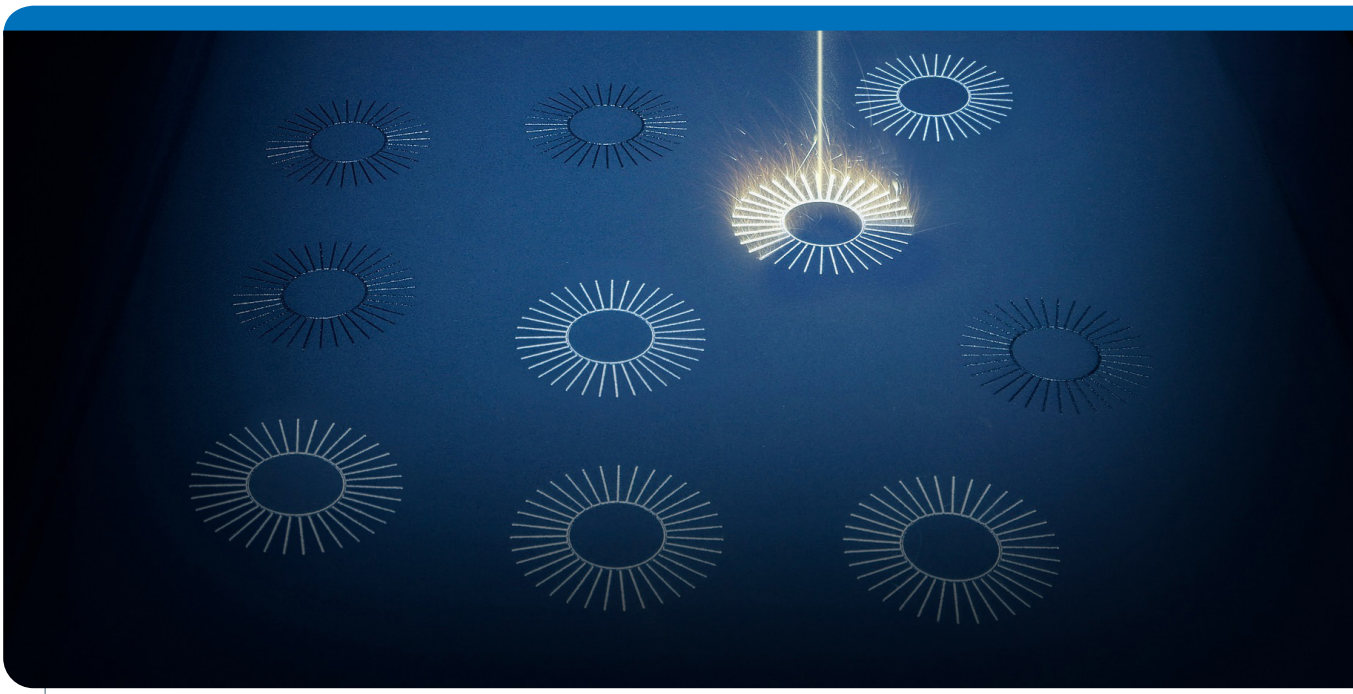

Application Note 001

Elemental Analysis solutions in Additive Manufacturing

A Powder Metallurgy case study

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Introduction

Additive Manufacturing (AM), also referred to as 3D printing, is a term describing the process of joining certain materials to create objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methods. The additive manufacturing process allows a high degree of geometrical freedom and is thus a cost-effective way to produce highly complex structures even for small output numbers.

The most common technique used in additive manufacturing is powder bed selective laser melting,

which shares similar challenges to welding, especially when it comes to light elements such as oxygen and hydrogen. But not only the additive manufacturing process itself needs to be monitored, the powder production, storage and recycling also play a major role when it comes to quality control, process optimization and cost reduction. Elemental analysis of major and trace elements as well as the analysis of light elements (CS/ONH/Ar) are thus essential in judging the quality of the powder or the printed/finished product.

The amount of argon or nitrogen can tell whether either of the gases have been used for powder atomization. Oxygen and hydrogen can be added by i.e., wrong storage (alteration by humidity) and can degrade the mechanical properties of the printed product. The amount of sulfur in powder and printed product can also have a negative influence on the material's properties, while carbon is used as an alloying element for steel powders and can also be added during binder jetting. These light elements (CS/ONH/Ar) can be analyzed using either combustion analysis for CS or inert gas fusion for ONH/Ar.

Major and minor alloying elements can be monitored using XRF analyses from ppm to 100%. WDXRF provides the best sensitivity and resolution for metal and metal powder applications. As certified reference material for metal powders is scarce, solid metal calibrations can be set up and corrected in order to quantify the corresponding elements in metal powders, too.

Insights into a Customer's Laboratory – Rosswag GmbH

The more than 100 years old German forging company Rosswag GmbH, with its innovative AM subdivision Rosswag Engineering set up a holistic metal AM process chain, from metal powder production up to 3D printing of metal parts and material analysis. The metal powder is produced via inert gas atomization on an AU3000 Atomizer from Blue Power Casting Systems GmbH (Figure 2) and specifically tuned to gain a high yield in the typical Laser Powder-Bed Fusion (LPBF) particle size range of 15 µm to 63 µm.

The LPBF production systems, used at Rosswag Engineering, are three SLM 280 with two lasers each from SLM Solutions Group AG (Figure 1). These systems pose a very reliable compromise between industrial production and research and development capabilities. Rosswag has already qualified more than 40 different metal materials and produced more than 60 000 parts on these systems.

The process chain at Rosswag GmbH was certified by TÜV Süd for quality management in additive manufacturing processes, quality assurance, reproducible and traceable processes, and controlled material handling. This now makes Rosswag GmbH certified powder producers as well as part manufacturers. To receive the certification, the fulfillment of DIN SPEC 17071:2019 was required. Part of this is their elemental analysis procedure, which includes determination of major and trace elements with their S8 TIGER and light elements with their G8 GALILEO (ONH) and G4 ICARUS (CS).

Figure 1: LPBF systems in the Rosswag Engineering laboratory
Source: Rosswag Engineering

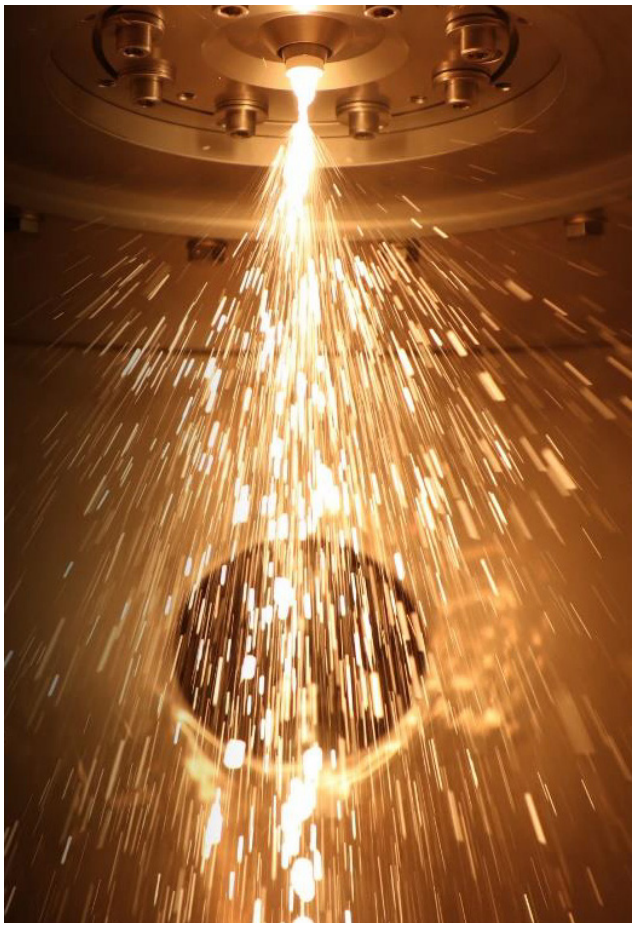


Figure 2: Gas atomization at Rosswag Engineering
Source: Rosswag Engineering

A complementary analytical method for Elemental Analysis

Stainless Steel 316L (1.4404, Fe base) was chosen as sample material for this complementary study. The metal powder was atomized under Nitrogen (N2), and the spherical particles have a diameter of 10-45 µm (d10,3 ca. 21 µm – d90,3 ca. 44.3 µm; SPHT90,3 ca. 0.96) at a density of 4.61 g/cm^3. The solid AM specimens were printed using the following process parameters: Laser power of 235 W, scan speed of 770 mm/s, hatch distance of 0.12 mm and layer thickness of 50 µm.

For an ideal quality control of the whole additive manufacturing process, elemental analysis should be carried out on the raw material as well as the intermediate and final product. For inert gas fusion and combustion analysis this requires the metal powders as well as small 3D-printed cubes of approximately 5 mm edge length (dependent on material). For X-ray fluorescence, metal powders as well as 3D-printed discs with dimensions of 39.5 x 0.5 mm are sufficient.

Figure 3: Printed metal cubes (5.0 mm edge length)

Figure 4: Printed and grinded metal disc (40 mm diameter, 5.0 mm thickness)

Figure 5: Original metal powder

Method Setups

CS/ONH Analysis

For the analysis of ultra-light element (C & ONH) and Sulfur (S), the following instrument settings were applied for best performance and detection:

Instrument	G4 ICARUS		G8 GALILEO		
Technique	Combustion Gas Analysis		Inert Gas Fusion (IGF)		
Element	C	S	O	N	H
Detector	IR	UV	IR	TCD	TCD
Power Level	4	4	65%	65%	29%
Temperature	N/A	N/A	~2400°C	~2400°C	~1400°C
Fluxes	1x W	1x W	Ni capsule	Ni capsule	Ni capsule

Table 1: Summary of method setups used for light element analysis

WDXRF Analysis

All other elements (including Sulfur) are analyzed by WDXRF using a global Fe base metal calibration which is suitable for low alloy and high alloy steel matrices. For some elements, automatic line switches are applied to allow best precision for low and high concentration levels. These elements include Fe, Ni and Cr on the S8 TIGER Series 2, and Fe on the S6 JAGUAR.

Additional crystals beside the standard configuration (XS-55, PET, LiF200) are XS-Ge-C (higher resolution and sensitivity for P and S) on the S6 JAGUAR, and XS-Ge-C and LiF220 (higher resolution for transitions metals) on the S8 TIGER Series 2.

The analytical WDXRF method was set up using solid standards due to the lack of certified reference materials for metal powders. This is achieved by applying a drift correction to transfer sensitivities for solid samples to powders with additional adjustments of the evaluation models.

Number	Analyte Line	Generator Voltage (kV)	Tube (mA)	Collimator (°)	Analyzer Crystal	Detector
1	Sn KA1	50	8	0.66	LiF200	HighSenseXE
2	Mo KA1	50	8	0.66	LiF200	HighSenseXE
3	Nb KA1	50	8	0.66	LiF200	HighSenseXE
4	W LB1	50	8	0.66	LiF200	HighSenseXE
5	Cu KA1	50	8	0.66	LiF200	HighSenseXE
6	Ni KA1	50	8	0.66	LiF200	HighSenseXE
7	Fe KB1	50	8	0.66	LiF200	HighSenseXE
8	Co KA1	50	8	0.66	LiF200	HighSenseXE
9	Fe KB1	50	8	0.66	LiF200	HighSenseXE
10	Mn KA1	50	8	0.66	LiF200	HighSenseXE
11	Cr KA1	50	8	0.66	LiF200	HighSenseXE
12	V KA1	50	8	0.66	LiF200	HighSenseXE
13	Ti KA1	50	8	0.66	LiF200	Flow Counter
14	S KA1	30	13.3	0.66	XS-Ge-C	Flow Counter
15	P KA1	30	13.3	0.66	XS-Ge-C	Flow Counter
16	Si KA1	30	13.3	0.66	PET	Flow Counter
17	Al KA1	30	13.3	0.66	PET	Flow Counter

Table 2: Summary of recommended WDXRF measurement parameters on the S6 JAGUAR

Number	Analyte Line	Generator Voltage (kV)	Tube (mA)	Collimator (°)	Analyzer Crystal	Detector
1	Sn KA1	60	67	0.46	LiF200	Scintillation counter
2	Mo KA1	60	67	0.23	LiF220	Scintillation counter
3	Nb KA1	60	67	0.23	LiF220	Scintillation counter
4	W LA1	60	67	0.23	LiF220	Scintillation counter
5	Cu KA1	60	67	0.23	LiF200	Scintillation counter
6	Ni KA1	60	67	0.23	LiF220	Scintillation counter
7	Ni KA1	50	81	0.23	LiF200	Scintillation counter
8	Fe KB1	50	81	0.23	LiF200	Scintillation counter
9	Co KA1	60	67	0.23	LiF200	Scintillation counter
10	Fe KA1	50	81	0.23	LiF220	Scintillation counter
11	Mn KA1	60	67	0.23	LiF220	Scintillation counter
12	Cr KA1	60	67	0.23	LiF220	Scintillation counter
13	Cr KA1	50	81	0.23	LiF200	Scintillation counter
14	V KA1	50	81	0.46	LiF200	Flow Counter
15	Ti KA1	50	81	0.46	LiF200	Flow Counter
16	S KA1	30	135	0.23	XS-Ge-C	Flow Counter
17	P KA1	30	135	0.46	XS-Ge-C	Flow Counter
18	Si KA1	30	135	0.46	PET	Flow Counter
19	Al KA1	30	135	0.46	PET	Flow Counter

Table 3: Summary of recommended WDXRF measurement parameters on the S8 TIGER Series 2

Why do XRF and CS/ONH techniques complement each other so well?

As soon as samples contain higher amounts of molybdenum (Mo), the analysis of trace level concentrations of Sulfur becomes challenging due to an overlap of Mo LA1 on S KA1. In this example, the analysis of sulfur is more efficient and reliable using combustion analysis. Carbon at higher concentrations in cast or pig iron is a standard application on WDXRF spectrometers. At relevant concentrations for steel applications, the measurement signal is significantly lower and surface polishing will get more important. Higher sensitivity and precision will be reached using combustion analysis.

Oxygen and nitrogen measurements by XRF are limited to specific sample matrices (light to intermediate) and special preparation (solid or pressed pellets without binder). In heavier metal matrices (e.g., Fe and Ni base), concentrations and absorption depth of these light elements is too low. Hydrogen cannot be determined by XRF at all. As such, inert gas fusion can be used as a second complementary techniques beside combustion/fusion analysis (CS/ONH).

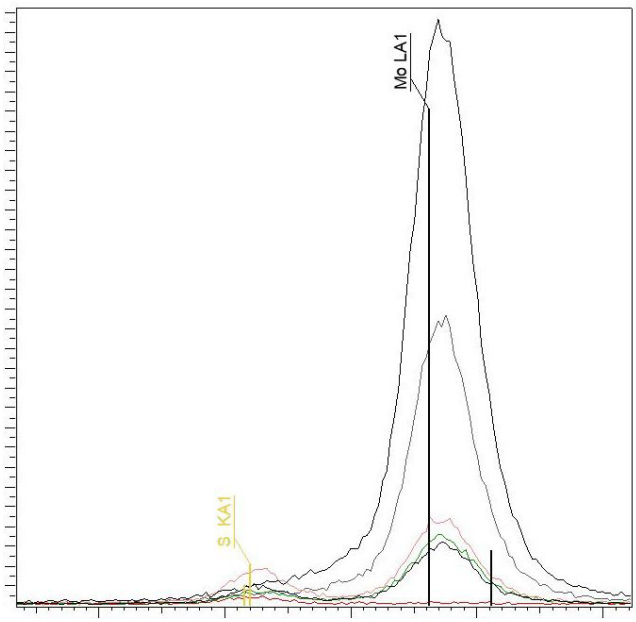


Figure 6: Example of the overlap of Mo LA1 on S KA1

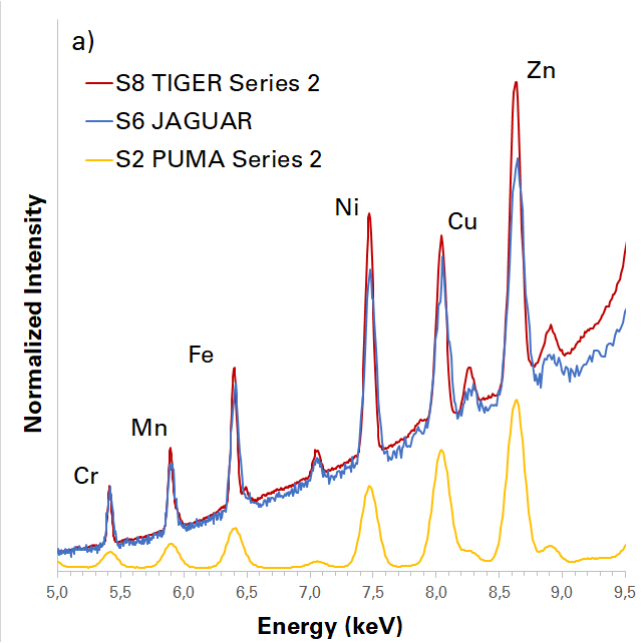


Figure 7a): Intensity and resolution comparison of a fused bead with 100 ppm of several elements measured/scanned on EDXRF and WDXRF instruments (S2 PUMA Series 2 - 40 kV, 500 µm Al; S6 JAGUAR - 50 kV, LiF200; S8 TIGER Series 2 - 50 kV, LiF200; intensities normalized to tube current)

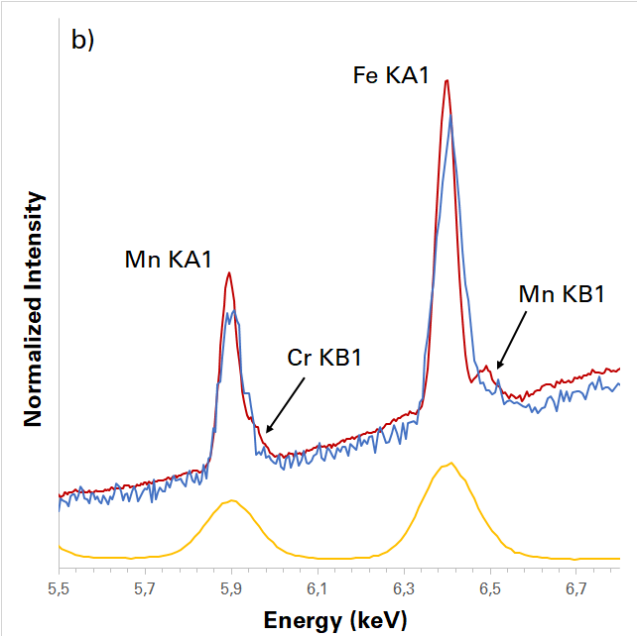


Figure 7b): Detailed view at Mn KA1 and Fe KA1 with overlaps by Cr KB1 and Mn KB1, respectively. Please note that for comparison, lowest resolution on the S8 TIGER was used.

Why favoring WDXRF over EDXRF?

EDXRF and WDXRF techniques are both capable of analyze the whole elemental range from Na to Am in metal matrices (depending on the alloy and base material). EDXRF techniques combine element groups into measurement ranges to find a good agreement of sensitivity and resolution. For some applications and elements, this will be good enough and EDXRF will be the technique of choice. WDXRF techniques provide higher resolution across the whole elemental range, which is beneficial in case of spectral overlaps (e.g., transition metal and/or major alloying elements). Moreover, the sensitivity for lighter elements is significantly better on WDXRF instruments, allowing better LOD, accuracy and precision.

Selected data from case study

The current study, which uses fresh and used powders as well as theoretical end products (cubes and discs), shows good agreement between powders and solid printed products. Small deviations between powders and solids in WDXRF analysis are related to the non-perfect package density in a powder sample. Fresh and used powders do not show significant differences.

In this case study we can see that carbon, sulfur and oxygen concentrations are within the expected concentration ranges of the manufacturer, while nitrogen is lower. Hydrogen was not characterized by the manufacturer. The oxygen concentration and standard deviation are higher in the printed product compared to the powders, though within the expected range. Does oxygen increase during the printing process itself? Is oxygen present in form of inhomogeneous distributed inclusions causing a higher standard deviation? This final question could be answered by i.e., optical inspection. Nitrogen is just below the expected concentration range. In steel, the nitrogen concentration is usually in a range between 10-5 000 ppm. A difference between 786 and 900 ppm is thus neglectable.

The investigated powder was furthermore atomized using nitrogen gas; therefore, a lower-than-expected Nitrogen concentration is non-critical. The decrease of nitrogen between powders and printed product, though only minorly resolved, could further be evaluated: Does nitrogen degas during the printing process? Is it more difficult to be released from a solid piece than a powder during fusion? This just highlights how light elemental analysis can be used to address quality assurance and production processes.

Light elements (CS/ONH)

ID	C (ppm)	S (ppm)	O (ppm)	N (ppm)	H (ppm)
Fresh Powder	212 ± 3.2	52 ± 1.5	406 ± 3.0	854 ± 4.9	2.98 ± 0.13
Used Powder	213 ± 5.7	53 ± 1.9	384 ± 1.4	858 ± 6.0	2.73 ± 0.16
Printed Product	212 ± 19.7	56 ± 2.0	458 ± 1.6	786 ± 6.7	2.06 ± 0.23
Range from producer	170 – 300	50 – 300	235 – 400	900 – 1000	-

Table 4: Summary of light element concentrations in new and old powder, the product as well as the range of concentrations given by the powder producer. Number of analysis for old powder, new powder and printed product = 10

Major and minor elements (WDXRF)

Powders	Al (%)	Si (%)	P (%)	S (%)	V (%)	Cr (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Nb (%)	Mo(%)	Sn (%)	W (%)
Fresh Powder	0.004	0.390	0.017	0.001	0.019	18.082	0.659	0.019	12.600	0.022	0.003	2.359	0.002	0.011
Used Powder	0.004	0.400	0.017	0.001	0.020	17.912	0.659	0.022	12.756	0.022	0.004	2.363	0.002	0.012

Table 5: Quantitative WDXRF results of fresh metal powder and used metal powder (detected elements only) Powders

Discs	Al (%)	Si (%)	P (%)	S (%)	V (%)	Cr (%)	Mn (%)	Co (%)	Ni (%)	Cu (%)	Nb (%)	Mo(%)	Sn (%)	W (%)
Min	0.013	0.690	0.020	0.002	0.022	17.932	0.686	0.027	13.021	0.025	0.003	2.372	0.002	0.009
Max	0.025	0.700	0.021	0.002	0.023	17.986	0.689	0.028	13.074	0.030	0.004	2.380	0.003	0.011
Average	0.017	0.697	0.020	0.002	0.023	17.964	0.687	0.028	13.047	0.027	0.004	2.377	0.002	0.010
SD	0.005	0.005	0.000	0.000	0.000	0.023	0.001	0.000	0.022	0.002	0.000	0.003	0.000	0.001
RSD	31.36	0.68	2.32	0.00	2.08	0.13	0.21	1.70	0.17	8.84	12.86	0.14	20.20	9.12

Table 6: Quantitative WDXRF results of printed & grinded metal discs (detected elements only)

Four Cases of Elemental Analysis in Powder Metallurgy

There are four cases in which elemental analysis of powders becomes useful:

1. When powders are directly produced on site
2. When powders are bought in from external producers
3. When binders are added i.e., for binder jetting
4. When powders are recycled and reused over several build jobs

In the first case, elemental analysis can help in determining the quality of the powder manufacturing process. Is the material we are planning to produce chemically identifiable? Has the chemical composition changed between raw material and finished powder? Is the material chemically homogeneous?

In the second case, elemental analysis can be used for validation of the material's chemical characterization given by the manufacturer. Is the quantity of light elements still the same? Has it increased or decreased since it was characterized? Is the major element composition matching the description of the manufacturer?

Case three focusses mainly on the addition of carbon from binder material during binder jetting. In a later de-binding process, carbon is removed. This removal needs to be monitored i.e., by combustion analysis.

In case four, the powder is recycled and reused over several production cycles. In between the cycles, the powder is prepared via sieving and drying. To ensure the quality over the cycles, a control of the physical properties as well as of the chemical alloy composition must be maintained for reproducibility and serial applications.

Further quality control criteria for additive manufacturing

To complete quality control of the raw material and finished product, the following techniques can be used to characterize and evaluate the material:

Powders

- Characterization of the particle size distribution
- Particle shape determination (e.g., sphericity)
- Flowability
- Surface roughness and surface to volume ratio
- Humidity
- Chemical analysis (combustion, inert gas fusion, XRF)

Finished product

- Metallographic investigation of texture and porosity
- Chemical analysis (combustion, inert gas fusion, XRF, OES)
- Hardness test
- Tension test
- Notched bar impact test
- Creep rupture test
- Compression test
- Optical and tactile dimensional inspection
- Non-destructive investigations including visual examination, ultrasound, penetration test and magnetic particle inspection

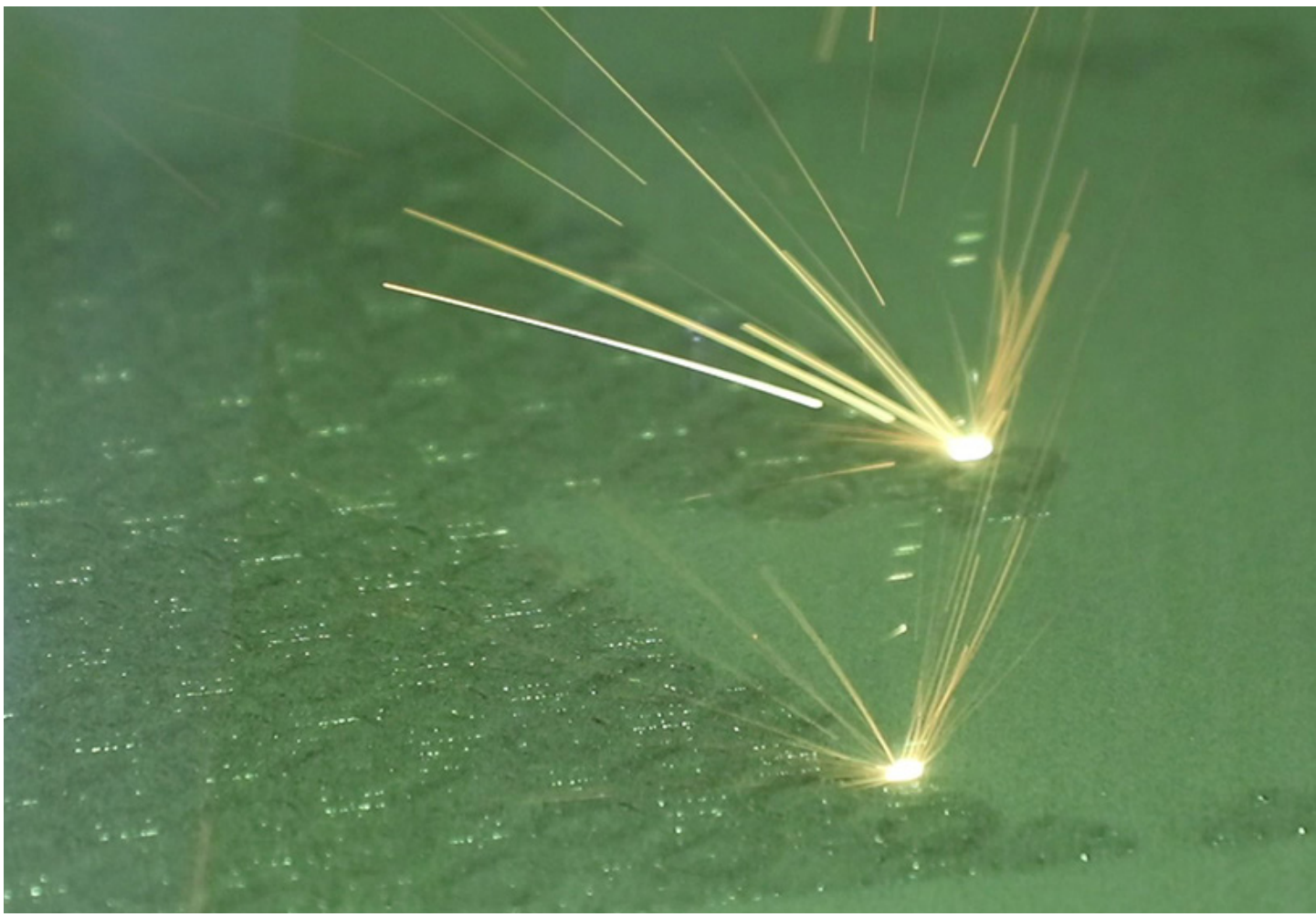


Figure 8: View into a LPBF system during a print job

Source: Rosswag Engineering

Result of the Analytical Co-operation

The Bruker Perspective

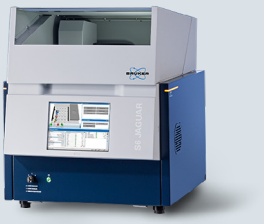
Direct feedback from the customer is essential for the improvement of methods, hardware, software, or sample preparation techniques. Without the exchange with Rosswag Engineering, this study would have not been possible. Rosswag Engineering provided us with the sample material and has participated in several discussions during and after the study. This included sample preparation, data evaluation as well as the discussion of calibration and method setups resulting in a more comprehensive understanding of elemental analysis in the additive manufacturing sector.

The Customer Perspective

The cooperation with Bruker leads to a better understanding when it comes to the analytical characterization of metal powders especially regarding their chemical alloy composition. In addition to Rosswag's decades of experience with conventional materials such as wrought metals, the analysis of metal powders and AM parts posed a new challenge. Bruker's support gave Rosswag the means to pursue their understanding in the limits and the validation of chemical analysis of powders compared to solid monolithic structures and to develop their own methods and techniques in this challenging field. This increased Rosswag's confidence in the elemental analysis of metal powders and hence resulted in an increase in quality and quality assurance over the whole AM process chain.

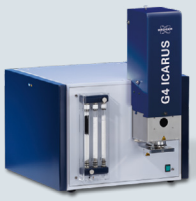
Summary

The G8 GALILEO, G6 LEONARDO, G4 ICARUS, S6 JAGUAR and S8 TIGER provide the required precision, accuracy, and reliability for elemental analysis in quality and process control in the additive manufacturing industry. Each system has its unique advantages, the choice for the particular systems being dependent on the analytical requirements of each individual application. The most common combination in additive manufacturing is the S8 TIGER for major elements, the G8 GALILEO for oxygen, nitrogen, hydrogen and argon and the G4 ICARUS for carbon and sulfur.



The **S6 JAGUAR** offers more analytical power than any other compact WDXRF instrument. It features a new compact goniometer, closely coupled optics and 400 W direct excitation power. The S6 JAGUAR covers the complete elemental range from F to Am, from low ppm to 100%. Its system components are well protected by our proven SampleCare technology, ensuring highest instrument uptime and lowest cost of operation, especially when running liquid or powder samples.

The **S8 TIGER Series 2** is the top-of-the-line WDXRF spectrometer of Bruker AXS. It provides best accuracy and precision for quality and process control using the new HighSense technology for ultimate sensitivity and low detection limits. Being the most versatile instrument, it can be equipped with up to eight analyzer crystals and four collimators and operates at maximum 4 kW. Optimal system uptime and lowest cost of operation is guaranteed with SampleCare technology, especially for the analysis of powders and liquids.



The **G4 ICARUS** is a dedicated instrument for carbon and sulfur analysis. It uses the principle of combustion by induction under a flow of pure oxygen gas. Accelerator materials aid melting of the sample, necessary to release carbon and sulfur, which react with pure oxygen to CO_2 and SO_2 and are measured by IR and IR or UV absorption, respectively.

Oxygen, nitrogen, hydrogen and argon in additive manufacturing can be analyzed with the **G8 GALILEO**. The G8 GALILEO uses the principle of inert gas fusion (O, N & H) and inert gas fusion mass spectrometry (Ar & H) with graphite crucibles in an electrode furnace under a flow of inert gas (N_2, He or Ar). Nitrogen and Hydrogen are detected as N_2 and H_2 by a thermal conductivity detector, oxygen as CO by IR absorption and Ar and low concentrations of H_2 (<0.01 ppm) by mass spectrometry.

Also using inert gas fusion as the measuring principle, the **G6 LEONARDO** can analyze oxygen, nitrogen and hydrogen. Though compared to the G8 GALILEO, the G6 LEONARDO is only available as single- (O/N/H) or dual element (ON/OH) configuration without the options of adding the mass spectrometer or other features (i.e., automatic cleaning, gas dosing).

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