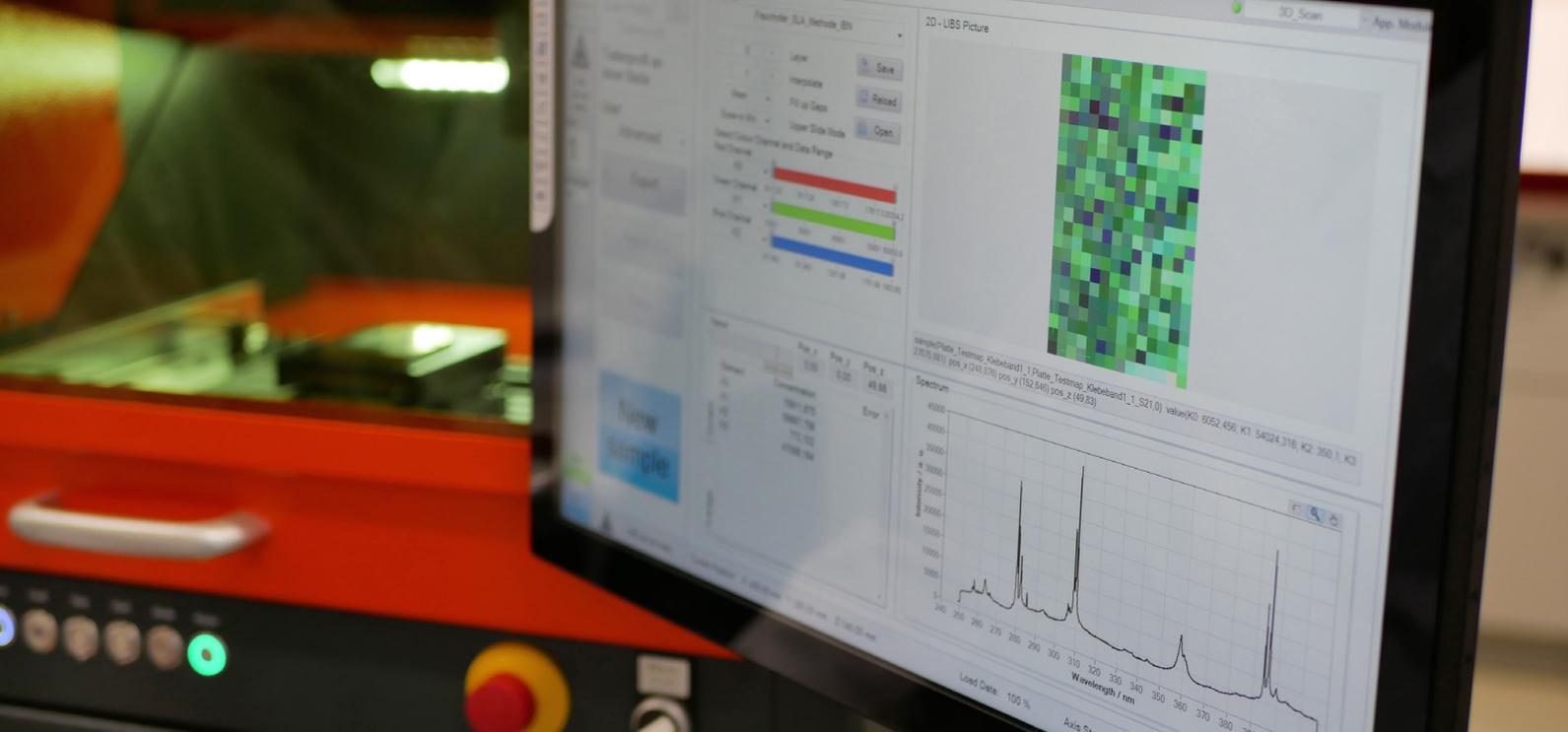




White Paper

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Visualization of the Chromium  
Distribution on Cr(III)-Passivated  
Galvanized Steel Sheets by Laser Induced  
Breakdown Spectroscopy (LIBS)



## Introduction

The application of inorganic, usually Cr(III)-based, passivations to galvanized workpieces is a common process for improving the corrosion resistance of the zinc coating and maintaining its silvery-light gray appearance. Therefore, ensuring a homogeneous layer is of high importance in this process. For a modern and efficient production process, inline-capable measuring methods are to be developed to monitor and improve product quality and to increase bath life.

So far, either no or very expensive off-line measurement methods such as X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS) or scanning electron microscopy (SEM) are available in this area. Concepts for in-situ measurement of chromium layer homogeneity can make a significant contribution to process optimization and quality monitoring.

Laser induced breakdown spectroscopy (LIBS) is a method for sensitive elemental analysis that has recently been developed to industrial suitability. As an almost non-destructive measurement method, LIBS combines adequate lateral resolution and sufficiently high sensitivity - even for thin films - with very short analysis times. Thus, it offers a unique possibility for inline monitoring of process stability.

The present study was performed to demonstrate the benefit of LIBS analysis for testing chromium(III)-based passivation coatings on galvanized steel products. Coated samples were prepared by immersion of galvanized test plates into a chromium(III) bath. The chromium(III) concentration of the passivation solution was varied in a range from 0.5 vol% to 7.0 vol%, which includes the usual range in production, as well as covering the lower as well as the upper limit ranges. By evaluating the complex LIBS spectra, the homogeneity of the chromium(III) coatings can be evaluated. In addition, correlations with the used chromium(III) concentration in the passivation bath were found. This means that LIBS analysis can also provide in-situ information on passivation bath solution and detect or avoid inadequately coated workpieces. This can potentially reduce complaints and expensive follow-up work.

## Experimental

### Sample Preparation

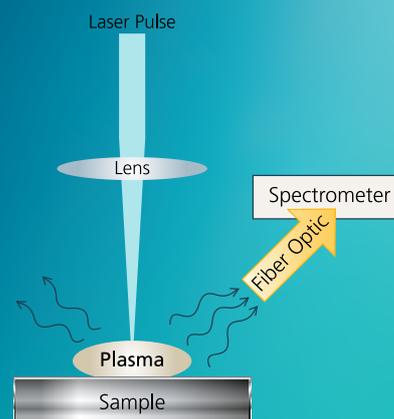
In the experiments described here, tests were carried out on steel plates measuring 150 x 80 x 0.7 mm. The samples were pretreated in the usual process by passing through an alkaline degreasing, hydrochloric acid pickling and fluxing agent, in each case with intermediate rinsing steps, and thinly zinc-coated in a zinc-5% aluminum alloy in accordance with DIN 50997. Subsequently, the still hot samples were passivated by immersion in the Cr(III)-containing aqueous passivation solution while maintaining the specified plate and solution temperature. Since the samples were passivated directly after galvanizing, no further cleaning was necessary. In a preliminary test, defects in the passivation were created intentionally by covering individual areas with tape before the dip treatment (Fig. 1). After it could be demonstrated that these defects could be detected perfectly by LIBS analytics (Fig. 2), all samples were only half immersed in the further tests so that there was a defined separation between the passivated lower area covered with chromium and the non-passivated upper area. This was advantageous for the subsequent presentation of the LIBS results. At the end of the dwell time in the passivation solution, which was kept constant throughout the tests, the samples were removed from the solution and allowed to air dry. With the thickness of the steel plates used (0.7 mm), the cooling process lasted only about 30 seconds.



Figure 1: Detail photo of specifically generated defect in Cr(III) passivation.

### Measuring Principle of LIBS

A high-energy laser pulse is irradiated onto the surface to be examined. The high intensity of the exciting radiation leads to heating, vaporization and partial ionization of a part of the sample surface. Since only a short period of interaction and ablation of the material takes place, there is hardly any heat transport into the sample. The recombination of electrons and ions produces a characteristic radiation which allows a precise elemental determination.



In this way, a total of nine galvanized steel plates were produced with various concentrations of chromium(III) in the passivation bath ranging from 0.5 vol% to 7.0 vol% by half-sided immersion (Fig. 3). Subsequently, the surfaces were analyzed for their chromium loading by LIBS.

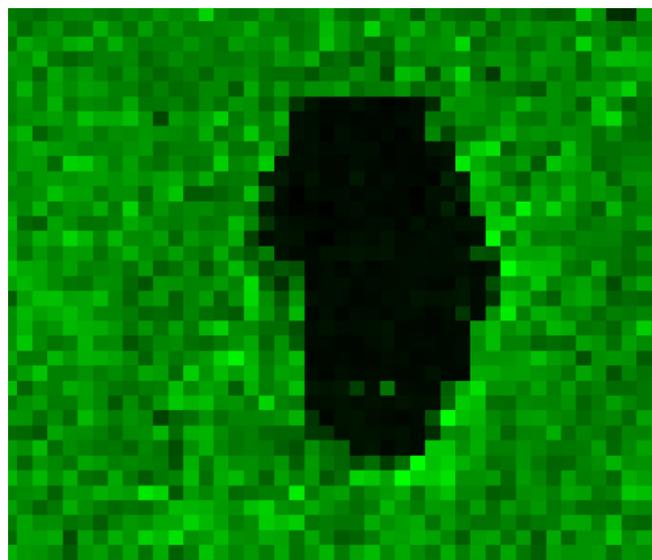


Figure 2: Distribution of the Cr signal measured by LIBS in the same sample area.

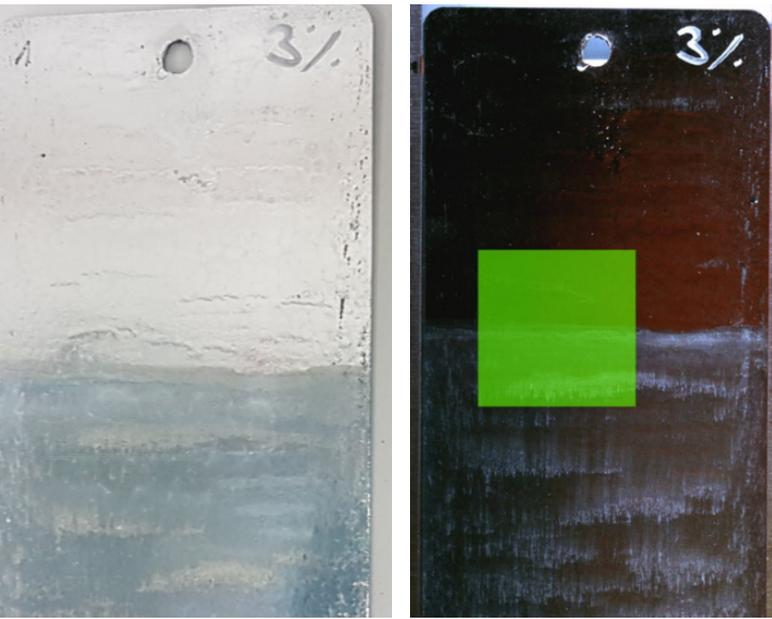


Figure 3: Zinc plate half coated with chromium(III) in a dip bath, green square shows the measuring area of the LIBS measurement.

The samples can be mounted in a sample holder system. The focal height of the samples was determined using the 4-point measurement mode, where only the focal height of the four corner points was determined, while all other points were interpolated.

All samples were analyzed with an x/y grid of 50 (to 70) x 70 points with an increment of 0.5 mm. Thus, the measured area was 25 (to 35) mm x 35 mm, with approximately half of the analyzed area coated with chromium(III). The analysis was performed as a point-to-point measurement with one laser pulse per integration time (shots per burst) at a laser shot repetition rate of 1000 Hz. At each measurement point three spectra were recorded and evaluated as different chromium layers. For evaluation, the peak area of the chromium line at 359.35 nm was integrated in the range from 359.073 nm to 359.714 nm after baseline correction and evaluated by single line analysis (SLA) using the SECOPTA software SEC Viewer (Fig. 4/5). The integrated peak areas of the chromium signal at each measurement point were shown as a 2D color plot (Fig. 6). The color scale correlates with the signal intensity (black = 0, light green = max).

A LIBS laboratory instrument based on a Nd:YAG laser with a wavelength of 1064 nm (FiberLIBS, SECOPTA analytics GmbH) was used for the study.

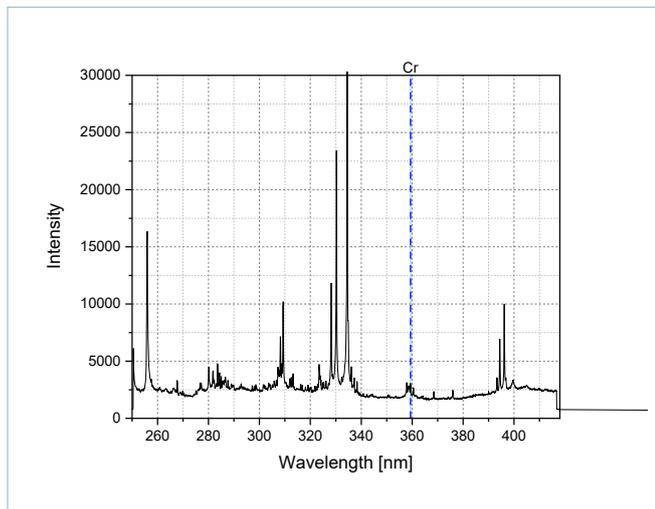


Figure 4: LIBS spectrum in the UV range.

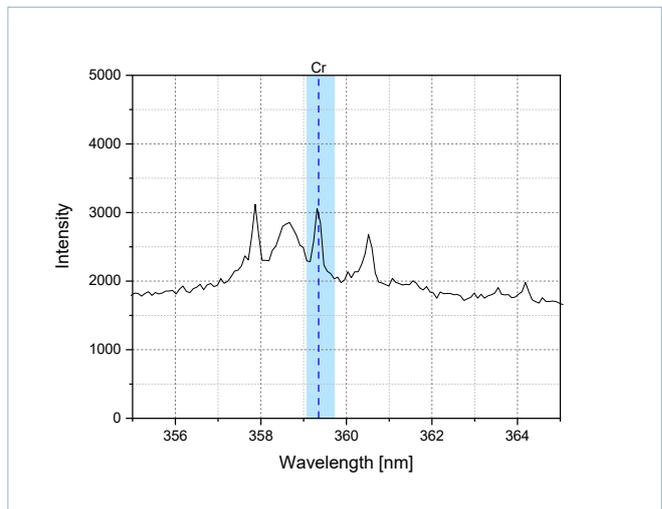


Figure 5: LIBS spectrum with marked chromium line at 359 nm, which was used for further evaluation.

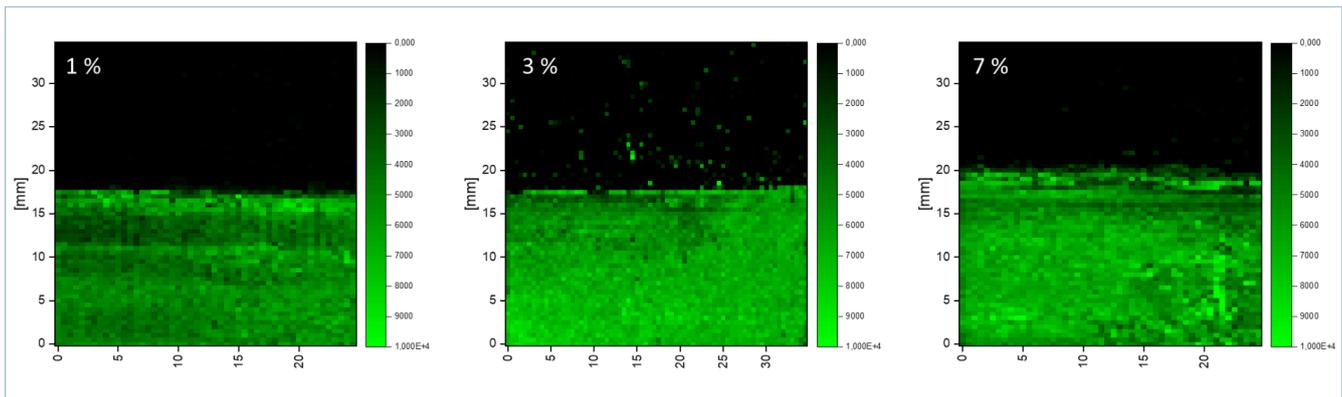


Figure 6: Exemplary representation of the chromium integrals for three selected samples (the darker the color, the less chromium is present).

## Results and Discussion

### LIBS Analysis of the Cr(III)-Containing Passivation Layers

Figure 6 shows exemplarily the 2D plots of the LIBS analysis for three out of nine samples. A clear separation between the chromium(III)-passivated (green) and the non-dipped area (black) can be seen. The lower parts of the sample show a more or less homogeneous chromium coverage. In some samples, chromium can also be found in spots on the upper (non-dipped) area. Splashes can occur due to the high temperature of the galvanized sheet during the dipping process, which causes the chromium(III)-containing passivation solution to reach the surface. The sometimes irregular, not quite sharp line of separation between the coated and uncoated surfaces is due to the manual performance of the dipping of the samples as well as the slight movement of the passivation solution induced by the dipping.

The 2D plots show very clearly that LIBS is a suitable method to test the homogeneity of even very thin coatings. This makes the method a powerful tool for process control. Defects become visible immediately, which allows a quick reaction in production and the adjustment of processes.

### Influence of the Cr(III) Concentration on the Coating Quality

In the following, it was investigated whether the determined LIBS signal intensities show a correlation to the chromium concentration of the respective immersion bath. For this purpose, the mean value of the chromium integral (including standard deviation) was determined for all 2D scans in the range from 0 to 15 mm height over the entire width (Figure 7). Figure 8 shows the plotting of these values versus the corresponding chromium(III) concentration of the immersion bath.

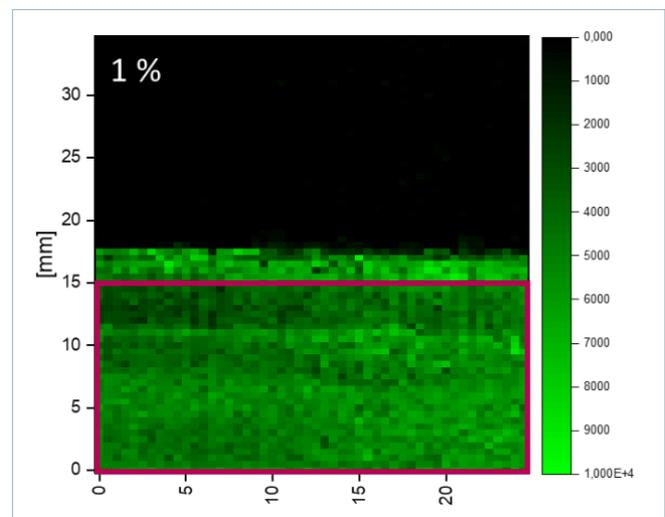


Figure 7: Zinc sheet passivated on half side in immersion bath with chromium(III) solution, red frame shows the area whose mean value was used for further evaluation.

It can be seen that the average signal intensity for chromium increases steadily up to a passivation bath concentration of about 2 %. There is a close correlation of the LIBS result with the chromium(III) concentration of the passivation bath.

From about 2 % up to the maximum tested bath concentration of 7 %, a relatively stable level of chromium(III) coating is formed on the zinc surface, within the usual application and measurement inaccuracies. Obviously, the saturation level in the passivation layer has been reached.

For the individual chromium(III) bath concentrations, relatively high standard deviations were observed, which indicate correspondingly large local deviations in the chromium coverage or

chromium(III) layer thickness. However, these can be explained by the sample state and the treatment procedure, both of which correspond to the industrial boundary conditions.

For the investigated range of passivation solutions, it can be stated from our LIBS studies, that a chromium(III) concentration in the range of 2 % represents the optimum with regard to chromium coating on galvanized products. Higher concentrations have no advantage in terms of a thicker or more homogeneous chromium layer and may be uneconomical.

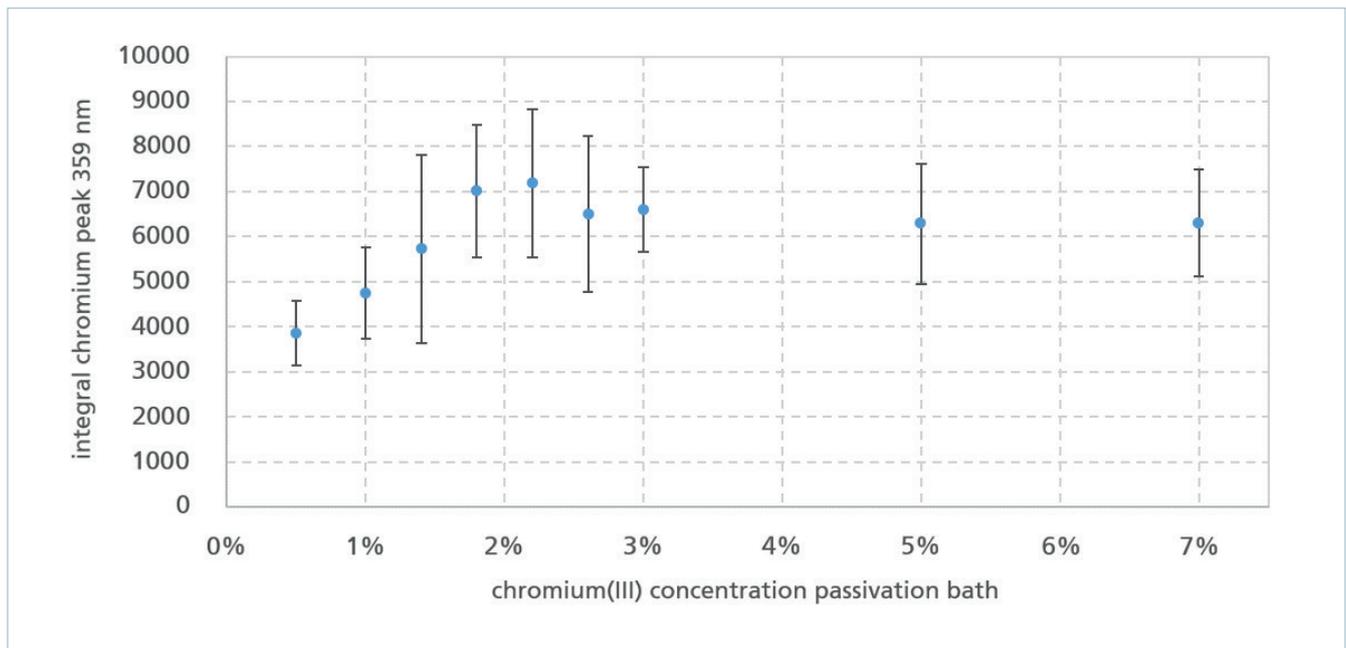


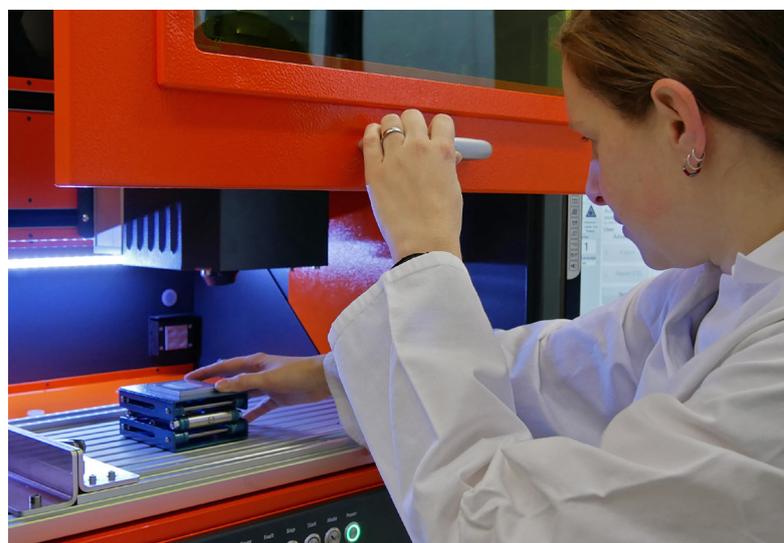
Figure 8: Mean values and standard deviation of chromium integrals over a large sample area, shown for the first layer analyzed.

## Summary

A total of nine samples with different chromium bath concentrations ranging from 0.5 vol% to 7.0 vol% were analyzed by LIBS. Evaluation of the chromium peak at 359 nm was performed for a wide sample section around the immersion border, and the lateral chromium distribution was shown in 2D color plots. By averaging the integrals over larger chromium-coated areas, differences between samples with different concentrations of chromium immersion can be clearly determined and evaluated.

It can be seen that the best chromium coatings were produced with about 2 vol% chromium(III) concentration. With higher concentrations the signal intensity and therefore the chromium content does not increase further, indicating that the coatings have a constant thickness at higher bath concentrations.

Our results demonstrate that LIBS analysis can help to control metal coatings and that it is a suitable tool to optimize process parameters.



*Figure 9: As a nearly non-destructive measurement method, LIBS combines adequate lateral resolution and sufficiently high sensitivity.*

## Imprint

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