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ARCHIVES of FOUNDRY ENGINEERING

ISSN (2299-2944)
Volume 18
Issue 1/2018

65 – 70

12/1

DOI: 10.24425/118813

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

Method of Selecting the Reclamation Temperature of Spent Moulding Sands with Organic Binders

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Received 28.08.2017; accepted in revised form 10.10.2017

Abstract

The thermal reclamation process as a utilisation method of spent moulding and core sands is more costly than other reclamation methods, but in the majority of cases it simultaneously provides the best cleaning of mineral matrices from organic binders. Thus, the application of the thermal analysis methods (TG-DSC), by determining the temperature range within which a degradation followed by a destruction of bounded organic binders in moulding sands, can contribute to the optimisation of the thermal reclamation process and to the limiting its realisation costs. The thermal analysis results of furan resin, one of the most often applied binder in foundry practice, are presented in the hereby paper. The influence of the heating rate of the sample - placed in the thermal analyser - on its degradation and destruction process under oxygen-free (argon) and oxygen (air) conditions, were compared. The recorded TG and DSC curves were used for analysing these processes as the temperature as well as the time function. The obtained results were analysed with regard to determining the required temperature of the thermal reclamation of the investigated organic binder. The usefulness of the developed methodology was found out, however under conditions of meeting several essential requirements concerning the repeatability of performed analyses.

Keywords: TG and DSC thermal analysis, Organic binders, Thermal destruction, Thermal reclamation

1. Introduction

A thermal reclamation of spent moulding and core sands constitutes a burning process of organic synthetic resins being binders of these sands.

In dependence of the initial composition of moulding or core sands, its multiple usage in the foundry plant and the kind of the applied alloy, the amount of material undergoing burning (oxidation) can vary from 1% to 7%. The remaining part of the moulding or core sand constitutes grain matrix (high-silica sand, zirconium sand, olivine sand), which within the applied temperature range, is not taking part in the burning process. However, this grain matrix participates in effects related to the heat flow and its accumulation.

The thermal reclamation as the burning process of spent organic binders is not the energy source. On the contrary, it requires significant energy expenditures for its realisation. When there is a large amount of the collected binder, the process can occur for some time intrinsically, without energy supplied to the burned deposit of the reclaimed moulding sand [1].

Due to a significant energy-consumption of the process, looking for solutions lowering its costs, seems justified. The thermal analysis constitutes the investigation allowing to recognise properties of binders used for preparing moulding or core sands, especially in consideration of their degradation and destruction

under the determined temperatures, thus providing guidelines for the reclamation treatments of various organic binders.

A sample weight, grain size, heating rate and atmosphere in a furnace are factors influencing the result. The quantitative composition of the sample, durability of individual substances and the range of their decomposition [2-4] can be determined by the performed analysis. Recognition of this process should contribute to the proper performing of the treatment and the proper temperature selection of the thermal reclamation of spent moulding and core sands.

2. Investigation methodology

A percentage amount of the bound organic binder in fresh, spent or reclaimed moulding sands can be different. The thermal degradation state of the applied resin is also not the same. A moulding sand in contact with liquid metal undergoes a degradation and destruction, in dependence on its placement in the mould, and this causes the emission of gases to the surroundings [5-8]. Therefore, in each case, it is necessary to create conditions allowing to achieve a complete burning (oxidation) of the initial organic material, which corresponds to the fresh moulding sand composition. The thermal analysis performed for the hardened resin allowed to determine the heating rate influence, atmosphere in the analyser and also the type of the device in which the process was realised. Effects of individual treatments were determined by means of the thermogravimetry (TG) and differential scanning calorimetry (DSC). The performed analysis was aimed at verifying the developed methodology of selecting the required reclamation temperature, which was described in other publications of the author [9-10]. The shown below analysis has to determine mutual relations between the process time and temperature, two main factors deciding on the organic material destruction.

2.1. Materials applied in investigations

The sample of the binder prepared for investigations consisted of:

- urea-formaldehyde resin modified by furfuryl alcohol,
- hardener being a mixture of sulphonic and inorganic acids, modified by special additions.

Components in proportion 2:1 (resin: hardener) were mixed under conditions of a fast heat abstraction due to strongly occurring exothermic reaction of combining resin and hardener without a grain matrix. The sample of the material after binding was crushed and powderized in the mortar.

2.2. Thermal analysis

Main thermal investigations were performed by means of the thermal analyser TA Instruments SDT Q600 (DSC/TGA) (analyser I), which allows to perform TG measurements under the same measuring conditions, i.e. at the same temperature increase rate (e.g. 10°C/min), and the same gas flow rate (e.g. 100 ml/min). Measurements for each sample were made in the oxygen-free (argon) atmosphere as well as in the oxygen (air) atmosphere. Samples weight was approximately equal 20 mg. Crucibles of aluminium oxide, allowing measurements up to a temperature of 1500°C, were used [11].

The obtained results - for the selected conditions - were compared with the results obtained in another device: NETZSCH STA 449 F3 Jupiter® (analyser II), for the constant temperature increase rate (10°C/min) and the gas flow rate (40 ml/min). Measurements were performed in both atmospheres for resin samples weighing app. 30 mg. Platinum crucibles allowing measurements up to a temperature of 1000°C [12], were used.

3. Analysis of the results

The initial materials of which binder was made were tested as the first ones. The thermal analysis results of the tested resin are presented in Figure 1. Investigations were made in the thermal analyser I in the oxygen-free (argon) and oxygen (air) atmosphere with the constant gas flow rate (100 ml/min) and the constant temperature increase rate (10°C/min).

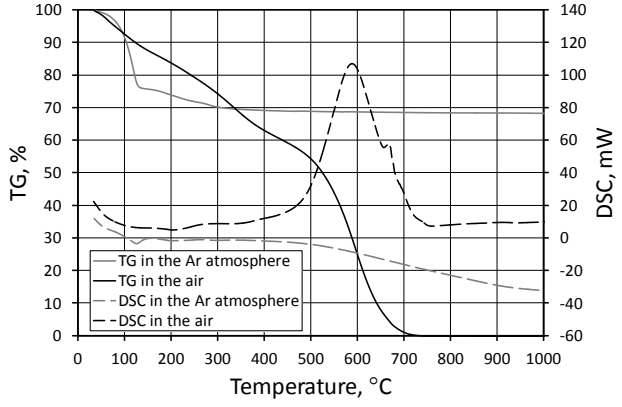

Fig. 1. Thermal analysis of resin in the oxygen-free and oxygen atmosphere at the constant heating rate of 10°C/min and gas flow rate of 100 ml/min (analyser I)

The mass loss of the liquid resin in the oxygen-free atmosphere is - in the tested temperature range - rather small and on the TG curve equals app. 32% (Fig. 1). The highest degradation of this organic material occurred up to a temperature of app. 120°C. The significant endothermic peak indicating the heat flow towards the sample, can be noticed on the DSC curve. As far as the temperature increases, a nearly constant heat exchange with the surroundings can be noticed (DSC curve in the argon atmosphere), for small mass changes of the tested sample. The situation is different when the analysis is realised in the oxygen atmosphere. Up to a temperature of 520°C resin undergoes degradation related to gasification of the tested material. This requires supplying heat to the material sample, which can be seen in a form of endothermic shape of the DSC curve in the oxygen atmosphere. Above a temperature of 520°C the proportional decrease of the sample mass - related to its burning - is seen on the TG curve and confirmed by the exothermic peak on the DSC curve. The maximum amount of the heat emitted to the surroundings occurs at a temperature of

590°C. However, the opinion that the recorded exothermic peak related to the temperature of physicochemical transformations in analysers is often even several dozen degrees higher than the values observed on the TG curves, can be found in references [13]. Resin undergoes the total burning in the thermal analyser at a temperature of 710°C (Fig. 1).

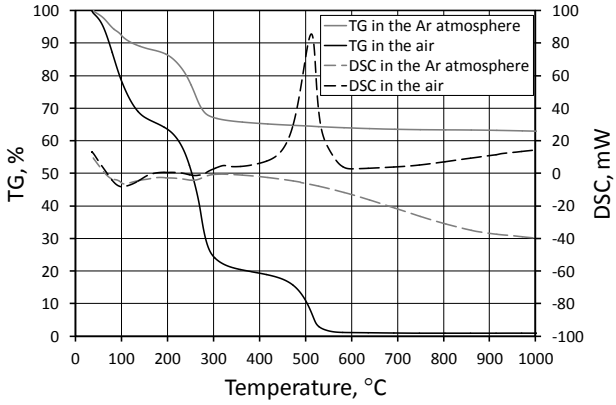

Fig. 2. Thermal analysis of the hardener in the oxygen-free and oxygen atmosphere at the constant heating rate of 10°C/min and gas flow rate of 100 ml/min (analyser I)

The thermal analysis results of the hardener are shown in Figure 2. In this case, the TG curve has more complex shape, caused probably by the hardener composition, since it is a mixture of a few acids and additions (chemical compounds). In the oxygen-free atmosphere the tested sample was loosing its weigh up to a temperature of 100°C as the result of loosing moisture, which is confirmed by a significant inclination of the TG curve, as well as by changes on the DSC curve (endothermic peak at this temperature). Above a temperature of 280°C, in the oxygen-free atmosphere, a small decrease of the sample mass - to 63% - is seen (with a visible endothermic effect on the DSC curve). The TG curve under oxygen conditions is more complex, since there is a visible mass change related to the sample burning from a temperature of 400°C. A distinct endothermic peak at a temperature of 520°C occurs on the DSC curve. The sample under the oxygen conditions changes its mass only negligibly, from a temperature of 570°C to 1000°C, with a non-flammable part being app. 1%. The characteristic element in both Figures (1 and 2) is the fact that the maximum value of the exothermic peak (related to samples burning) corresponds to the inflection point on the TG curve.

Looking for the optimal conditions of the thermal reclamation process the rate of temperature changes of the reclaimed spent moulding sand should be also taken into account. Therefore, the successive investigations, utilising the thermal analysis, concerned the influence of the heating rate of the bound binder (resin-hardener). The TG curves, presented as the temperature function (in the oxygen-free and oxygen atmosphere), for the heating rate in the analyser I, being: 5°/min, 10°/min, 15°/min, 20°/min, 25°/min and 30°/min, are shown in Figure 3 and 4.

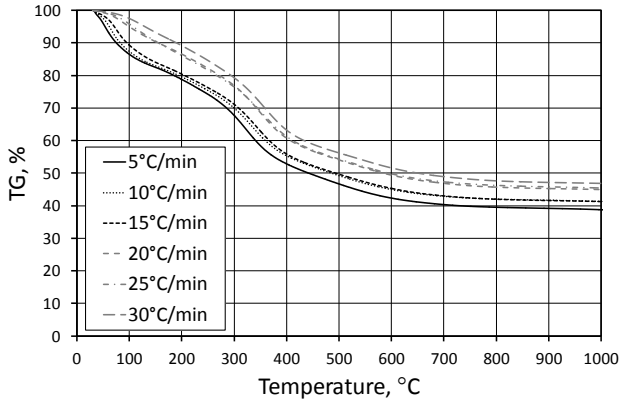

Fig. 3. Thermal analysis of the investigated binder in the oxygen-free atmosphere in dependence on the temperature, for various heating rates and the constant gas flow rate of 100 ml/min (analyser I)

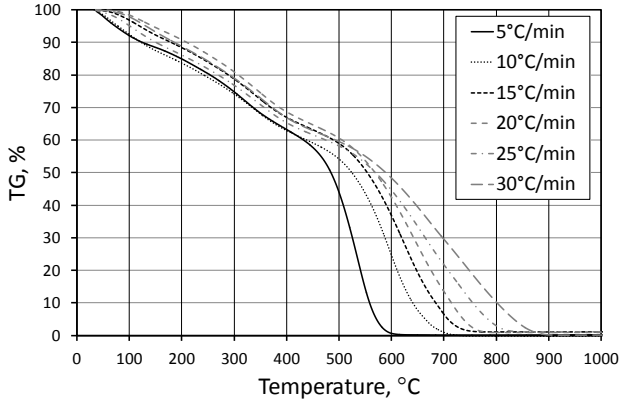

Fig. 4. Thermal analysis of the investigated binder in the oxygen atmosphere in dependence on the temperature, for various heating rates and the constant gas flow rate of 100 ml/min (analyser I)

It can be noticed, that the faster the temperature increase to the lower destruction degree the tested material sample is subjected in the oxygen-free atmosphere (Fig. 3) or at the higher temperature it undergoes total destruction in the oxygen atmosphere (Fig. 4) (at the tested temperature range). This situation is caused by the process duration time. When the same mass losses presented by means of the TG curve will be presented as the time function in the oxygen-free atmosphere (Fig. 5) the largest mass loss of the sample for the heating rate of 5°C/min is the result of the long time needed to reach a temperature of 1000°C. However, in the oxygen atmosphere the faster is the sample heating rate in the shorter time the higher temperature is obtained, and the total destruction time of the tested material is much shorter (Fig. 6).

On the bases of the developed, own method of selecting the required reclamation temperature (described in papers [9-10]) on the basis of the TG curves in the oxygen-free (argon) and oxygen (air) atmosphere - for the selected heating rates of the sample - the temperature needed for the thermal reclamation treatment was determined.

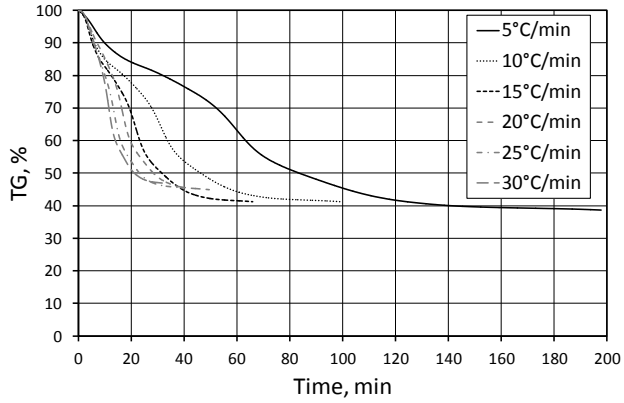

Fig. 5. Thermal analysis of the investigated binder in the oxygen-free atmosphere in dependence on the time, for various heating rates and the constant gas flow rate of 100 ml/min (analyser I)

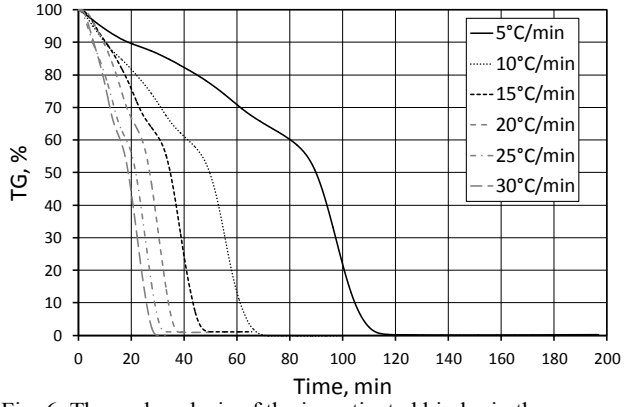

Fig. 6. Thermal analysis of the investigated binder in the oxygen atmosphere in dependence on the time, for various heating rates and the constant gas flow rate of 100 ml/min (analyser I)

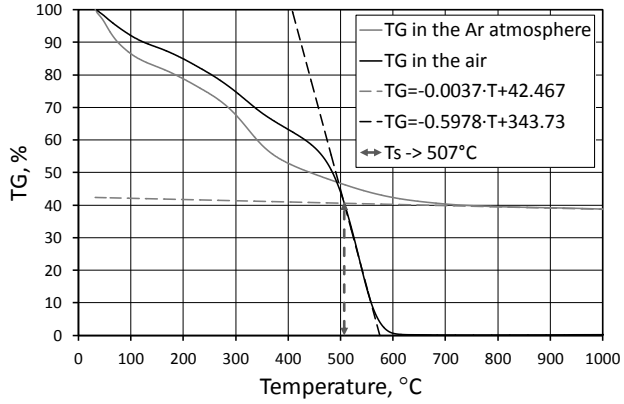

Fig. 7. Determination of the required temperature of the tested binder thermal reclamation, for the heating rate of 5°C/min and the constant gas flow rate of 100 ml/min (analyser I)

The results for the low heating rate, being 5°C/min, are presented in Figure 7. On the basis of the performed analysis the T_s temperature (required burning temperature) of 507°C was determined. For the twice higher heating rate, being 10°C/min, the determined T_s temperature was 551°C (Fig. 8). When the heating rate was increased six times i.e. to 30°C/min, the determined required temperature of the thermal reclamation increased to 598.5°C (Fig. 9). The T_s temperatures for all applied heating rates are presented in Table 1.

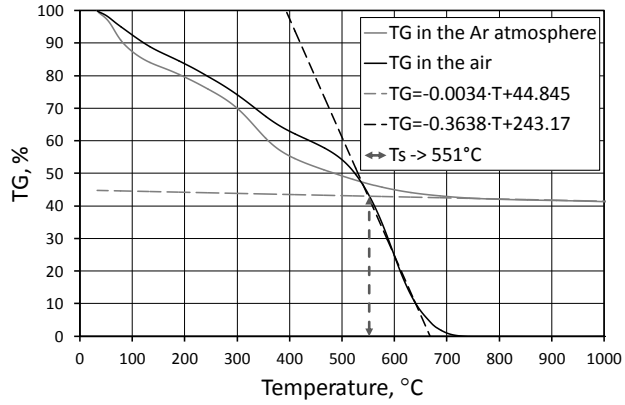

Fig. 8. Determination of the required temperature of the tested binder thermal reclamation, for the heating rate of 10°C/min and the constant gas flow rate of 100 ml/min (analyser I)

Table 1
Required reclamation temperatures for various heating rates of the sample

Heating rate [°C/min]	5	10	15	20	25	30
T_s [°C]	507	551	577	580	583	598.5

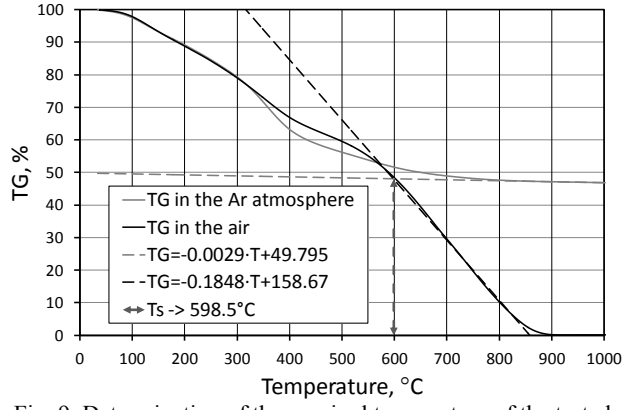

Fig. 9. Determination of the required temperature of the tested binder thermal reclamation, for the heating rate of 30°C/min and the constant gas flow rate of 100 ml/min (analyser I)

As can be noticed, along with the increased heating rate of the tested binder, the higher value of the thermal reclamation required temperature was obtained. The heating rate change of the constant step does not cause a proportional change of the analysed parameter.

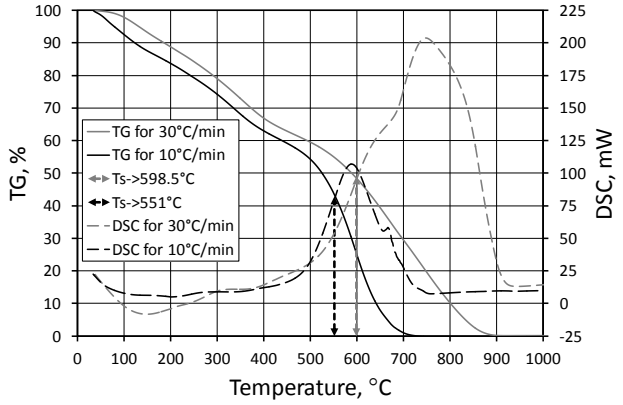

Fig. 10. TG and DSC thermal analyses of the tested binder, in the oxygen atmosphere, in dependence of temperature, for various heating rates and the constant gas flow rate of 100 ml/min (analyser I)

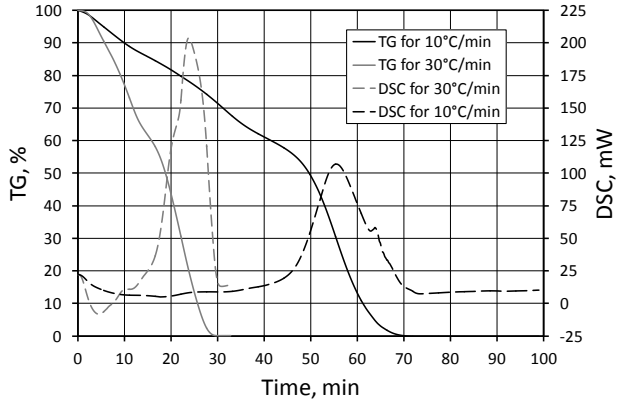

Fig. 11. TG and DSC thermal analyses of the tested binder, in the oxygen atmosphere, in dependence of time, for various heating rates and the constant gas flow rate of 100 ml/min (analyser I)

The TG i DSC curves in dependence of the temperature are presented in Figure 10 for the selected heating rates: 10°C/min and 30°C/min. It was found, that for the lower heating rate the exothermic peak related to the binder burning has the lower value at the lower temperature. The higher heating rate generates the higher in its value heat flow at the higher temperature. The same TG and DSC changes are presented as a time function of the process duration in Figure 11. From the same mass of the tested sample the same amount of energy is obtained. The surface area under DSC curves in a time function, for the exothermic peaks has the same values, in addition to which for the faster heating this peak is sharper and more compressed, while for the lower heating rate it is more distributed in time and of a lower intensity. When analysing the results of the performed investigations (compare Fig. 8 with 10 and Fig. 9 with 10) the repeated regularity that the determined required reclamation temperatures coincide with the inflection points of TG and DSC curves - for the given heating rates - was noticed.

The results of the thermal analysis performed in the oxygen-free and oxygen atmosphere of the same binder from another production process (realised in the analyser II), are shown in Figure 12 [9]. For the same heating rate another gas flow rate - being 40 ml/min - recommended for this type of the device, was applied. On the bases of the obtained results, it can be stated that the flow rate can decide the obtained TG curve shape. The higher gas flow in the time unit, especially creating the oxidising atmosphere, shortens the time of the total binder destruction. It can also influence the increasing mass loss in the oxygen-free atmosphere. Another reason of discrepancies of the required burning temperature in both analysers, can be the result of different binder compositions, regardless of the same trade name. This is confirmed by the other, not yet published by the author, tests.

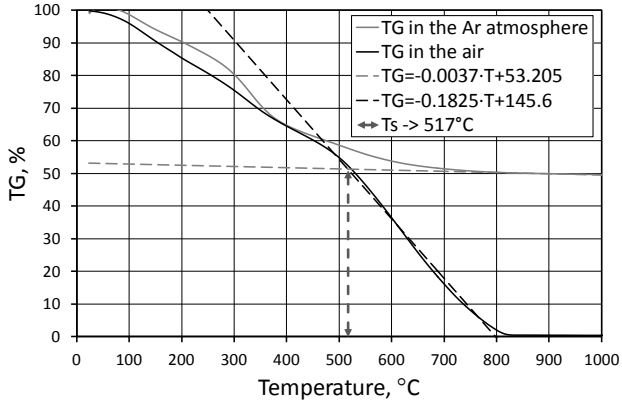

Fig. 12. Determination of the required temperature of the tested binder thermal reclamation, for the heating rate of 10°C/min and the constant gas flow rate of 40 ml/min (analyser II)

4. Conclusions

The performed investigations confirm the suitability of the developed methodology of determining the required temperature of the thermal reclamation of spent moulding and core sands, provided that several essential factors will be taken into consideration.

The first essential criterion constitutes the information that the determined required reclamation temperature concerns only the given batch of the tested binder. The thermal analysis methods are used, among others, for verifying the production repeatability of various kinds of materials, e.g. in pharmacy and in food and chemical industries.

The second essential criterion is using the same equipment for comparative measurements. When the same product is tested in two different devices (often of another construction) different results can be obtained.

The third important factor constitute the application of the same work conditions of the analyser. It was proved during investigations that the heating rate influences the thermal analysis

results. Therefore, assuming the constant method, which will create conditions allowing comparing of the results, seems reasonable.

The performed investigations indicate that the sample heating rate is very essential. In looking for the required temperature of the thermal reclamation - it should be taken into consideration - that not only the temperature but also time is the essential parameter in the thermal process.

The thermal analysis results under oxidising conditions (in the air) can also depend on the amount of the gas flowing through the analyser. On the one hand at a larger flow more oxygen needed for oxidative burning (accelerating the thermal process) is supplied, but on the other hand it can be cooling the analysed material sample (delaying the thermal process).

Acknowledgements

This work was elaborated under research and development study no 11.11.170.318, task 2

References

[1] Łucarz, M., Dereń, M. (2017). Conditions of thermal reclamation process realization on a sample of spent moulding sand from an aluminum alloy foundry plant. *Archives o f Foundry Engineering.* 17(2), 197-201. DOI: 10.1515/afe-2017-0074.

[2] Dziewulska-Kułaczkowska, A. (2007). Application of thermal analysis methods for the examination of chemical compounds. *Laboratorium.* 7-8, 18-22. (in Polish).

[3] Pielichowski, J. & Pielichowski, K. (1995). Application of thermal analysis for the investigation of polymer degradation processes. *Journal of Thermal Analysis.* 43, 505-508.

[4] Janowska, G., Przygocki, W., Włochowicz, A. (2007). *Flammability of polymers and polymeric materials.* Warszawa: Wydawnictwo Naukowo-Techniczne. (in Polish).

[5] Żymankowska-Kumon, S., Bobrowski, A. & Grabowska, B. (2016). Comparison of the emission of aromatic hydrocarbons from moulding sands with furfural resin with the low content of furfuryl alcohol and different activators, *Archives of Foundry Engineering.* 16(4), 187-190. DOI: 10.1515/afe-2016-0107.

[6] Holtzer, M., Bobrowski, A., Dańko, R., Kmita, A., Kubecki, M., Żymankowska-Kumon, S. & Górny, M. (2014). Emission of polycyclic aromatic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene and xylene (BTEX) from the furan moulding sands with addition of the reclaim. *Metalurgija.* 53(4), 451-454.

[7] Kubecki, M., Holtzer, M. & Żymankowska, S. (2013). Investigations of the Temperature Influence on Formation of Compounds from the BTEX Group During the Thermal Decomposition of Furan Resin. *Archives of Foundry Engineering.* 13(2), 85-90. DOI: 10.2478/afe-2013-0042.

[8] Grabowska, B., Szucki, M., Suchy, J.Sz., Eichholz, S. & Hodor, K. (2013). Thermal degradation behavior of cellulose-based material for gating systems in iron casting production. *Polimery*. 58(1), 39-44.

[9] Łucarz, M. (2015). Setting temperature for thermal reclamation of used moulding sands on the basis of thermal analysis. *Metalurgija.* 54(2), 319-322.

[10] Łucarz, M.; Grabowska, B.; Grabowski., G. (2014). Determination of parameters of the moulding sand reclamation process, on the thermal analysis base. *Archives of Metallurgy and Materials.* 59(3), 1023-1027. DOI: 10.2478/amm-2014-0171.

[11] https://www.tainstruments.com/pdf/brochure/sdt.pdf

[12] https://www.netzsch-thermal-analysis.com/pl/produkty-rozwiazania/jednoczesna-analiza-termiczna/sta-449-f3-jupiter/ (in Polish).

[13] Wesołowski, M. (2007). Modern methods of thermal analysis. Basic concepts and definitions. *Laboratorium.* 3, 40-44. (in Polish).