

A R C H I V E S o f F O U N D R Y E N G I N E E R I N G

ISSN (1897-3310) Volume 14 Special Issue 3/2014

 $105 - 109$

21/3

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

Gas Generation Properties of Materials Used in the Sand Mould Technology – Modified Research Method

J. Zych *, J. Mocek, T. Snopkiewicz

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

Received 21.07.2014; accepted in revised form 22.08.2014

Abstract

The paper presents a new methodology for research on gas generation property of materials used for sand forms and cores, models made of foamed polystyrene, protective layers, etc. In the form of an example, full analysis has been presented of gas generation property of a selected furan resin bonded sand, stating the course and kinetics of gas generation, their intensity in the time function, and in the heating temperature function. The description is of quantitative nature. The existence of peaks in gas generation intensity was observed at several temperature values. The results are well-correlated with the inclination to form surface defects of casts made in furnace resin bonded sands. This is the first study on gas generation kinetics in the mass heating temperature function.

Keywords: Moulding mass gas generation property, Research methodology, Generation kinetics

1. Introduction

The impact of high temperature of liquid metal on the casting mould leads to increase in gas (air) volume, which fills the niche of the mould and fills the pores of sand form, leading to decomposition and gasification of many mass components, binders, additives and protective components layers). In the casting practice, gases generated while filling the moulds and cast solidification constitute one of major problems rendering it difficult to produce casts without defects.

The source of gases generated and increasing their volume while heating depends on form technology. Most frequently, in the sand form technology, these are organic bonds, additives to masses, and water in the wet mass technology. In the metal form technology, these are protective layers placed on the forms to increase their durability. In the full-mould casting, the source of gas is the evaporative model made of expanded polystyrene.

In many technologies, gases may be generated by protective layers that most frequently contain over 60% water or alcohol solvent and additives in the form of bonds and various modifiers that change their rheological properties.

To assess the inclination of the aforementioned materials to generate gases, two method groups are applied: one refers to tests in laboratory conditions $[1, 2, 3, 9, 10]$, while the other – to tests in conditions similar to conditions occurring directly in the mould [1, 4 - 7]. In the first case, sample of the material tested (e.g. mass) is heated in a sealed flask to be placed in a tubular furnace. The generated gas volume is measured while heating the mass sample to the selected temperature [3]. According to the second method [1] and its later variations [4 - 7], a sample of the mass tested, forming some sort of a core, is covered with liquid metal in the mould. During mass heating, volume of gas generated from the sample heated is measured.

As all measurement methods, the methods described also have their advantages and disadvantages. Neither of them, in the current solution, allows for determining gas generation 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 material heated is summed up with the increase in the volume of air heated that fills the measurement flask (in the laboratory sample), or forms cavities in a porous sample (intergranular voids).

This paper presents a new method which eliminates sources of potential measurement errors and creates conditions for studying kinetics of gas generation in the temperature function $\begin{bmatrix} 8 \end{bmatrix}$. Measured volumes of gases produced are recorded in real time.

2. Own study

2.1. New research methodology

The modified method for analysis of moulding material gas generation properties belongs to the first group, namely the group of laboratory methods. The modification shall involve several key elements of the measurement methodology. And so:

- continuous measurement of the quantity of gases generated,
- continuous measurement of the temperature of mass sample heated,
- calibration of measurement flask has been introduced by initial measurement of increase in the volume of air heated which filled the measurement flask,
- operating volume of the flask has been minimised to limit the effect of gas expansion without mass sample.

Stations for gas generation analysis

Figure 1 presents the laboratory station for analysis of moulding sand gas generation properties. The mass sample to be analysed is placed in a glass flask with a plug. After heating the tubular furnace and mass sample placement in the flask, the flask is closed, and the generated gas is directed to the measurement section where total gas volume is measured.

Fig. 1. Laboratory station for analysis of moulding mass gas generation properties

Such total gas volume comprises gas generated from decomposition of mass bonds, and gas volume resulting from heating of air present in the "cold" flask.

The greater the volume of the flask and the greater the temperature of gas heating in the flask, the greater is the component being the derivative of gas heating.

Modified stations for gas generation analysis

Figure 2 presents the diagram of a new station for analysis of gas generation kinetics and assessment of moulding mass gas generation properties. The test probe with the mass tested (B) is introduced in the tubular sylite furnace PSR-1(Fig.2 A2) with temperature controlled using thermocouple (A3), as well as power supply and digital regulator (A4). On the "unused" side of the furnace operating pipe, thermo-insulating wool has been placed (A1), to limit temperature drops caused by air flow. Test probe (B), where the sample of mass tested is placed, has been designed and built as a unilaterally closed pipe. To increase resistance to thermal shocks, the test probe has been made of refractory steel. On the other side, the test probe is equipped with a sealed valve (Fig. 2 B4). Closing valve allows for directing the gas formed from the sample to the measurement system. The same valve, after disconnecting from the probe (pipe), allows for replacement of the mass analysed (P). After measurement, the test probe is emptied of the tested (heated) mass and cleared from its remains.

Fig. 2. General view of the station for analysis of gas generation kinetics and assessment of core and moulding mass gas generation properties (description in the text)

To reduce the volume of "inactive" space of the test probe, an insert is placed inside it (Fig. 2. B3). On the outer surface of the test probe, pipe (B2) – guiderail has been placed – with ceramic insulators where thermocouple conductors of "S" type have been inserted (Pt -PtRh10). Thermocouple junction is placed in the area with the tested mass sample. Such a solution assures exact temperature control of mass tested (P). Thermocouple conductors at the end of the test probe have been connected to the compensation conductor (B6) and temperature recorder.

Fig. 3. Sketch of the measurement test probe

Air filling the cold test probe that increased its volume as a result of heating, as well as gas generated in the test probe from decomposition of the binder of the mass tested, are directed via a complex of conductors $(B5)$ to the measurement system $-$ to measure their volume. The system comprises a three-way pipe distributing gas to the low-pressure meter (Fig. 4C) and to the glass container with water $(D1)$.

Fig. 4. Diagram of the generated gas volume measurement section

Gas products of organic binder decomposition usually include $CO₂$, which rather easily dissolves in water, and thus can be a source of measurement error. In order to reduce $CO₂$ solubility in water, use water previously saturated with carbon dioxide, or water with salts dissolved in it.

In the bottom section of the vessel with water, there is a drain closed with a plug with a drain pipe. Gas is introduced via the top valve to the vessel with water pushes the water from the vessel in such volume as it occupies in the vessel itself. Water flowing out via bottom valve from the vessel is first directed via rubber hose to the pressure "regulator" (hydrostatic pressure) – stand (D2), and then to the outlet zone of the pipe. Under the outlet zone of the pipe, a vessel has been placed (D4), set on a tensometric laboratory scale furnished with electronic system for data collection and transmission to the computer. The thermocouple placed in the test probe (Fig. 2.B) has been connected to the computer via Agilent 34970A recorder (Fig. 2.E). Simultaneously, data are gathered on sample temperature and – indirectly - volume of gases generated at a particular time. Because specific density of water amounts to $1g/cm³$, number of grams of water pushed out by the gas flowing into the vessel
corresponds to its volume, which facilitates the corresponds to its volume, which facilitates the measurement/calculation procedure.

Measurement method

Test probe filled with a mass sample tested is entered into the furnace heated to a predefined temperature. Mass is weighed using laboratory scale with the accuracy of up to 0.01g. Mass quantity is to assure accurate measurement, namely must be large enough to produce "lots" of gas, yet small enough so as not to

exceed the measurement range of the scales (by water pushed out during the measurement), and so that the material tested is poured in a loose, thin layer. Thin layer of mass sample assures quick heating of its entire volume and at the same time gasification (incineration) across the entire volume of the material tested. The weighed portion of the mass is poured into a clean test probe, and then a roller (B3) is inserted to reduce the "dead volume" of the measurement system (test probe). After connecting the pipes, water table is equalised in the vessel and outflow level – location of drain pipe outlet. After water levelling, the manometer indicates 0 mm water column. After pressure equalisation, software recording the volume of water pushed out from the vessel and recording temperature of the heated mass sample is activated. Together with heating the test probe, gas volume increases in the probe, which while flowing out to the vessel with water induces the commencement of water flowing out. At the same time, in online mode, the quantity of outflowing water is recorded, as well as the temperature of mass heated. When the push-out of a greater water volume by gas generated is rather quick, the water table level in the vessel will decrease – pressure meter will show value different than 0 mm. Then, the location of outflowing pipe is corrected continuously so that the pressure difference in the vessel and in the outflowing pipe is restored to the value close to $0 \text{ mm H}_2\Omega$.

Duration of one measurement depends on temperature to which mass is heated, and amounts to several to several dozen minutes.

Test probe calibration

Operating volume of the test probe in the version described amounts to approx. 40 cm³. While heating the test probe with the tested mass, two processes occur in parallel: increase in the volume of heated air that fills the probe, and generation of hot gas from decomposition (incineration) of mass components. While measuring summary volume of gas pushed out from the tank, falsified image of mass gas generation properties is obtained. It could be referred to as **total or apparent gas generation property.** Total volume of gases flowing out from the test probe largely depends on the proportion between the operating volume of the probe and volume (weight) of mass sample. The greater the operating volume of the test probe, the more "falsified" is the image of actual mass gas generation property.

In order to allow for determining actual volume of gases generated from mass decomposition, it is necessary to determine increase in the volume of air alone in the test probe heated to selected temperature. The measurement can be referred to as test probe "calibration" and involves recording of increase in gas (air) volume in the test probe during its heating to selected temperature. In order to measure actual gas generation property of mass tested, from the recorded volumes of gas generated from the sample (and at the same time heated air), the result of calibration performed for the same temperature conditions must be deducted. The results obtained must be divided by the input quantity of mass tested – the result obtained will be the volume of gas generated at a particular temperature per 1g of mass tested. Consequently, it is possible to calculate the binder itself per weight. For this purpose, mass composition must be known with percentage share of the binder. In such a case, we can refer to specific gas generation property, namely referred to 1g of binder (not mass).

2.2. Results

The paper presents the results of tests of the mass with organic binder – furan resin. The research was carried out for the mass with fresh sand matrix and matrix after mass thermal regeneration. 1.2% resin and 0.55% hardener has been applied, solution of PTS acid. Figure 5 presents source results of measurements, comprising: record of temperature changes, record of changes to volume of gas flowing out from the test probe when heating the very test probe (calibration) and test probe with furan mass. The mass is heated to approx. 950°C. The test probe contained 5g of previously dried mass. For calibration, 5g of dry silicon sand was used.

Fig. 5. Records of changes to temperature and volume of gases flowing out of the test probe when heating samples weighing 5g

Fig. 6. Gas generation records when heating the test probe with: a/ mass with regenerated matrix, b/ regenerated matrix by itself, c/ mass with matrix – fresh sand

Figure 6 presents gas generation records for three types of materials tested: masses with fresh matrix, regenerated matrix itself (without new binder), masses with regenerated matrix. The volume of gases generated from the mass with regenerated matrix is over double than from the mass with fresh matrix. The matrix

itself, characterised with 2.0% losses on heating, generates more gases than mass with fresh sand.

Gas generation kinetics

In technological processes, when executing casts, not only total volume of gases generated from the mass is important. Kinetics of the process is also of major significance, namely how quickly gases are produced, and at what temperature they are formed most intensively. The developed research method allows for determining both such values. Figure 7 presents gas generation kinetics in the heating time function. It can be seen that they are generated with the highest intensively during the first minute of heating, while after approx. 30 s. curves record the second peak, although gas generation intensity is already lower.

Fig. 7. Intensity of gas generation from three types of furan mass

Figure 8 presents the kinetics of gas generation depending on mass temperature. Masses with furan resin begin producing gases rather intensively already after exceeding 100° C. At the temperature of approx. 850 - 900°C, the process of gas generation actually ends. Kinetics record three peaks, first in the area of temperatures 200 - 300°C, the second at the temperature of 500 - 600°C, and the third at the temperature of 700 - 800°C. Gas generation covers broad temperature range, and further peaks can form one of the causes of surface defects, such as: pitting, orange peel, or gas porosity.

Fig. 8. Impact of temperature on the intensity of gas generation from three types of furan mass

3. Conclusions

The executed tests of gas generation properties of furan masses using the new measurement method allow for drawing the following conclusions:

- The new method for analysis of gas generation properties, like none of the applied so far, allows for monitoring kinetics of gas generation from materials used in sand mould technology.
- Furan masses generate gases while being heated (e.g. by liquid metal) with varying intensity, the highest at the temperature within the interval of 500 - 600°C.
- The new testing method can be applied for assessment of not just moulding mass with binders, but also protective layers, models of foamed polystyrene, etc.

Acknowledgements

The study was performed in the framework of the statute: Nr 11.11.170.318. zad. 4

References

- [1] Lewandowski, J.L. (1997). Materials for molds. Kraków. (in Polish)
- [2] Lewandowski, J.L., Solarski, W. & Pawłowski, Z. (1993). Classification of molding and core in terms of the ability to create gas*. Przegląd Odlewnictwa.* 5. (in Polish)
- [3] Urbanik, E. (1964). Unpublished doctoral dissertation AGH, Wydział Odlewnictwa Kraków. (in Polish)
- [4] Holtzer, M., Dańko, J., Lewandowski, J.L., and others, *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; Biuletynyn Urzędu Patentowego ; ISSN: 0137-8015 ;2013 nr 21, s. 26.
- [5] Holtzer, M., Dańko, R., Dańko, J., Kubecki, M., Żymankowska-Kumon, S., Bobrowski, A., Śpiewok, W. (2013). *Severity rating of binding materials used for molding and core of the new generation.* AGH Akademia Górniczo-Hutnicza im. Stanisława Staszica w Krakowie. Kraków: Wydawnictwo Naukowe Akapit. (in Polish)
- [6] Bobrowski, A., Holtzer, M., Dańko, R. & Żymankowska Kumon, S. (2013). Analysis of gases emitted during a thermal decomposition of the selected phenolic binders. *Metalurgia International.* 18(spec. 7), 259-261. ISSN 1582*-* 2214
- [7] Holtzer M., and others. (2012). *Emission tests dangerous compounds with masses of bentonite and lustrous carbon carriers in contact with liquid metal*. Przegląd Odlewnictwa. 62(3-4), 124-132. (in Polish)
- [8] Mocek, J., Zych, J., Krubnik Ł. (2014). Selected problems casting of Al - Si technology complete form*,* Kraków – Starachowice: XVII International Scientific - Technical Conference of Non-Ferrous Foundry. (in Polish)
- [9] Żółkiewicz Z.: *The kinetics of thermal decomposition, and impact polystyrene model resulting gases on the content of hydrogen, nitrogen and oxygen in gray cast iron, in a "full mold process"*. Unpublished doctoral dissertation, AGH.
- [10] Pacyniak, T. (2013). *Full mold method. Selected aspects.* Łódź: Monografie Politechniki Łódzkiej. (in Polish)

.