This article presents a gas evolution study of a novel, cellulose-based mixture with such mineral additives as expanded perlite, expanded vermiculite and microspheres. Inorganic alumina-silica binder was used to produce an uniform, bound mixture. The results have shown that the novel, cellulose-based mixture, obtained from waste paper, with mineral additives, emits smaller amounts of gas, while retaining the same thermal resistance.

Keywords: gas evolution, modified cellulose mixture

1. Introduction

The sequence of liberation of different kinds of gases and compounds from mould materials is a natural process that occurs during the thermal treatment of materials [1-8]. This also happens during the process of casting iron-based alloys, when disposable auxiliary and mould materials are used. Different ceramic materials, which may have some disadvantages, but which contaminate the mould compound and prove difficult in mechanical processing, are usually used at high temperatures. There is an alternative solution available on the market. It is a cellulose-based material [9] which solves the problem of mechanical processing while at the same time retaining similar thermal insulation capabilities. Unfortunately, it contains some organic binders, which are a source of intensive gas evolution during high-temperature thermal treatment [2,10].

Gases and chemical compounds emitted from moulding compound, core compound, gating systems and other auxiliary materials, are in direct contact with liquid metal during the process of casting, which may produce problematic surface casting defects [11-13]. They are also often harmful to the health and life of humans [3]. Therefore, the tendency to reduce the gas evolutions during the casting process is an obvious goal and the result of which is the seeking out of novel moulding compounds [14]. Different ceramic materials, which may have some disadvantages, but which contaminate the moulding compounds and prove difficult in mechanical treatment, are usually used to make casting systems for large and medium-sized casts.

This paper presents a gas evolution study of a cellulose-based mixture obtained from waste paper with the addition of minerals resistant to high-temperature, such as expanded perlite, expanded vermiculite and microspheres [14-19]. Being materials of high thermal resistance, the additives modify the thermal resistance parameters of the cellulose-based mixture. Owing to the characteristics of this modified novel mixture, it can be considered a short-time, one-off thermal barrier for contact with liquid metal [10,14,20,21].

2. Research materials and methodology

Fifteen versions of the mixture [14] of different compositions were used to study gas evolution. The mixture compositions consisted of EP-150 expanded perlite with a bulk density of 40-90 [kg/m³], FINE type expanded vermiculite with a bulk density of 100÷130 [kg/m³], F150 microspheres with a granulation of 50-150 [mm] and paper pulp obtained from EKOFIBER waste paper. The base paper pulp was made by mixing 250 [g] of water at a temperature of 80°C with 20 [g] of paper waste. Thus the obtained paper pulp was modified by the addition of expanded perlite, expanded vermiculite and microspheres. The amount of the aluminosilicate binder accounted for 32.4% of the sample weight. After thorough mixing, reference samples were created, which were then dried in a laboratory dryer at 130°C for 90 minutes in order to evaporate the water. Table 1 presents the composition of the samples.
### TABLE 1

Chemical composition of samples

| Sample | Paper pulp [g] | Expanded perlite [g] | Expanded vermiculite [g] | Microspheres [g] | Binder [g] |
|--------|----------------|---------------------|-------------------------|------------------|------------|
| ex1    | 270            | 15                  | 30                      | 80               | 189.6      |
| ex2    | 270            | 15                  | 30                      | 0                | 151.2      |
| ex3    | 270            | 15                  | 30                      | 160              | 251        |
| ex4    | 270            | 0                   | 30                      | 80               | 182.4      |
| ex5    | 270            | 30                  | 0                       | 80               | 182.4      |
| ex6    | 270            | 7.5                 | 15                      | 80               | 178.8      |
| ex7    | 270            | 7.5                 | 15                      | 0                | 140.4      |
| ex8    | 270            | 7.5                 | 15                      | 160              | 217.2      |
| ex9    | 270            | 0                   | 15                      | 80               | 175.2      |
| ex10   | 270            | 7.5                 | 15                      | 40               | 159.6      |
| ex11   | 270            | 7.5                 | 15                      | 40               | 168        |
| ex12   | 270            | 0                   | 0                       | 80               | 148.8      |
| ex13   | 270            | 0                   | 0                       | 80               | 206.4      |
| ex14   | 270            | 7.5                 | 15                      | 40               | 170.4      |
| ex15   | 270            | 7.5                 | 15                      | 40               | 170.4      |

The gas evolution was studied on a Type PGD Gasdurchmessgerat device manufactured by Georg Fischer. Each of the composition options was studied three times. The device diagram is shown in Fig. 1.

The gas evolution was measured at a temperature of 900°C +/- 2°C. The test samples were placed inside a preparation chamber (16) at room temperature and subsequently the whole measurement chamber (9) was blown through with nitrogen for 120 seconds. After a neutral nitrogen atmosphere was obtained, the vent valves and inlet valves were shut (18-19). After the system was closed, the mechanism (17) was released in order to shoot the sample (previously weighed on a laboratory balance) into the measurement chamber with a test temperature of 900°C +/- 2°C. The gas liberation was shown on the screen (6) and expressed in [cm³/g]. Additionally, the gas evolution of a sample of a commercially available, cellulose-based material [9] used for gating systems and the gas evolution of additives that were used, i.e. expanded perlite, expanded vermiculite and microspheres, was examined.

A composition with the lowest emissivity (ex6) was chosen from among the samples tested and a cylindrical sample with the dimensions of 600 mm Ø 60 mm was made. This experimental profile was put into a disposable mould made of silica sand with a bentonite binder and poured over with EN-GJL 250 grey cast iron melted in a PI30 type induction melting furnace with a capacity of 30 kg. The diagram of the measuring stand is shown in Fig. 2.

The temperature inside the commercial mould and that made of the (ex6) mixture was measured simultaneously while the experimental profile was being cast over with iron. When it had cooled down, samples were taken from the contact zone between the cast iron and the cylindrical mould made of modified cellulose. Microsections were made in order to analyse the microstructure. Metallographic tests were performed on crosswise microsections under a Nikon-MA200 microscope. The samples were etched with nital and a magnification of ×100 and ×500 was used.

### Results and discussion

Measurement of the gas liberation for pure expanded perlite and microspheres did not reveal any gas evolution during the tests. Pure expanded vermiculite showed a medium gas liberation of 65 +/- 16.2 [cm³/g]. The sample of commercially available cellulose mixture used in gating systems [9] showed an emissivity of 411 +/- 17.8 [cm³/g]. The measurement results of the gas evolution of our own samples (Table 1) per mass unit are shown in diagrams in Fig. 3-8.

An analysis of the graphs in Fig. 3-5 shows that an addition of microspheres reduces the gas evolution of the modified cellulose mixture. This effect is visible both when the mixture...
composition is not modified with an addition of expanded perlite and expanded vermiculite, and when both were added to the mixture.

Figures 6 and 7 show that expanded perlite or expanded vermiculite only slightly affect the gas evolution of the cellulose mixture modified with these additives. A synergistic addition of expanded perlite and expanded vermiculite, shown in Figure 8 also did not bring about any significant changes in the gas liberation of the mixtures under study.

Microstructure images obtained from cast iron samples taken from the contact zone between the cast iron and the cylindrical mould made from the modified composition of the (ex6) mixture is presented in Figures 9 and 10.

Observation of the microstructures in the contact zone did not reveal any gaseous micro-defects in the microstructures. At the same time, no non-metallic intrusions were noticed in the border zone in the cast iron sample where the liquid cooling-down metal came into contact with the experimental cylindrical sample.
Figure 11 shows the results of temperature measurements of the cooling-down cast iron inside a sample of (ex6) and a sample of a commercially available mixture.

The characteristics of the cooling down process is similar in both cases, although the process of temperature decrease is much slower for a commercially available sample in the temperature range of 1300-1190°C. The cooling-down rate equalises for both samples after a similar time of 380-420 seconds. An analysis of the temperature change shows that there is an exothermic effect for the commercially available cellulose profile and for the experimental ex6 profile, which maintains a constant temperature of the liquid metal for some time. The effect is associated with the presence of microspheres in both samples, which has also been observed in other studies [2,20,21].

4. Conclusion

The modified cellulose mixture developed by the authors considerably reduces gas evolution per unit mass compared to the liberation of a commercially available cellulose mixture [9] from 411 [cm³/g] to the range of 165÷366 [cm³/g], depending on its composition. The results have shown that using a different binder in our own mixes reduces the amount of gas generated during the high-temperature thermal treatment compared to the compounds used in the commercial mix, i.e. melamine-urea-formaldehyde resins [20].

With respect to the experimental compositions of the modified mixture, the best gas evolution reduction is observed with an increasing content of microspheres in it. It can be assumed that an addition of expanded perlite, which does not emit any gas, has no significant effect on the parameter in the samples under study, as the effect is immeasurable and it lies within the measurement error range.

It is similar with expanded vermiculite, although its gas evolution is approx. 65 [cm³/g]. Its effect on the gas liberation lies within the measurement error range and is not visible in the experiment result.

Owing to their thermal resistance [15-19,22], which is higher than that of the commercial mixture [2,9], materials for the pulp modification used in the study give the experimental mixtures a thermal resistance comparable to that of commercial products [20,21], while at the same time reducing gas evolution. This effect can be attributed to the temperatures characteristic of the additives used in the study. The softening temperature of expanded perlite ranges from 871 to 1093°C, and the melting range spans from 1260 to 1343°C. Microsphere sintering starts at a temperature of 1000°C with an estimated melting point of 1400°C. Expanded vermiculite coagulation takes place within a range from 1240 to 1430°C and its melting point has not been estimated. The level of characteristic temperatures for these materials may allow for their use as fillers for paper pulp made from paper waste in order to increase its working temperature, with a simultaneous gas evolution reduction compared to commercial products.
The analysis of microstructures did not confirm any negative effect on the quality of the cast iron cooling down in a cylindrical profile made from the experimental composition ex6, which is a cellulose-based modified mixture.

It is the authors’ long-term objective to optimise the composition of the modified cellulose mixture in order to achieve a higher thermal resistance compared to commercial products with a concurrent reduction of gas evolution.

REFERENCES

[1] Ł. Kaczmarek, P. Kula, J. Sawicki, S. Armand, T. Castro, P. Kruszysiński, A. Rochel, Arch. Metall. Mater. **54**(4), 1199-1207 (2009).
[2] R. Grabowska, M. Szucki, J. Suchy, S. Eichholz, K. Hodor, Polimery. **58**(1), 39-44 (2013).
[3] M. Holtzer, E. Bagińska, A. Baliński, K. Borla, A. Bydalek, J. Dąbko, K. Kowalski, M. Latała-Holtzer, M. Młyński, Cz. Podrzucki, J. Rożek, M. Żmudzińska, Wytyczne dla Branży Odlewniczej (in Polish), Ministry of Environment Press (2005).
[4] M.M. Sipos, Gießerei Rundschau. **62**, 32-33 (2015).
[5] S. Zymanksowa-Kumon, Arch. Foundry Eng. **14**(4), 149-152 (2014).
[6] A. Bobrowski, Arch. Foundry Eng. **14**(4), 17-20 (2014).
[7] J. Sawicki, M. Górecki, Ł. Kaczmarek, Z. Gawroński, K. Dybowskii, R. Pietrasik, W. Pawlak, Chiang. Mai. J. Sci. **40**(5), 886-897 (2013).
[8] L. Jamrozowicz. Arch.Metall. Mater. **58**(3), 891-894 (2013).
[9] http://www.foseco.com – (06-04-2014).
[10] Z. Zawieja, J. Sawicki, G. Gumienney, A. Sobczyk-Guzenda, Arch. Foundry Eng. **14**(3), 123-128 (2014).
[11] J. Campbell, The new metallurgy of cast metals-castings, Elsevier Ltd 2003.
[12] R.I. Naro, AFS Transactions. **107**, 839-851 (1999).
[13] M. Perzyk, A. Kochanski, J. Eng. Manuf. **222**, 1503-1516 (2008).
[14] Z. Zawieja, J. Sawicki, Polish Patent Application P. 408770 (2014).
[15] S.A. Suvorov, V.V. Skurikhin, Refract. Ind. Ceram+. **43**, 11-12 (2002).
[16] V.E. Peletskii, B.A. Shur, Refract. Ind. Ceram+. **48**, 356-358 (2007).
[17] W. Pichor, A. Janiec, Ceram. Ind. **35**(1), 527-530 (2009).
[18] R. Demirborga, R. Gul, Energ. Buildings. **35**, 1155-1159 (2003)
[19] M. Losiewicz, D. Halsey, J. Dews, P. Olomaiye, F. Harris, Constr. Build. Mater. **10**, 583-588 (1996).
[20] Z. Zawieja, J. Sawicki, Adv. Sci. Technol. Res. J. **9**(26), 83-88 (2015).
[21] Z. Zawieja, J. Sawicki, Arch. Foundry Eng. **16**(3), 91-94 (2015).
[22] A.D.Mazzoni, E.F. Aglietti, Thermochim. Acta, **327**, 117-123 (1999).