A novel approach for thermal evolution analysis of steel samples by using chips with granular morphology

Abstract

Herzog has recently launched a new module for the milling machine HS-F 1000 that allows the production of chips with a granular morphology especially suited for thermal evolution analysis. In this application note, we investigated the analytical reproducibility for the analysis of C, S and N using different steel material. Furthermore, we compared the analytical results of granular chips with those made from solid punched pieces. The relative standard deviation for the mean concentration of C was in the range between 0.7 and 2.4 %, for S between 0.2 and 3.9 % and for N between 0.2 and 4.4 %. The comparison between results from granular chips and solid pieces revealed no significant differences. The study demonstrates that the granular chips produced by the new module provide all conditions necessary for an easy handling and reliable combustion analysis.

Key words

• **Combustion analysis** • **Chips** • **Milling** • **Automation** • **Steel**

Introduction

Thermal evolution analysis is a destructive analysis method to determine the carbon (C), sulfur (S), nitrogen (N), oxygen (O) and hydrogen (H) content of iron and steel samples. For C and S analysis, the sample is filled into a ceramic crucible together with tungsten, tin or other types of accelerator. Subsequently, the specimen is heated to a temperature of approximately 2100 °C using a high-frequency induction furnace. The combustion gas is transported in a flow of pure oxygen to solid state IR detectors for measurement of the carbon dioxide and sulfur dioxide concentration.

For determination of O and N, the sample is fed into the analyzer from the outside and temporarily deposited in a sample loading port. A graphite crucible is placed directly under the sample holding area. After an outgas cycle for reducing the contamination of the crucible, the sample automatically drops into the hot crucible. A helium stream entrains the gases to be analyzed to the respective analyzing instruments. The O content is quantified as carbon monoxide or dioxide using IR detection while N is determined by using a thermal conductivity detector.

The collection of representative and processable

samples is a critical step in the analytical process. Samples might be taken from liquid metal as well as cast, wrought or finished products. Typical sample types used for analysis include punched pieces, slugs, pins, strips, chips, drillings and powders. The samples can be obtained either by manual or automatic procedures. Herzog offers various solutions for manual and automatic preparation of samples suitable for combustion analysis. One possibility is to punch small pieces out of double thickness samples or sample slices using the HUST punching machine. The punched pieces can either be removed and processed manually or sent pneumatically to a magazine or analyzer for automatic processing.

Another possibility is to collect chips that are produced during sample surface processing with a face milling cutter. Those chip collection units are integrated in nearly every automatic Herzog milling machine including the HS-F 1000, HS-FF 2000, HS-FF and HS-CF. The obtained chips can be either removed manually or can be pneumatically sent to a sample magazine. The chips obtained in this way are suitable for the analysis of C and S. However, due to their coiled shape and irregular size, they are hardly usable for automatic dosing or automatic introduction into the loading port of the N analyzer.

In this application note, we present a newly developed module for the production of chips especially suited for the analysis of C, S and N using thermal evolution methods. The chips show an evenly granular shape and uniform size distribution which makes automatic dosing and insertion into nitrogen analyzers particularly easy. We will demonstrate the C, S and N results of different steel and iron samples as obtained from analysis of granular chips. Furthermore, we will compare the analytical results made from punched pieces to those from granular chips.

Methods

The chips were produced in an automatic milling machine of the type HS-F 1000 with an integrated module for production of granular chips. All samples were manually inserted into the machine. In a first step, the top layer of the sample was removed by a face-milling cutter. Afterwards, the support of the HS-F 1000 transported the sample to the chip production module. Here, the sample was passed over a cylindrical milling cutter with 30 cutting edges (Figure 1).

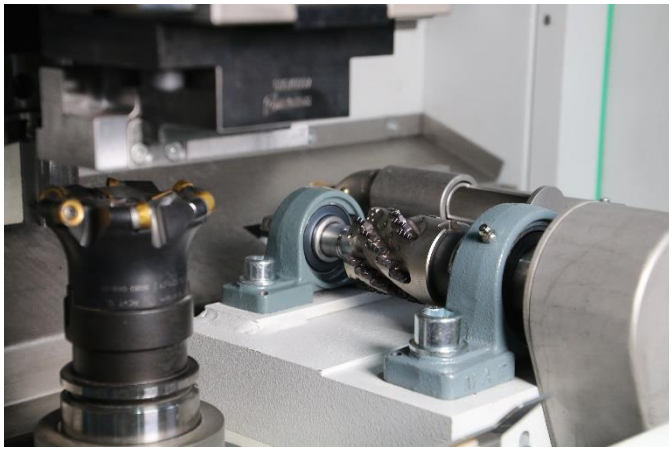

Figure 1: *The module for production of granular chips is fully integrated into the milling machine HS-F 1000. After removal of the uppermost layer by the face-milling cutter the sample is transported to the module.*

The produced chips were collected in a cup that was positioned on a special holder within the module. In all samples we were able to produce reproducible granular chips with an elongated narrow shape (Figure 2).

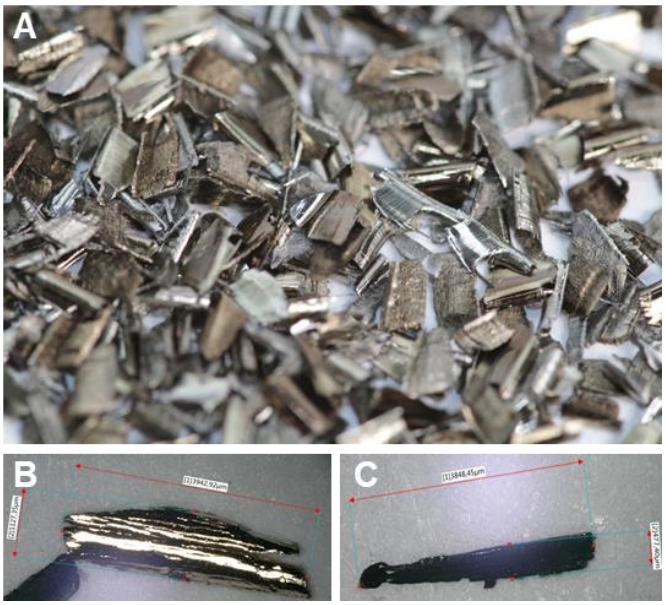

Figure 2: *(A) Macroscopic appearance of the granular chips. (B) Microscopic image of a granular chip produced from a brass sample. (C) Microscopic image of a granular chip produced from a steel sample.*

For determination of C and S, we weighed 500-1000 mg of the chips into a ceramic crucible according to the sample type to be analyzed. Subsequently, we added 1.5- 2.0 g tungsten as accelerator and introduced the crucible into the analyzer (Elementrac CS-i, Eltra, Haan Germany). For determination of N, we weighed 1000 mg of the chips and filled the sample material into the analyzer (Elementrac ONH-p2, Eltra, Haan, Germany) via the designated input.

In the first step, we tested the reproducibility of the C, S and N measurement by using granular chips. For C and S determination we used RH 31,23 (reference material), 42CrMoS4 (heat treated alloy steel), 1.3343 (high speed steel) and 1.4305 (free-cutting steel). For each material, we conducted ten trials and calculated the mean content (%), standard deviation (SD) and relative standard deviation (RSD). With the material RH 31,32, we carried out three test runs à 10 trials.

For N determination, we used the materials 42CrMoS4, 1.3343 and 1.4305 carrying out 10 trials each.

In a further step, we compared the analytical results of C and S made from punched pieces to those from granular chips. Both punched pieces and granular chips were obtained from the same sample specimen. We carried out three analyses from punched pieces and six analyses from granular chips. For this test series we used CK-15 (case hardened steel) and ST52-3 (unalloyed structural steel).

Results

Determination of C and S by using granular chips

For all tested materials we achieved reproducible results (Table 1 and 2). For RH31,32 the RSD of the C content was between 1.6 and 2.4 %. The RSD of the S content was between 2.4 and 3.9 %. For the other materials the RSD of C was between 0.7 and 1.0 % and of S between 0.2 and 3.8 %. All batches of chips produced by the cylindrical cutter module were easy to handle and could be weighed and filled into the crucible without any problems.

Material	Mean (%)	Standard Deviation (%)	Relative Standard Deviation (%)
RH 31,32 (1)	0.0237	0.0005	2.4
RH 31,32 (2)	0.0237	0.0005	2.1
RH 31,32 (3)	0.0237	0.0004	1.6
42CrMoS4	0.4206	0.0040	1.0
1.3343	0.3808	0.0029	0.8
1.4305	0.0468	0.0003	0.7

Table 1: *Results for carbon after combustion analysis of granular chips obtained from various materials.*

Material	Mean (%)	Standard Deviation (%)	Relative Standard Deviation (%)
RH 31,32 (1)	0.0095	0.0003	3.9
RH 31,32 (2)	0.0090	0.0002	2.4
RH 31,32 (3)	0.0091	0.0002	2.7
42CrMoS4	0.0222	0.0005	2.3
1.3343	0.0050	0.0002	3.8
1.4305	0.3678	0.0007	0.2

Table 2: *Results for sulfur after combustion analysis of granular chips obtained from various materials.*

Determination of N by using granular chips

As shown in Table 3 the RSD of the N content in all three tested materials was between 0.2 and 4.4 %. All tested chips were easy to handle and could be filled into the sample holding without any problems. In particular, it was not necessary to pack the chips in air-tight tin or nickel capsules.

Material	Mean (%)	Standard Deviation (%)	Relative Standard Deviation (%)
42CrMoS4	0.0033	0.0009	2.9
1.3343	0.0112	0.0005	4.4
1.4305	0.0824	0.0019	0.2

Table 3: *Results for nitrogen after combustion analysis of granular chips obtained from various materials.*

Comparison of C and S analysis made from punched pieces to those from granular chips

The comparison of the C and S analysis between punched pieces and granular chips revealed no significant differences. For CK-15, the mean C content (SD, RSD) of punched pieces was 0.1560 % (0.0016 %, 1.0 %), the mean S content was 0.0305 % (0.0003 %, 0.8 %). The mean C and S content for granular chips was 0.1489 % (0.0016 %, 1.1 %) and 0.0300 % (0.0003 %, 1.1 %) (Figure 3). For ST52-3, analysis of punched pieces revealed mean values for C and S of 0.1497 % (0.0033 %, 2.2 %) and 0.0116 % (0.0003 %, 2.9 %). Analyses made from granular chips revealed mean C and S values of 0.1764 % (0.0012 %, 0.7 %) and 0.0118 % (0.003 %, 2.9 %).

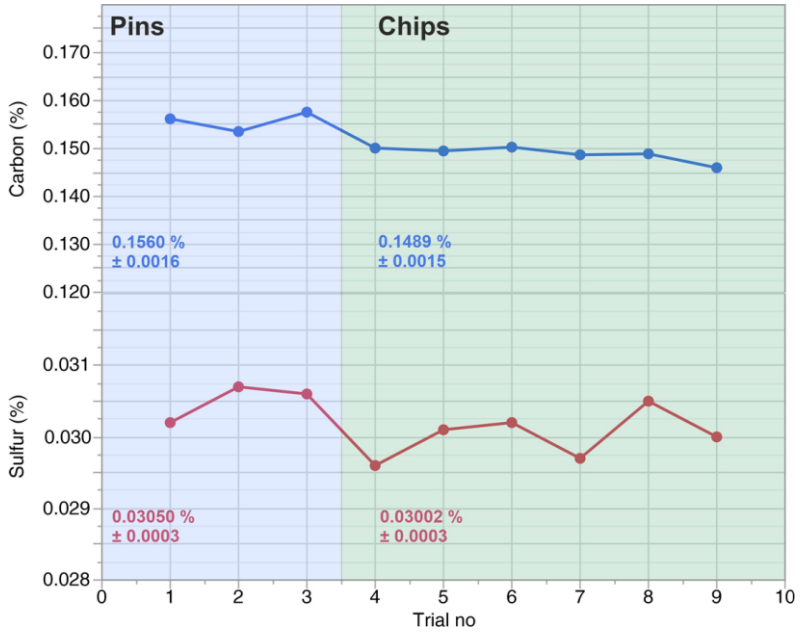

Figure 3: *Analysis results for carbon and sulfur obtained from a CK-15 steel sample. We initially analyzed three solid pins punched out of the material followed by a batch of six chip samples.*

Discussion

There are three main conclusions that can be drawn from this study. First, the granular chips produced by the cylindrical milling cutter module in the HS-F 1000 meet all requirements for automatic handling and analysis. The applied technology enables the reproducible breaking of the chips during the milling process leading to a uniform and even morphology. The granular chips can be easily and precisely dispensed using an automatic dosing device. Furthermore, they can be automatically transported from the milling machine to the analyzer by using a pneumatic tube system. The smooth shape prevents the chips from getting caught on the inside of the transportation tube. This avoids cross-contamination between subsequent samples.

At the same time, the smooth morphology enables the filling of chips into the sample holding area of ONH- analyzers. These properties allow all possibilities for fully-automated preparation and combustion analysis of chips from steel and iron samples.

Second, the analysis of granular chips resulted in an excellent repeatability. Accordingly, the RSD of the C content was between 0.7 and 2.4 %. For S and N, the RSD was between 0.2 and 4.4 %. These values of variance are in the same range as previously reported in other studies [1, 2].

We did not observe any property of the chips that may impair their precise and accurate analysis by thermal evolution methods. On the contrary, sample preparation using a cylindrical milling cutter seems to be particularly suitable for achieving reliable analytical values for C, S and N.

The third finding of this study also supports the assumption that sample preparation by a cylindrical milling cutter does not interfere with combustion analysis. The comparison of the analytical results from solid pieces to those from granular chips did not reveal any significant differences.

Both the solid piece as well as the granular chips were from the identical specimen. This is a clear indication that the mechanical stress caused by the milling process was so low that it had no significant effect on the analytical outcome for C, S and N.

In conclusion, the granular chip module presented in this application note is a suitable tool for both manual and automatic combustion analysis of steel and iron samples. For an automated solution, the module for granular chip production can be connected to a magazine via a pneumatic connection. In this case, the operator removes the sample and inserts it manually into the analyzer. Alternatively, the module can be connected to the Herzog CNSLab. Here, the chips are automatically received, weighed, filled into the crucible and introduced into the combustion analyzer. The whole process is fully-automatic; an intervention by the operator is not necessary.

References

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