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Thermal degradation behavior of cellulose-based material for gating systems in iron casting production

Summary — This study presents a fragment of research aimed at determining the thermal stability of a cellulose-based composite material used for building gating systems for large iron castings. The behavior of the material itself at elevated temperatures is of major significance for the mould filling process. In this research, thermal analysis methods (DTG, TG, DSC) were used to explain the course of the thermal degradation of the analysed material by establishing thermal effects of transformations occurring during its heating as well as its structural and mass changes. The research was conducted at the temperature range of 40—1000 °C. The degradation process was found to start at the temperature of approx. 300 °C, and the total mass loss at the range of 300—750 °C amounted to 48.8 %. The mass loss observed is accompanied by very strong exothermal effects. The remaining part of the sample mass which had not decomposed up to the temperature of 1000 °C (approx. 51.2 %) probably represents the carbon fibres and ceramic clay present in the material, because these decompose at a temperature higher than the range of the performed thermal analysis and higher than the temperature of the liquid metal fed into the gating system (about 1300—1400 °C). In addition, volatile products of degradation were analysed using IR spectrum and the thermogravimetry (TG) method coupled online with mass spectrometry (MS). In the temperature range 300—750 °C signals for small molecular masses were noticed, which indicates that the degradation process and fragmentation of polymer chains in the cellulose occur as well as formation of small particle compounds, primarily H_2O and CO_2. No signals given off by aromatic compounds were detected.

Keywords: cellulose, thermal analysis, thermal degradation, EG Runner, gating system, large castings.

DEGRADACJA TERMICZNA MATERIAŁU NA BAZIE CELULOZY STOSOWANEGO DO BUDOWY UKŁADÓW WLEWOWYCH DO ODLEWÓW ŻELIWNYCH

Streszczenie — Przedstawiono wycinek badań dotyczących termicznej stabilności wieloskładnikowego tworzywa na bazie celulozy, stosowanego do budowy układów wlewowych przeznaczonych do wielkogabarytowych odlewów żeliwnych. Zachowanie się samego materiału w podwyższonej temperaturze ma istotne znaczenie dla procesu zalewania formy odlewniczej ciekłym metalem. Metodami analizy termicznej (DTG, TG, DSC) badano przebieg degradacji termicznej stosowanego tworzywa, ustalając efekty cieplne przemian zachodzących podczas jego ogrzewania, zmiany strukturalne oraz masę. Analizę prowadzono w temperaturze z zakresu 40—1000 °C. Ustalono, że proces degradacji rozpoczyna się w temp. ok. 300 °C, a całkowity ubytek masy w temperaturze z zakresu 300—750 °C wynosi 48,8 %. Zaobserwowanym ubytkom masy towarzyszą bardzo silne efekty egzotermiczne. Pozostała część masy próbki nie uległa rozkładowi do temp. 1000 °C (ok. 51,2 %), co prawdopodobnie jest związane z obecnością w składzie włókien węglowych oraz materiałów ceramicznych, rozkładających się w temperaturze o wartości powyżej zakresu przeprowadzanej analizy termicznej, a zarazem powyżej temperatury ciekłego metalu wprowadzanego do układu wlewowego (ok. 1300—1400 °C). Przeprowadzono ponadto analizę lotnych produktów rozkładu, stosując metodę spektroskopii IR oraz termograwimetrii (TG), sprzężonej „*on-line*" ze spektrometrią masową (MS). W temperaturze z zakresu 300—750 °C stwierdzono sygnały odpowiadające małym ciężarom cząsteczkowym, świadczące o zachodzeniu procesu degradacji, fragmentaryzacji łańcuchów polimerowych w celulozie i tworzeniu się mało-

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cząsteczkowych związków, w tym przede wszystkim H_2O i CO_2. Nie stwierdzono obecności sygnałów pochodzących od związków aromatycznych.

Słowa kluczowe: celuloza, analiza termiczna, degradacja termiczna, EG Runner, układy wlewowe, odlewy wielkogabarytowe.

INTRODUCTION

Casting is currently one of the most widespread and fastest growing methods of producing machine and equipment parts. It represents a broad industrial field combining the knowledge from many, frequently separate scientific disciplines like material engineering, metallurgy, chemistry, environmental protection, computer modelling or mechanics. Among the many problems and challenges found in foundries, the production of large iron castings, which can weigh several dozen tons, is one of the most demanding and difficult. Casts of this type are used in the power engineering, ship-building and machine industries. Due to their large sizes, frequently complicated shapes and custom production, the manufacture of such casts is a highly advanced subject which requires the use of specialised tools and solutions, including the appropriate technological process supported by computer simulation results [1—3].

One of the main challenges in this kind of tasks is to design and fabricate the gating systems, *i.e.* the channels pouring liquid metal into the mould cavity. Large iron casts are usually made in self-hardening sands moulds (quartz sand, resin, hardener) [4]. The gating system is constructed of ready ceramic semi-finished products, so-called shapes. The range of shapes available in the market is standardized and comprises such basic elements as pipes, elbows, T-pipes, constrictors *etc*. The advantage of this approach is that technological solutions of any complexity can be built. Gating systems of this type are also highly heat and erosion resistant. On the other hand, after the cast is knocked out, the majority of the casting sand can be reused after the appropriate processing, but this is not true for shapes, which are destroyed after a single use and usually landfilled. Due to the use of ready ceramic semi-finished products this significantly increases the quantity of production waste, which is a serious problem in the light of new legal regulations [5, 6]. A new development on the global market is called HOLLOTEX EG Runner. This is a trademark of products for building gating systems in iron casting foundries, which, according to the producer, are made mainly of cellulose [7]. This makes it possible to construct the channels for liquid metal when the mould is being prepared, and during its filling, the cellulose is completely destroyed by the heat, thus significantly reducing the quantity of waste that cannot be recycled. In addition, these shapes are much lighter and easier to work (cut, fit) than their ceramic counterparts. Figure 1 shows a simplified diagram of the technology for large iron casts production using this new type of gating systems.

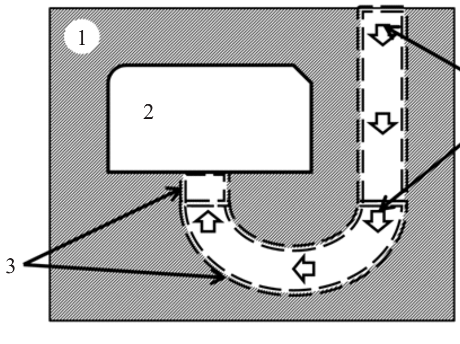

Fig. 1. A simplified diagram of the technology for producing large iron casts, where: 1 — sand mould, 2 — mould cavity, 3 — EG Runner gating system, 4 — direction of liquid metal flow

The use of a cellulose-based material to fabricate the gating system undoubtedly yields many benefits, but questions arise about its behavior in the high temperature (1300—1400 °C) prevailing when iron casts are produced. What is particularly important here are problems like the oxidation kinetics of EG Runner systems, the thermal effects accompanying this process and the impact of gases produced during the thermal destruction of the shapes on both the casting alloy and the environment. The wide-ranging thermal analysis performed as part of this work will make it possible to understand phenomena occurring when liquid metal flows through gating system of the new type [8, 9].

EXPERIMENTAL

Materials

A cellulose-based composite material used for manufacturing semi-finished products (shapes) for making gating systems, sold under the HOLLOTEX EG Runner trademark by Foseco (Fig. 2). Material composition: cel-

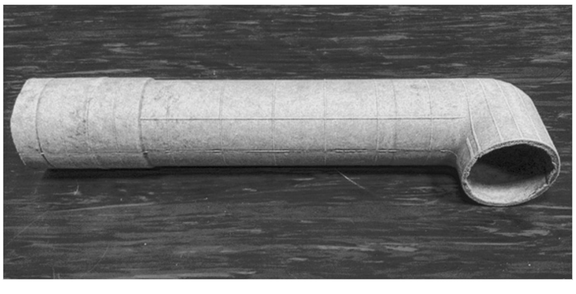

Fig. 2. An example EG Runner shape

lulose reinforced with carbon fibre and aluminosilicates (10 wt. %) [7].

Thermal analysis methods

Experimental research was carried out at the NETZSCH Applications Laboratory.

The NETZSCH STA 449 F3 Jupiter®, NETZSCH QMS Aëolos® and the NETZSCH TG 209 F1 Iris® coupled with the BRUKER Optics FT-IR TENSOR™ were used for thermal analysis.

The NETZSCH model STA 449 F3 Jupiter® simultaneous thermal analyzer can be used to measure the mass change and transformation energetics of a wide range of materials. The top-loading STA can be equipped with various easy exchangeable TG, TG-DTA or true TG-DSC sensors and with different furnaces to accommodate different application areas. The system employed for this work was equipped with a silicon carbide furnace capable of operation from the room temperature up to 1550 °C. The system is vacuum tight, allowing measurements to be conducted under pure inert, reducing oxidizing atmospheres. Heating rates of up to 50 °C/min can be employed and the digital resolution of the balance is 1 μg/digit. Data acquisition and evaluation, as well as instrument control, are carried out using a MS-Windows™ software package. The software allows computing the mass change rate, mass change steps, onset and peak temperatures, inflection points, peak area integration, *etc*.

The Thermo-Microbalance NETZSCH TG 209 F1 Iris® with an effective resolution of 0.1 μg enables highly precise measurements under pure gas atmospheres from ambient temperature up to 1000 °C. Internal mass flow controllers (MFC) guarantee a highly precise gas flow adjustment of three different gases.

Data exchange between NETZSCH PROTEUS® software and Bruker OPUS™ software is done online during the measurement. This guarantees simultaneous start and stop of the measurement as well as data exchange during the measurement.

Table 1. Measurement parameters

Parameter	STA-MS	TG-FT-IR
Temperature program	40—1000 °C	RT — 1000 °C
Heating rate	10 °C/min	10 °C/min
Atmosphere	synthetic air	air
Flow rate	70 cm^3/min	40 cm^3/min
Sample holder	TG-DSC Type S	sample carrier for corrosive gases
Crucible	platinum with pierced lids	Al_2O_3 (0,085 cm^3)
Sample mass	11.44 mg	13.746 mg

The basic measurement parameters are collected in Table 1.

RESULTS AND DISCUSSION

Thermal analysis STA-MS

Figure 3 depicts the mass changes and heat flow rate of the cellulose sample. Five mass loss steps of 0.3 %, 16.9 %, 14.5 %, 8.9 % and 8.2 % were observed (the total mass loss up to the temperature of 750 °C amounts to 48.8 %). Maxima in the rate of mass change occurred at 76 °C, 332 °C, 447 °C, 498 °C and 756 °C.

The first mass loss step which is due to the release of moisture was accompanied by an endothermic effect of 10 J/g (the dehydration of physically-bound water) visible in the DSC signal which was strongly exothermic during all other mass loss steps.

This finding is due to the stepwise burning of the sample above the approximate temperature of 200 °C. An enthalpy value of 5.9 kJ/g is determined. At the temperature range of 330—500 °C, three exothermal effects due to the destruction of the organic part of the material (mainly cellulose) are observed in sequence. At the first stage cellulose destruction, the weak C-O-C and C-C bonds in the glycoside bond decompose. The reaction whereby side groups are detached with C-O bonds breaking leads to the cellulose chain being depolymerized, and then glucosan radicals are regrouped and levoglucosan is produced. At the final stage, levoglucosan is destroyed to tar products (including alcohols, ketones, aldehydes, acids) which volatilize, of which CO_2 is the main component [10—13].

At 764 °C, the TG/DSC curve shows the last mass loss (8.2 %) accompanied by an exothermal effect (1.5 kJ/g). This effect may be due to a modification of the material whose contents include ceramic clays (mainly aluminosilicates) [13, 14].

The remainder of the sample mass (approx. 51.2 %) which has not decomposed up to the temperature of 1000 °C probably contains organics and inorganics found in the composition of the analysed material (including carbon fibres) which degrade at temperatures higher than those of the liquid metal poured (1300—1400 °C) [15, 16]. For this reason the temperature range selected for conducting this research work, from 40 °C to 1000 °C, seems to be sufficient to observe all the phenomena significant from the technological perspective.

Figure 4 presents the temperature dependence of the MS signals with mass numbers 18 and 44 which are due to the release of H_2O and CO_2. These MS signals confirm the release of moisture at lowest temperatures and the burn-up of the sample at higher temperatures, causing the evolvement of H_2O and CO_2 which are typical for cellulose containing a lot of hydroxyl groups. At about 600 °C, only carbon is left which is gradually combusted, up to about 800 °C.

At 335 °C, further mass numbers like 39, 41, 55 and 68 were detected in traces which are attributed to organic molecules and fragments (Fig. 5).

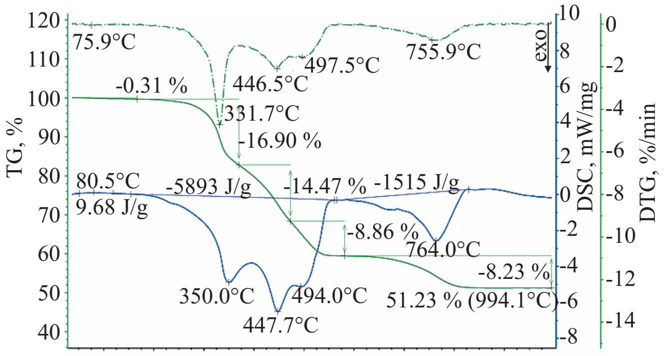

Fig. 3. Temperature-dependent mass change (TG), rate of mass change (DTG, dashed line) and heat flow rate (DSC) of the cellulose sample

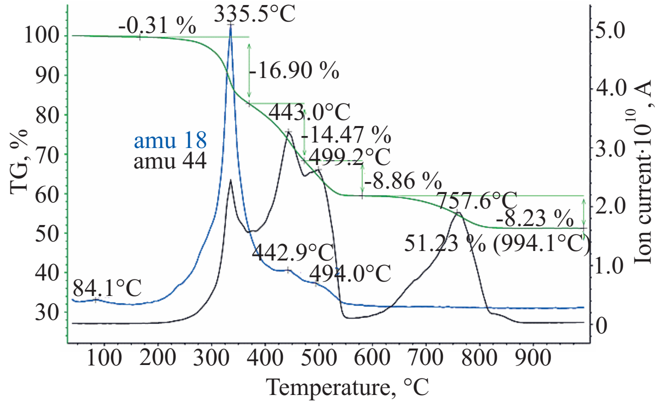

Fig. 4. Temperature-dependent mass change (TG) and results of mass spectroscopy (ion current for mass numbers 18 and 44)

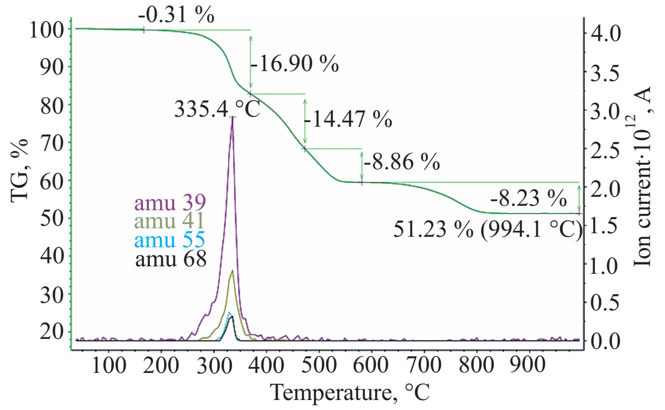

Fig. 5. Temperature-dependent mass change (TG) and results of mass spectroscopy (ion current for mass numbers 39, 41, 55 and 68)

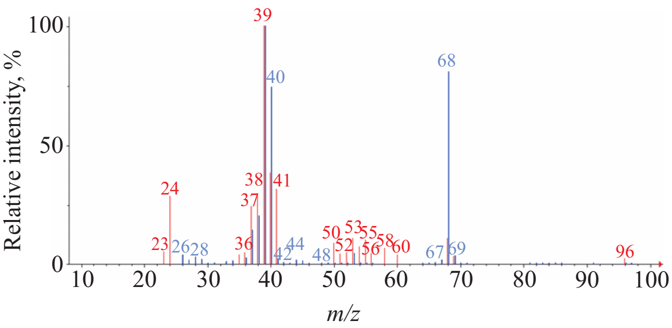

Fig. 6. Mass spectrum of the cellulose sample measured at 335 °C (red) in comparison with the NIST literature spectrum of 3-methyl-2,5-furandione ($C_5H_4O_3$, blue)

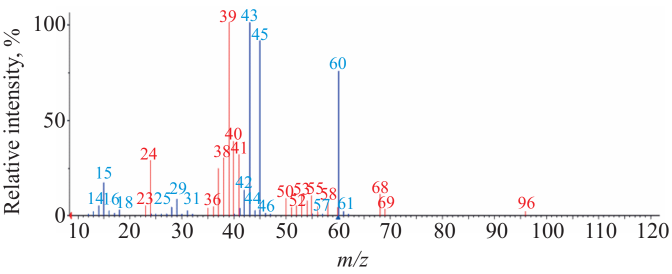

Fig. 7. Mass spectrum of the cellulose sample measured at 335 °C (red) in comparison with the NIST literature spectrum of acetic acid ($C_2H_4O_2$, blue)

Figure 6 displays an example comparison of the mass spectrum with the NIST library.

The molecules of 3-methyl-2,5-furandione could be identified. Acetic acid could furthermore be evolved (Fig. 7). Due to the measurement in air and due to the strong evolvement of CO_2, the mass numbers around 28, 32 and 44 are dominated by N_2, O_2 and CO_2. As a consequence, other molecules like carbon monoxide, formic acid or methanol (see TG-FT-IR results, Fig. 12) which would show these mass numbers could not be detected.

Thermal analysis TG-FT-IR

Figure 8 shows the TG results of the measurement of the sample in the temperature range from room temperature to 1000 °C under air atmosphere with the heating rate of 10 °C/min. TG depicts the relative mass change of the sample (black), the mass-loss rate signal as the first

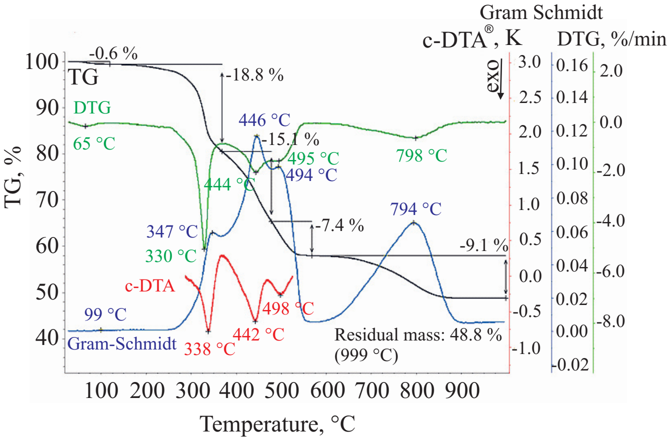

Fig. 8. TG- (black), DTG- (green) Gram-Schmidt- (blue) and c-DTA-results (red) of the sample

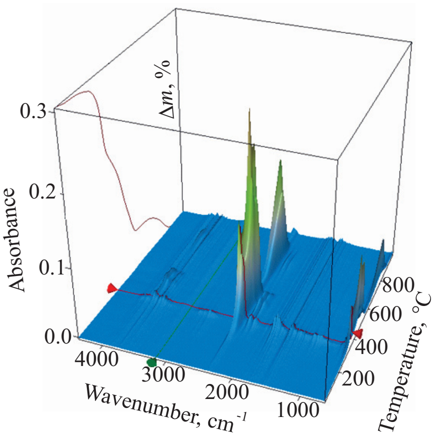

Fig. 9. 3D view of all detected IR-spectra versus temperature including the TG results at the side face

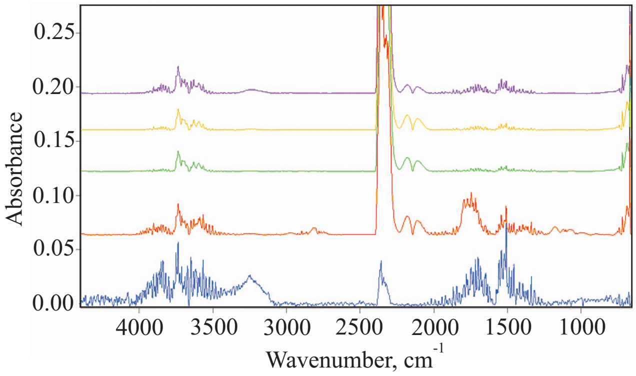

Fig. 10. Extracted IR spectra of the specimen at 74 °C (blue), 340 °C (red), 446 °C (green), 495 °C (orange) and 795 °C (purple)

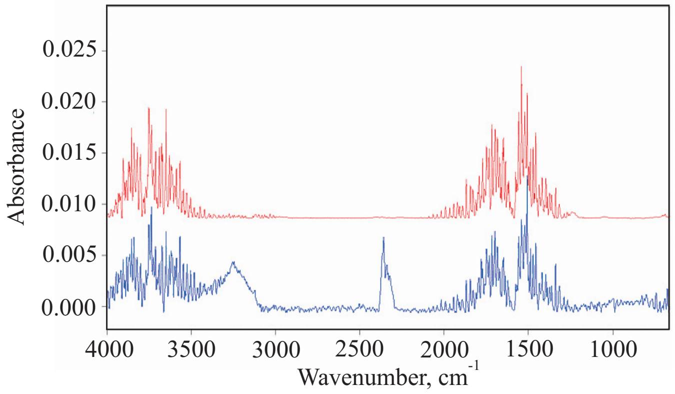

Fig. 11. Comparison of the extracted IR-spectrum at 74 °C (blue) with the library spectrum of water (red)

derivative of TG (DTG, green) and the Gram-Schmidt trace (blue curve) as the overall IR intensities. Along with the DTG curve, the intensities of the Gram-Schmidt trace increase as soon as a mass loss is detected. It is more or less the mirrored view of the DTG curve and this shows that the gases are interacting with the infrared beam as soon as they are released and transferred to the gas cell.

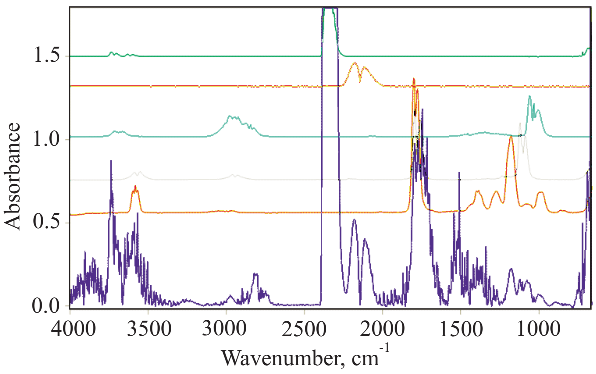

Fig. 12. Comparison of the extracted IR-spectrum at 340 °C (blue) with the library spectra of CO (red), CO_2 (green), acetic acid (orange), formic acid (purple) and methanol (turquoise)

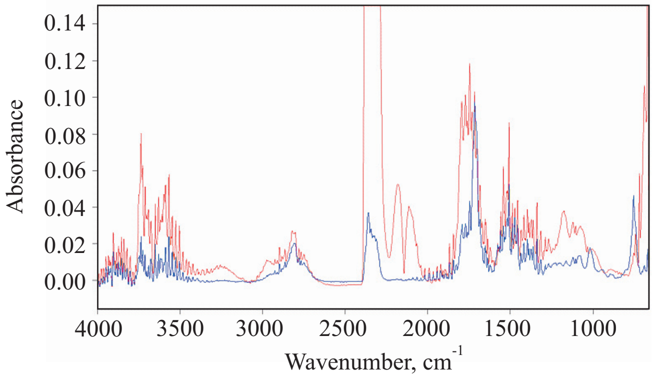

Fig. 13. Comparison of the extracted IR-spectrum at 340 °C (red) with the extracted spectrum of fructose (blue)

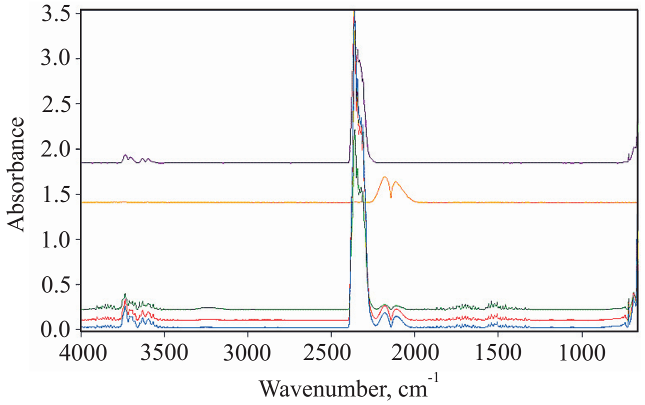

Fig. 14. Comparison of the extracted IR-spectra at 446 °C (blue), 495 °C (red) and 795 °C (green) with the library spectra of CO_2 (purple) and CO (orange)

The c-DTA signal implies the *calculated Differential Thermo Analysis* signal where the signal of the sample temperature is used to calculate the difference between the theoretical and the real temperature.

Five mass loss steps can be detected (0.6 %, 18.8 %, 15.1 %, 7.4 % and 9.1 %). The residual mass at the end of the temperature program is about 49 %.

The c-DTA signal is shown as an example in the temperature range from 300 °C to 550 °C. Here, comparable to the STA results, three exothermic peaks can be detected.

A collection of all detected IR-spectra is shown as a 3-dimensional cube in Figure 9.

From the labelbox one can clearly see the communication beetwen the two software applications. Not only the IR data, for example the Gram-Schmidt-trace, is transferred to the Proteus software, but also the sample mass is transferred from the Proteus to the Opus software.

From this 3-dimensional plot single spectra at the Gram-Schmidt maxima were extracted (Fig. 10) and compared to library data (Figs. 11 to 14).

The first mass loss step is due to the release of water (Fig. 11).

During the second step acetic acid, formic acid, methanol, CO and CO_2 can be detected (Fig. 12).

Additionally, the extracted spectrum was compared to an extracted spectrum of a fructose sample which should represent the evolvement of the cellulose base units (Fig. 13).

The last mass loss steps are due to the release of CO and CO_2 in different concentrations (Fig. 14).

CONCLUSIONS

The completed thermal analysis allows determining of the behavior of the material exposed to temperatures ranging from 40 °C to 1000 °C.

The thermal curves are of complex shapes as the material degrade in several stages, due to its composition and physical/chemical properties. The thermal curves show that the degradation process starts at approx. 300 °C. It was found that the degradation, mainly of the organic part of the sample, continued to the temperature of approx. 750 °C with the total mass loss of 48.8 %. The mass loss in this temperature range is accompanied by very strong exothermal effects, which may have an impact on the liquid metal temperature. The remaining part of the sample mass, which had not degraded up to the temperature of 1000 °C (approx. 51.2 %) probably represents carbon fibres present in the material, because these decompose at a temperature higher than the range of the thermal analysis completed and higher than the temperature of the liquid metal poured into the gating system.

Based on the analysis of volatile products of material decomposition, carried out using IR spectrum and the thermogravimetric (TG) method coupled on-line with mass spectrometry (MS), signals of low molecular weights were detected. These represent the evidence, that the degradation and fragmentation of polymer chains in the cellulose occur as well as formation of small particle compounds, primarily H_2O and CO_2. In addition, the IR spectrum analysis led to the finding that destruction products in the form of organics — acetic acid and methanol — can form. No signals coming from aromatic compounds were detected, which is significant when assessing the harmfulness of material destruction products released, as well as their environmental impact. In addition, as the organic part of the material, mainly cellulose, is burned out (practically in 50 %), the quantity of waste generated in the manufacturing cycle is reduced.

Results of this research work may represent significant premises for developing optimum technologies of producing large iron castings using HOLLOTEX EG Runner gating systems.

ACKNOWLEDGMENT

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