand.

5. Oxygen atmosphere in casting mould

Oxygen has a negative impact on the quality of castings, resembling in this respect other elements which occur in the form of gas, e.g. hydrogen and nitrogen. It can occur in atomic form in the solution or form compounds such as oxides, oxysulphides, oxynitrides, etc. Oxygen can originate not only from the charge materials, but also from the thermal decomposition of moulding materials. It is responsible for a number of defects caused by the reaction of gas evolution [6,11,12].

6. Methodology of gas evolution measurements

This study describes the gas evolution measurements using three different proprietary methods:

- direct method of measurement of the gas evolution in sand mould during manufacture of test castings from ductile iron,
- indirect method of measurement of the gas volume evolved from moulding materials with continuous online recording,
- pressure-assisted, indirect method of measurement of the amount of gas evolved from moulding materials during testing of the gas evolution tendency with continuous online recording.

6.1. Direct measurement in mould

The direct method of measurement presented in Figure 1 consists in this that during the process of making test casting from ductile iron, changes in the gas evolution are monitored in a continuous manner. The measuring points are located in close proximity to the nearest metal-mould interface, i.e. at a distance of approx. 3 mm. Each time, the temperature of gases is measured at each of the measuring points. Additionally, the pressure of gases is measured at selected points in the mould along with the measurement of the content of hydrogen (H_2O) and oxygen (O_2) in these gases. The mould making process is kept under control. The measuring points are standard ø 50 mm shaped elements with fixed perforated copper tubes provided with K type thermocouples. Both ø 50 mm shaped elements and casting mould are made from the tested sand. Gases are discharged outside the mould by means of air-tight copper tubes connected through short rubber hoses with gas sensors, which include a pressure gauge, a pellistor for the measurement of hydrogen content and a lambda sensor for the measurement of oxygen content in a mixture of the evolved gases.

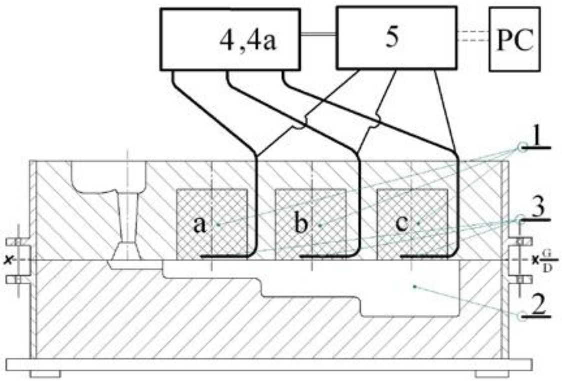

Fig. 1. Test stand for direct measurement of gas evolution rate from moulding sands: 1) mould elements (height of mould cavity under the measuring point: a-13 mm, b-26 mm, c-40 mm), 2) mould cavity with the gating system, 3) gas sampling location, 4) and 4a) gas sensors, 5) Agilent recorder [8, 9]

The whole mould shown in Figure 1 is made from the tested sand. The obtained results of measurements are recorded continuously with the Agilent 73358a recorder at a frequency of 2 times per second, to be next entered to EXCEL spreadsheets.
The spreadsheet with entered data allows multiple and detailed analysis of the obtained results using proper algorithms [10].

6.2. Indirect method for testing the gas forming tendency of moulding sands

The indirect method of measurement of the gas volume formed during the thermal destruction of moulding materials consists in this that 5 grams of the tested material (e.g. moulding sand) are poured into a volumetric flask made of heat-resistant steel. Figure 2 shows a schematic diagram of the test stand for indirect measurement of the gas evolution rate. The sand sample is a crushed fragment of the mould prepared in a controlled manner. A corundum rod, limiting the volume of air filling the flask, is next inserted into the steel flask.

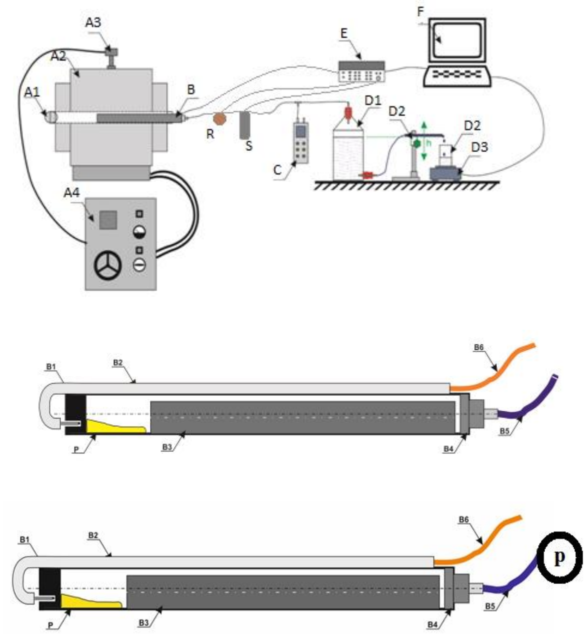

Fig. 2. Schematic diagram of the test stand for indirect gas evolution measurement [7] showing measuring flasks used in: a) volumetric method [7], b) pressure-assisted method

The whole is screwed tightly using a plug with quick coupling for the hose that discharges gases. The gases flow in series through the chamber with the pellistor, and then through the chamber with the lambda probe, and finally over the water surface in the cylinder. The cylinder filled with water allows an accurate measurement of the outflowing gas volume. The measuring flask is fitted with an S-type thermocouple that measures the temperature of the tested mould material. The measurements are recorded by the Agilent recorder at a sampling frequency of every half a second. Then the steel measuring flask with the sample is put in a tubular furnace heated to 1000^{o}C. The time of measurement and of heating the sand sample up to about 900°C is close to 1000 s. After cooling the flask with the tested sand sample, the measurement is carried out once again, this time on the superheated sand sample.

6.3 Pressure-assisted indirect method for testing the gas forming tendency

The pressure-assisted indirect method of measurement of the gas forming tendency of the tested sands uses samples prepared in the same way as in the method described above, illustrated in Figure 2 (measuring flask b). A hose that discharges gases from the measuring flask is made blank by placing a pressure gauge in the closing plug. The indications of the pressure gauge and thermocouple are recorded by the Agilent recorder. The volume of empty spaces in the sampler is 18 cm^3. Other steps in this measurement method are the same as in the volumetric method. In order to check the tightness of the measuring system after 1000 s of the measurement, the measuring flask is removed from the tubular furnace, cooled to ambient temperature and released from the gases. The result of measurement in this method is the instantaneous gas pressure in the flask during measurement related to the instantaneous temperature *j* of the sand sample.

7. The results of gas atmosphere measurements by direct method

The developed, analyzed and recorded results obtained for the test castings are as follows:

- in contrast to castings made in previous studies, the test castings shown in Figure 3 are characterized by high surface quality; the surface obtained in moulds with alkyd resins is smooth and covered entirely with lustrous carbon (silvery colour),

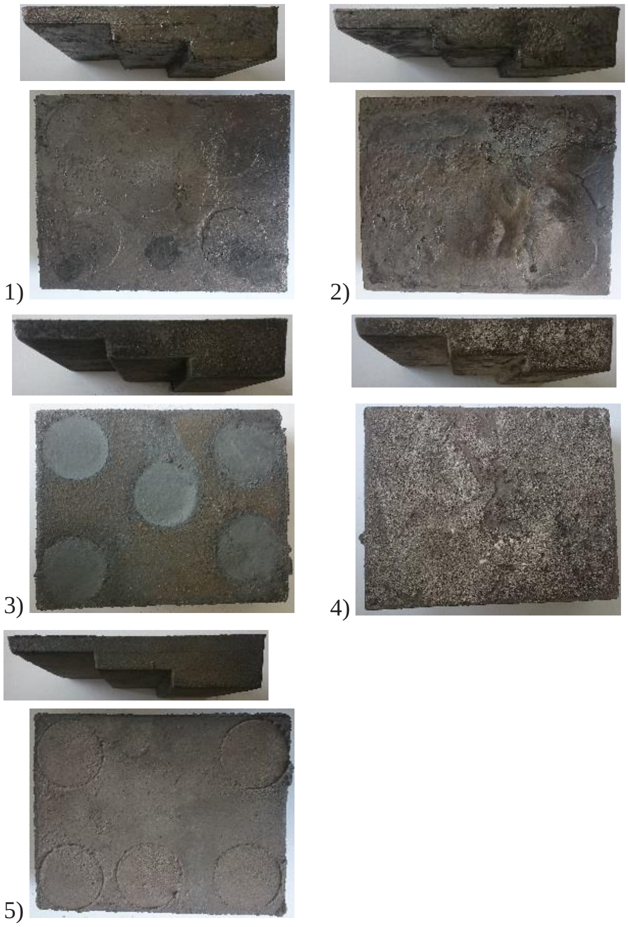

Fig. 3. Sample ductile iron castings during direct gas evolution test. Castings made in sand moulds with: 1) SL resin, 2) SL 2002 resin, 3) furan resin, 4) bentonite and coal dust, 5) Besil binder

- the lowest surface roughness have castings made in sand moulds with alkyd resins. Slightly inferior quality with small burn-on defects in the thick part of the casting have castings made in bentonite-bonded moulds with the addition of coal dust,
- castings made in sand moulds with furan resin have additionally the burn-on defects caused by the first layer of sand grains sticking to the whole surface of the casting,
- the most difficult to clean are castings made in silica sand-based mixtures modified with Besil water glass,
- sands with coal dust and bentonite show the highest gas forming tendency, i.e. above 10 cm^3 from 1 gram of sand [5].

Studies of sand moulds with alkyd resins

To 100 parts by weight of silica sand, 1.3% by weight of the SL or SL 2002 alkyd resin was added. After thorough mixing in a rotary mixer, the addition of 25% of hardener in relation to the resin content was introduced. After mixing the whole and compacting the sand in the mould, the sand was binding for at least 24 hours. Thus prepared mould or fragments of mould were next tested for the gas forming tendency.

7.1 Gas pressure in casting mould

During this gas evolution test, instantaneous gas pressures in the mould made from a typical green bentonite sand with the addition of coal dust exceeded even 350 Pa [8]. The pressure values obtained for the sands with the SL and SL2002 resins, depicted in Figures 4 and 5, respectively, did not exceed 70 Pa. These values are representative of the process of filling the sand mould cavity with casting alloy (the gating system has no overflow) and prove good permeability of the mould [8]. Gases emitted by the sand as a result of its thermal destruction indicate a pressure of maximum 25 Pa. The values of the pressure remained unchanged regardless of the location of the measuring point in the mould, i.e. above the casting with a wall thickness of 13, 26, 40 mm. Pressure drops and differences in maximum temperatures were caused by the formation of shrinkage cavities above the upper surface and by the combustion of gases on the surface of the mould.

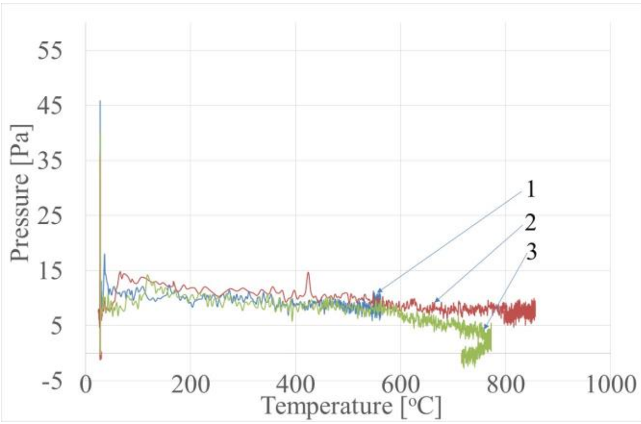

Fig. 4. Pressure of gases released from mould with the SL2002 resin during pouring of ductile iron castings with the wall thickness: 1) 13 mm, 2) 26 mm, 3) 40 mm

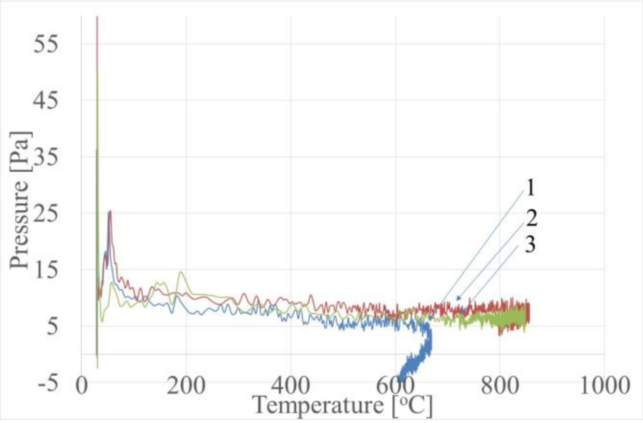

Fig. 5. Pressure of gases released from mould with the SL resin during pouring of ductile iron castings with the wall thickness: 1) 13mm, 2) 26mm, 3) 40mm

The average metallostatic pressure for the test casting was 4.9 kPa, and therefore pressure-assisted gas penetration from the mould into the casting before its solidification was highly unlikely [6,13].

7.2 Hydrogen content in gases flowing out of the zone heated by molten alloy

Hydrogen content in gases flowing out at the points of measurement is illustrated in Figure 6. The maximum hydrogen content, depending on the casting wall thickness, is observed under the measuring points, and for the 40 mm thick casting wall it exceeds 40%. For the 13 mm thick casting wall, the maximum hydrogen content does not exceed 28% and, depending on the type of resin, it occurs in the period of 60 to 100 s. Hydrogen starts evolving intensively already after 20 s from the beginning of the test mould pouring.

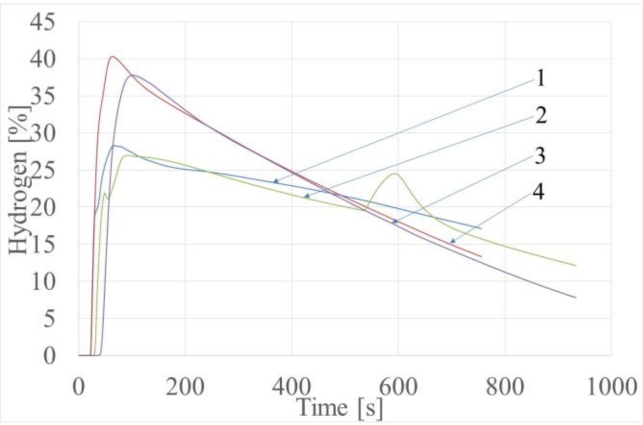

Fig. 6. Hydrogen content in gases evolved during casting of ductile iron: 1) casting thickness 13 mm, sand with the SL resin, 2) casting thickness 13 mm, sand with the SL 2002 resin, 3) casting thickness 40 mm, sand with the SL resin, 4) casting thickness 40 mm, sand with the SL 2002 resin

Figure 7 shows changes in hydrogen content related to the instantaneous temperature at the mould measuring points. At least two maxima are observed in the hydrogen content increase. Both depend on casting wall thickness, and for the 13 mm thick walls they occur at temperatures above 100°C and 300°C, while for the 40 mm thick walls – at 200°C and up to 550°C. The hydrogen evolution rate differs and depends on the resin type (SL or SL2002).

Figure 7 also shows the increase in hydrogen content in the gas mixture evolved during casting of ductile iron related to the mould temperature at sampling points.

The maximum increase in hydrogen content does not exceed 3.5 [%/s] and each time it occurs in two different temperature ranges from 100 to 550°C.

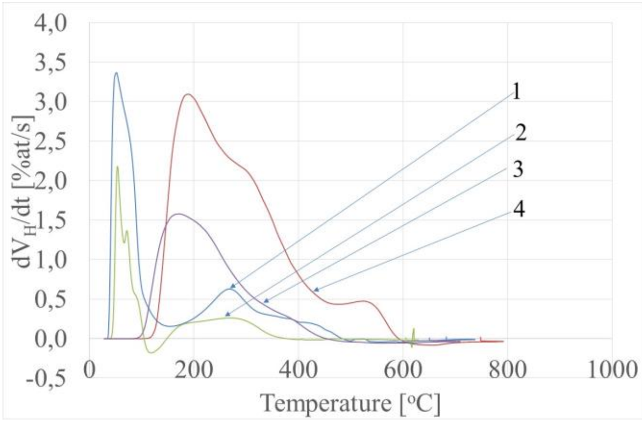

Fig. 7. Changes in hydrogen content in gases evolved during casting of ductile iron related to the mould temperature: 1) casting thickness 13 mm, sand with the SL resin, 2) casting thickness 13 mm, sand with the SL 2002 resin, 3) casting thickness 40 mm, sand with the SL resin, 4) casting thickness 40 mm, sand with the SL 2002 resin

7.3. Oxygen content in gases evolved during casting

Fig. 8 shows pressure and changes in the partial pressure of oxygen in gases emitted during casting of ductile iron related to the mould temperature. Starting with the temperature of 150°C, the oxygen content is decreasing very significantly, and the minimum of $6*10^{-7}$ at takes place when the mould temperature at the sampling point is above 400°C.

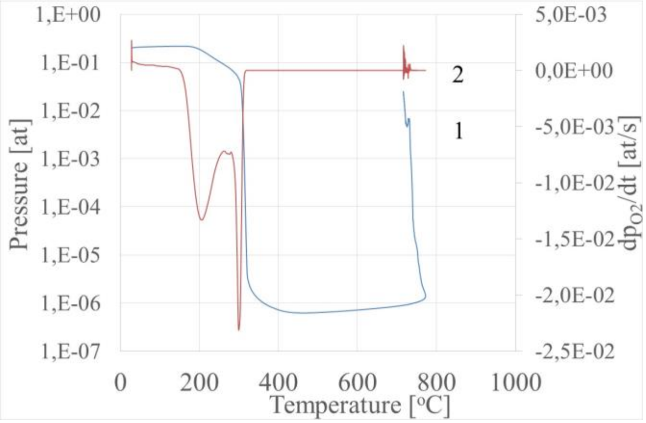

Fig. 8. Oxygen content in gases evolved during casting of ductile iron related to the mould temperature: 1) partial pressure, 2) changes in pressure

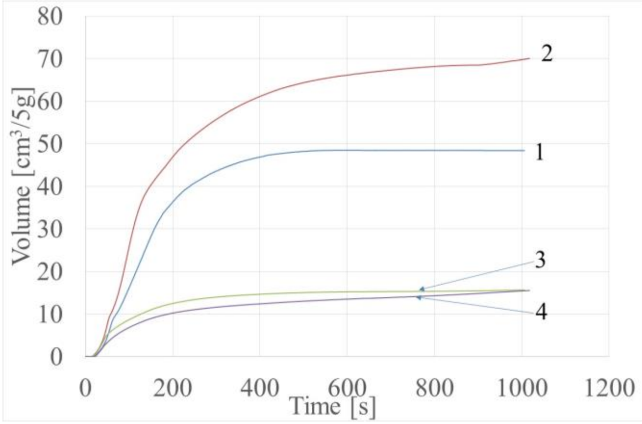

Fig. 9. Gas volume released during heating up 5 grams of the sand with: 1) SL resin, 2) SL2002 resin, 3) SL resin (reheating), 4) SL2002 resin (reheating)

The maximum decreases in oxygen content of $1.2*10^{-2}$ at/s and $2.3*10^{-2}$ at/s occur at 200 and 300°C, respectively, and the source of this effect should be searched in the reactions of oxidation and reduction of organic compounds. Low oxygen content at high temperature causes the release of lustrous carbon [12] at the ductile iron test casting/sand mould interface (Figs. 3.1 and 3.2).

The sand with the SL resin has its second maximum at a temperature slightly lower than the temperature observed for the sand with the SL2002 resin, but it reaches constant values (0.04 cm^3/s from one gram of the sand) at temperatures up to 620°C (Fig. 10 curve 3).

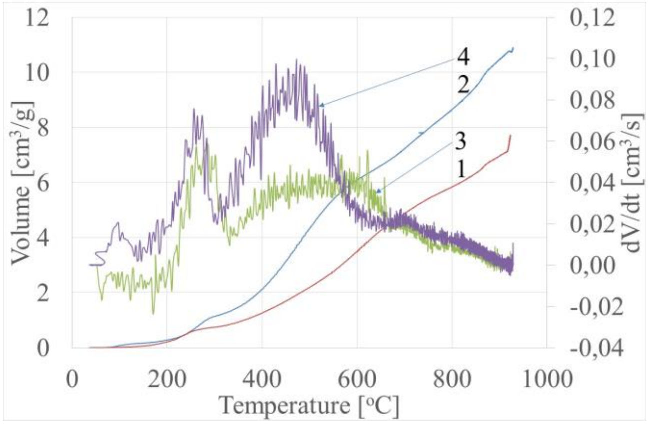

Fig. 10 Gas forming tendency and its changes observed in the sand with: 1) SL resin, 2) SL2002 resin, 3) SL resin (instantaneous values), 4) SL2002 resin (instantaneous values)

8. The results of gas forming tendency measurements by indirect method

The results of indirect volumetric measurements of the gas forming tendency of the tested sands are shown in Figure 9. The average volume of gases emitted from 5 grams of the sand with the SL resin is 48 cm^3, while for the sand with the SL 2002 resin it is 70 cm^3. The repeated measurement of the gas forming tendency of the burnt down sand represented by curves 3 and 4 (Fig. 9) is 15 cm^3 from 5 grams and it is used for calibration of the device. Figure 10 illustrates the gas forming tendency and changes in this tendency observed in the tested sands. Curve 1 shows the gas forming tendency of the sand with the SL resin amounting to 7.7 cm^3/g. According to the classification proposed by J. L. Lewandowski [3], this value denotes the sand with a medium gas forming tendency. Curve 2 illustrates the test results of the gas forming tendency obtained for the sand with the SL2002 resin. This is the gas-generating sand yielding 11 cm^3/g of the gaseous products. The highest gas evolution rates occur at two temperatures, i.e. 250°C and 480°C.

9. Pressure-assisted indirect gas formation measurement

The pressure-assisted method of indirect measurement developed for the purpose of this study allows measuring and recording the gas forming tendency as a function of the test time and test material temperature. The results of pressure-assisted measurements of gas forming tendency carried out on sands with alkyd resins are shown in Figures 11 and 12. At the present stage of studies, these results still can not be interpreted in a quantitative way. The simple method of measurement allows comparing the tested moulding materials in terms of their gas forming tendency.

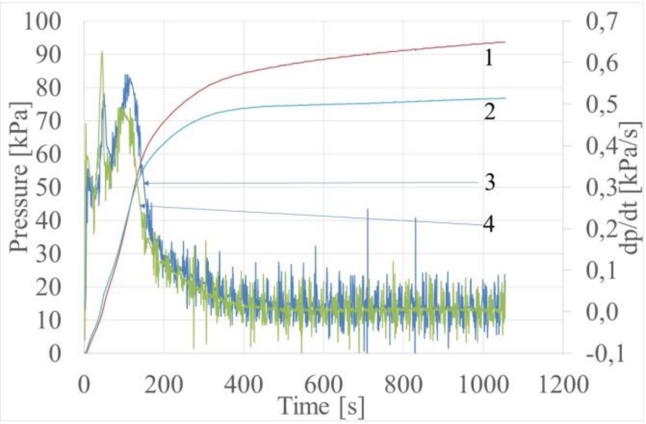

Fig. 11 Pressure of gases and increase in this pressure during gas evolution test: 1) pressure for sand with the SL resin, 2) pressure for sand with the SL 2002 resin, 3) pressure increase for sand with the SL resin, 4) pressure increase for sand with the SL 2002 resin

The increasing pressure creates the experimental conditions closer to the conditions occurring directly in the casting mould. The temperature-related pressure increases depicted by curves 3 and 4 in Figure 12 are similar to the results of the volumetric measurements depicted by curves 3 and 4 in Figure 10. The maximum pressure increase after 50 and 100 s depicted by curves 3 and 4 in Figure 11 suggests that a temporary increase in gas evolution rate from the sand with alkyd resin may be the cause of gas-originated defects in castings.

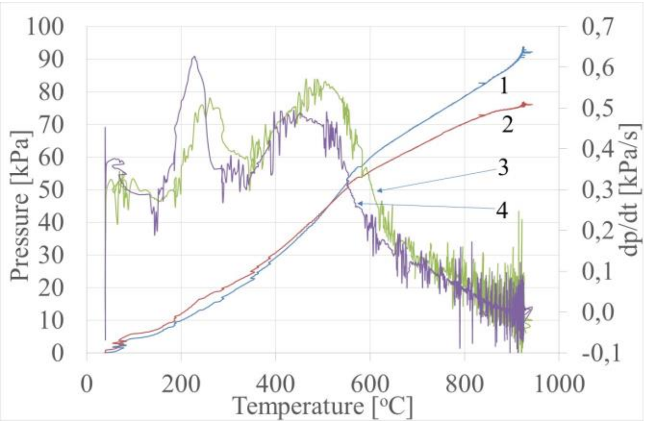

Fig. 12. Temperature-related pressure of gases and changes in this pressure during gas evolution test: 1) pressure for sand with the SL resin, 2) pressure for sand with the SL 2002 resin, 3) pressure increase for sand with the SL resin, 4) pressure increase for sand with the SL 2002 resin

10. Conclusions

1. The sand with the SL resin can be defined as the sand characterized by a medium gas forming tendency (7.7 cm^3/g), while the sand with the SL2002 resin can be defined as the sand characterized by a high gas forming tendency (11 cm^3/g).
2. The applied methods of measurement of the gas forming tendency allow for continuous recording of the gas evolution process, while analysis of the gas forming tendency related to the temperature of the material tested shows kinetics of this evolution (increases in temperature).
3. Hydrogen in maximum amounts exceeding 40 at% is evolved after less than 100 s.
4. The partial oxygen pressure of 6*10^{-7}at results in the release of lustrous carbon on the surface of ductile iron castings made in moulds bonded with alkyd resins.
5. Gases emitted above the thicker iron casting wall (40 mm) have partial concentration of hydrogen higher than the gases emitted above the thinner wall (13 mm).
6. The instantaneous increase in pressure reaches its highest value immediately after pouring the sand mould with alkyd resin.
7. The method of pressure-assisted indirect measurement allows determining the gas evolution rate in a qualitative way, but it is expected that more advanced research will also enable a quantitative measurement of the gas forming tendency of the foundry moulding sands.

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