In-situ monitoring of the material composition in PBF-LB via optical emission spectroscopy

Anna R. Ziefuss¹, Rene Streubel¹, Philipp Gabriel¹, Florian Eibl², Stephan Barcikowski³

¹ Technical Chemistry I and Center for Nanointegration Duisburg-Essen (CENIDE), University Duisburg-Essen, Universitätsstraße 7, 45141 Essen, Germany
² Aconity GmbH, Kaiserstraße 98, 52134 Herzogenrath, Germany

Abstract

Powder bed fusion using a laser beam of metals (PBF-LB/M) is a widely used additive manufacturing (AM) technique that enables the material-efficient fabrication of complex geometries in metallic parts. However, achieving high-quality parts with desired properties heavily depends on variances in the manufacturing process and powder composition, making quality control an indispensable aspect of almost all applications. Today, mainly grayscale imaging or pyrometry are employed, whereas in situ recording of chemical (compositional) information has rarely been done during LBF-LB/M. This pilot study explores the feasibility of in-situ optical emission spectroscopy (OES) for elemental analysis of metallic samples during PBF-LB, at the example of Nd-Fe-B. Our findings suggest that the local emissivity of Fe and Nd lines can serve as a reliable indicator to determine the temperature and elemental concentration in the plasma. The results showed that Online-OES during PBF-LB enables tracking of how Nd content in as-build parts critically depends on the laser parameter used while printing the part.

Keywords

Optical emissivity
Laser powder bed fusion of metals
As-build part quality
MQP-S
Introduction

Powder bed fusion using a laser beam of metals (PBF-LB/M) is an established AM technique to produce parts in complex geometries required for various applications.\cite{1, 2} In this process, a laser beam melts the metal powder feedstock to obtain dense components after solidification.\cite{3} However, the high solidification rates, in the range of $10^5$ K/s \cite{4}, can lead to microcracks, non-equilibrium structures with phase segregation, and columnar grain growth, which typically affect the material strength.\cite{5}

Therefore, the quality of PBF-LB/M-manufactured products heavily depends on the manufacturing process. As a result, quality control of components manufactured using additive manufacturing (AM) and developing a digital data twin \cite{6} are increasingly important. Quality control is a crucial aspect for almost all applications and typically involves verifying the surface quality of as-built parts, their geometric properties, composition, and functionality. In situ quality control instrumentation has several advantages over post-processing measures, however, today, mainly cameras or pyrometers are available as PBF-LB machine upgrades. Here, one possibility is the online camera-supported observation of individual layers during the PBF-LB, which can lead to the identification of defects in each printed line.\cite{7} In addition, in-situ pyrometry and thermography are used for process monitoring and regulation \cite{8}, at least in research, but they cannot make any statements about the chemical composition. Today, sensors that gather chemical or compositional information are rarely embedded in quality control development strategies.

Since the laser parameters have a decisive influence on the material behavior in the AM process, they determine the resulting properties of the component. Parameters that are not optimally adapted to the raw powder result in, for example, insufficient density and surface quality of the respective element or too high internal mechanical stresses, which leads to insufficient (static and dynamic) strength.\cite{9}

Moreover, deviation of the element distribution in the powder bed (down to the individual microparticles) from the nominal composition, e.g., due to powder batch variances, can lead to undesirable malfunctions in functional components. In addition, the chemical composition can change during the process due to vapor pressure differences in the alloy feedstocks, which, dependent on the induced thermal stress, results in strong deviations in the as-build part composition from the powder composition. It is known from the literature that melts sputter particles taken from the PBF-L/M process have a
very different composition from that of the raw powder.[10] Tracking the chemical composition layer-by-layer or even spot-by-spot during PBF-LB/M (with the perspective of compositional 3D reconstruction) is crucial to correlate the changes in the composition with the microstructure formation and the properties of the 3D part and to generate a high-quality control capability of the manufactured parts.[6] Note that some established ex-situ methods are available for analyzing the chemical composition of the manufactured parts in PBF-LB/M, both non-destructive (e.g., X-ray fluorescence (XRF)) and destructive (e.g., energy-dispersive X-ray spectroscopy (EDX) or inductively coupled plasma mass spectrometry, ICP-MS). However, such ex-situ methods require tedious and time-consuming preparation and are unsuitable for full 3D reconstruction, which is required for high-level quality control. Numerous computational applications for object modeling, process simulation, and product reliability are currently in the scientific development or testing stage.[11] In parallel, experimental quality control must be further expanded to open the technology of PBF-LB/M to new levels of complex industrial and commercial use, allowing to embed of the chemical composition data in the digital twin.

In-situ spectroscopic measurements using optical emission spectroscopy (OES) can contribute to the analysis and quality documentation of the process behavior and a much better understanding of the material behavior. However, such techniques in connection with PBF-LB/M machines are currently not available.

Consequently, this study shall pave the way for developing an in-situ analysis method that analyzes the composition of an as-build part during PBF-LB/M via in-situ OES. We selected Nd-Fe-B-based permanent magnet powder as model material, as i) its spectral lines are within the measurement range of our OES system and at least for high temperatures clearly differentiable [12] and ii) permanent magnet AM by laser powder bed fusion, is an emerging application, with many material-related issues and sometimes narrow processing windows that need to be better understood.[13]

**Results and Discussion**

The generation of laser-induced plasma during PBF-LB/M can adversely affect the quality and reliability of the produced parts as metals when heated to high temperatures, readily react with oxygen. These chemical reactions can result in defects
such as porosity and cracks, which can negatively impact the mechanical properties of the final part, compromising its strength and reliability.\cite{14} To mitigate these negative effects, various strategies can be employed, such as optimizing laser parameters, using an appropriate shielding gas, and controlling the process environment to reduce plasma formation and spatters.\cite{4, 10} Additionally, advanced monitoring and control systems can be employed to detect and correct any deviations in the process, ensuring the quality and reliability of the final part.

To mitigate the negative effects of laser-induced plasma/plume on the PBF-LB process, a shielding gas is often introduced into the interaction zone during processing to suppress plasma formation over the powder bed and to remove any disruptive factors that may be created during the process. According to Ref \cite{1}, the flow rate of the shielding gas can have an inverse relationship with the spectral intensity in the powder bed, as a greater amount of the laser-induced plasma/plume can be removed with a higher flow rate of the inert gas. Consequently, the temperature at the top surface of the powder bed decreases, which can significantly influence spectral intensity in optical emission spectroscopy. Compared to the study in Ref \cite{1}, we used a rather fast volumetric flow of the shielding gas of 72.9 mm/s during processing, which led to a drastic decrease in the thermal radiation of the plasma. It is essential to minimize the impact of the gas flow on the emission signal to create a reliable system. To achieve this, we have positioned the spectrometer at a 45° angle to the laser beam, providing a top-side view of the process with respect to the gas flow direction. The experimental configuration is illustrated in Figure 1.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Schematic of PBF-LB system with the off-axis coupled optical components for in-situ OES.}
\end{figure}
Figure 2 presents two distinct OES-spectra recorded in situ during PBF-LB of MQP-S. These spectra are obtained from two printing jobs utilizing different parameter sets, with high or low areal energy density (AED), respectively. The black curve represents the emission profile during high AED printing with exceedingly high laser power and low scan rate (450 W, 800 mm/s). On the other hand, the grey line represents the OES intensity profile resulting from printing with realistic parameters (75 W, 2300 mm/s), as referenced. Characteristic Fe I and Nd I lines with established atomic parameters [12], in particular transition probability (A) and lower-level energies (g), were selected (marked in blue (Nd I) and violet (Fe I) in Fig. 2A).

![Figure 2](image.png)

**Figure 2:** A) Raw OES-spectra recorded during PBF-LB single line scans performed with 450 W, 800 mm/s (black) and 75 W, 2600 mm/s (grey) on the Nd-Fe-B-based powder MQP-S. B) Multi-element Saha-Boltzmann Plot of MQP-S alloy of the two main elements Fe and Nd.

Note that potential spectral interferences [15] or self-absorbing processes [16, 17] cannot be ruled out and may impact subsequent calculations resulting in larger statistical deviations. Using the local emissivity of the chosen lines, Saha-Boltzmann plots were generated for various intensity profiles (Figure 2B). The values for g and A were acquired from the NIST database. These plots were fitted to straight lines with varying slopes, demonstrating the temperature difference caused by the two distinct parameter sets during PBF-LB. The graph distinguishes between emission lines originating from Nd and Fe, which will prove statistical significance in a subsequent step. While printing with parameter set 1 (high AED) results in a temperature of 5605 ± 595 K, printing with parameter set 2 (realistic AED) results in 2-times lower Temperatures of 2266 ± 1242 K. It should be noted that the higher temperature value
is in accordance with recent literature. However, the in-situ OES-derived temperature values from Nd slightly differ from a linear regression of the data points generated from the local emissivity of Fe (see dashed line in Fig. 1B), indicating a different concentration of both elements in the plasma than in the sample. [15] In contrast, the lower temperature value is significantly higher than anticipated based on previous research. [18] Nonetheless, the statistical deviation from a linear fit is considerable, indicating the presence of potential interferences in the spectral lines at lower temperatures (moderate AED) that need to be addressed in future studies.

In order to assess the elemental composition derived from the OES spectra, a calibration was conducted for two distinct local emissivity’s at a fixed wavelength across varying temperatures. To achieve this, theoretical spectra were simulated using the NIST database [12], and the ratio between the intensity of Fe I at 372.0 nm and Nd I at 495.2 nm was calculated. These spectral lines are both prominent and intense for their respective elements. Figure 3A presents the results as a function of the Nd content for different temperatures. We fitted the respective curves with a non-linear fit function \( y = a \cdot \frac{1}{x} \) which shows a good correlation for values below 20 at% Nd.

Figure 3B illustrates the correlation between the local emissivity of Fe at 372.0 nm and Nd at 492.5 nm. Our observations reveal that the correlation factor exhibits no significant changes below 2000 K, but there is a linear increase in the correlation factor above this temperature threshold. The Saha-Boltzmann plot provides the temperature, enabling direct determination of the correlation factor from Fig 3B. This factor can then

![Figure 3: A) Plot of the Fe/Nd optical emission intensity at 372.0 nm (Fe I) and 492.5 nm (NdI) at different temperatures, under variation of the Nd content. Note that we only simulated the signal for Nd and Fe without considering further elements in the feedstocks. B) Plot of the fit parameter a (from Fig 3A), describing the correlation between the peak intensity ratio of Fe/Nd at 372.0 nm (Fe I) and 492.5 nm (NdI), and the Nd content plotted against their corresponding electronic temperature.](image)
be used to calculate the Nd content in the vapor phase. Our study shows that the high-power PBF-LB results in an in-situ measured Nd content of $8.7 \pm 0.9$ at%, indicating a slight increase in the plasma's Nd content compared to the feedstock MQP-S powder that nominally contains $7.5$ at% Nd.

Notably, the Saha-Boltzmann plot indicates different concentrations of Fe and Nd in the plasma compared to the sample. In contrast, using moderate energy density printing parameters, the print job results in an Nd content of $1.14 \pm 8.86$ at%. Here, the statistical deviation is higher due to the substantial temperature variation. Note that spectral interferences for the Nd/Fe system are expected to be higher at lower temperatures. By enhancing the effectiveness of the herein-shown measurement technique, incl. the evaluation routine, future works can expand on the accuracy of quality control measures.

**Conclusion**

In conclusion, our study utilized OES to record signals in situ that relate to the elemental composition in the processed area during laser powder bed fusion. Our results demonstrate that the local emissivity of Fe and Nd lines can be used to determine both the temperature and elemental concentration in the plasma during PBF-LB of Nd-Fe-B-based permanent magnet powder. However, potential spectral interferences and self-absorbing processes must be addressed in future studies to obtain more accurate results. We found that high-power (high-AED) PBF-LB resulted in an Nd content that is slightly (1.2%) higher than the raw powder's nominal Nd content. In contrast, printing parameters with moderate laser energy input resulted in a significantly lower Nd content and higher statistical variance. In perspective, matching of the absolute elemental concentration values of the feedstock powder and the in-situ emitting plume could be achieved by correction factors once the system is calibrated for a given material. Of course, ex situ validation of the compositional data acquired in situ would be the consequent next step.

But for quality control purposes, instead of absolute composition values, already tracing compositional changes via in situ recording of emission line intensities and emission line ratios would be a big step forward beyond melt pool imaging or pyrometry used today. It would be straightforward to combine the datasets of elemental concentration and laser melt spot position, to create a 3D file with data voxels that
contain composition-relevant information, and embed that into the digital twin, useful for quality control, in the future. Overall, our pilot study provides valuable insights into the in situ OES analysis of PBF-LB additive manufacturing processes. It highlights the possibility of expanding the digital data twin by a material vector. These findings could aid in speeding up PBF-LB parameter studies and ultimately improve the quality of additively manufactured metallic parts.

Method section

PBF-LB processing, including in-situ determination of the elemental composition

The DMP 350_B machine with a reduced build volume from 3D Systems GmbH was used for this study. The powder used was MQP-S-11-9-20001 from Magnequench. Three cycles of vacuum withdrawal and argon flooding were performed to ensure a residual oxygen content of <100 ppm in the build volume, measured in situ by an oxygen sensor. Two different sets of parameters were used:

- Parameter Set 1 (high AED): Power of 450 W, a speed of 800mm/s, a hatch distance of 100 µm, and a layer thickness of 30 µm.
- Parameter Set 2 (moderate AED): Power of 75 W, a speed of 2600mm/s, a hatch distance of 30 µm, and a layer thickness of 30 µm.

As a test job, a cube with a side length of 1 cm and a height of 2 mm was printed directly onto a 316L stainless steel build plate without using any support structures. OES spectra were taken using an Ocean Optic spectrometer (200 nm – 535 nm) and the Ocean FX-Platform software. The spectral lines were assigned using the Specline software from Plasus GmbH. The exposure time for the spectrometer was 100 ms for Parameter Set 1 and 10 ms for Parameter Set 2.

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Conflicts of interest
The authors declare no conflicts.

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