Multiple wavelength stratigraphy by laser-induced breakdown spectroscopy

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Introduction

High-power solid-state ns-lasers promise to enable stratigraphic investigations via Laser-Induced Breakdown Spectroscopy (LIBS) in industry and conservation science. In this context, the effect of laser wavelength on ablation behaviour – in particular, on the ablation rate *h* – is of great interest.

In the present study, the four most common wavelengths for ns-pulsed Nd:YAG lasers were used to ablate and analyse an industrial Ni-Co alloy coating on steel. Ablation rates and effective absorption coefficient were determined and compared.

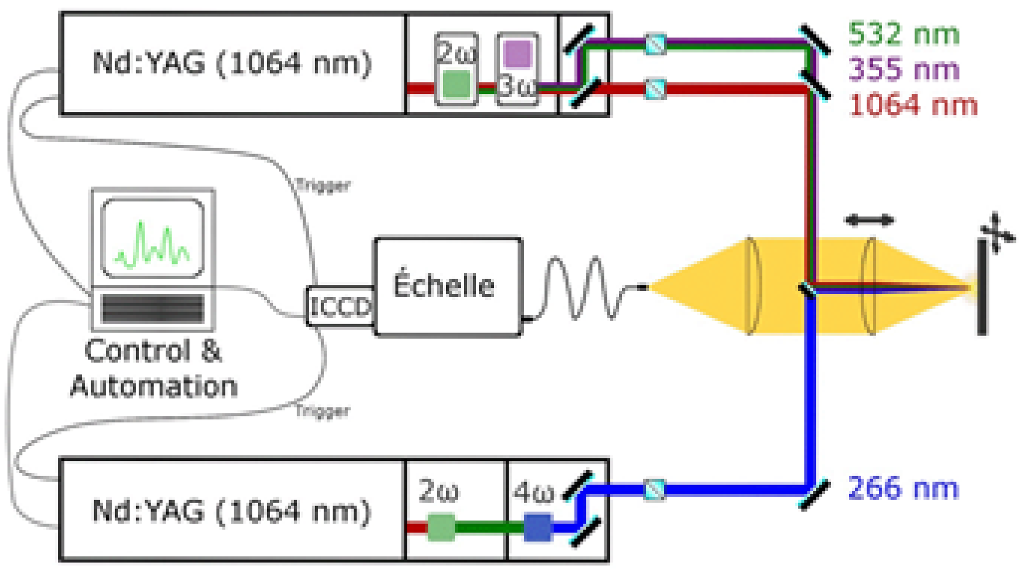

Fig. 1: Scheme of the LIBS setup

Experimental

The sample is a steel sheet, galvano-coated with ~20 µm of a Ni-Co alloy (~20% w/w Co). Layer thickness was determined by EDX analysis of a polished cross-section (Fig. 2).

LIBS measurements were performed at 1064, 532, 355, and 266 nm. Sample spectra are the result of 25 individual measurements. For each pulse, the correlation coefficient *r* with standard spectra of Ni and Fe was calculated and then approximated by the empirical functions described in [1].

The ablation rate *h* was calculated using the layer thickness in terms of the breaching pulse number N_b.

From these numbers, it is possible to determine the effective absorption coefficient α_{eff} [3] according to

$$h = \frac{1}{\alpha_{eff}} \ln\left(\frac{F_0}{F_{th}}\right) \qquad (1)$$

where F_{th} is the ablation threshold, and F_0 is the maximum fluence of the laser pulse.

Due to effects such as heat conduction, α_{eff} is expected to be much smaller than the Lambert-Beer absorptivity [2]. For ns ablation at low fluences, wavelength-independent absorption depths can be expected, according to the thermal diffusion length L_{th}

$$L_{th} = \sqrt{2\kappa\tau} \qquad (2)$$

where κ is the thermal diffusivity and τ is the laser pulse length.

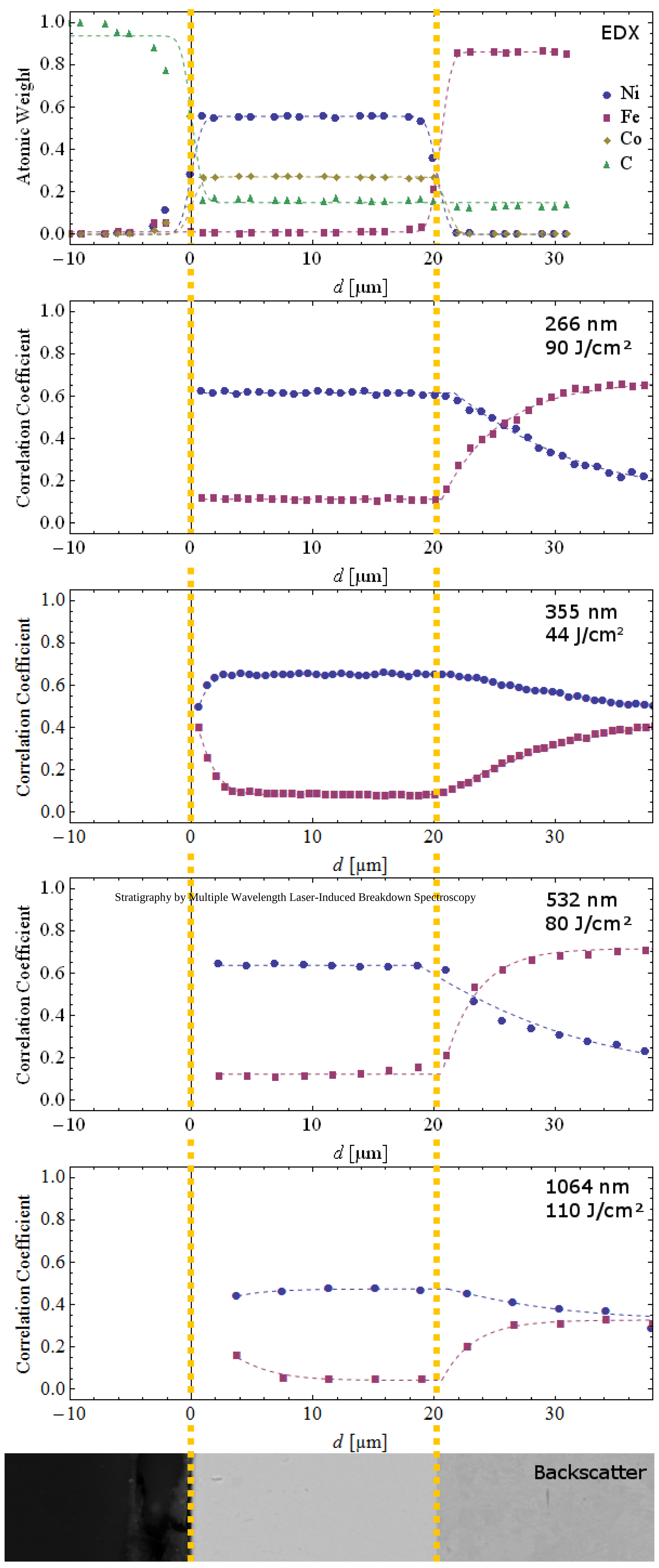

Fig. 2: Top: Atomic weights of the composite elements, determined by EDX vs. depth *d*
Middle: Correlation Coefficient *r* for Ni (blue) and Fe (purple) for various wavelengths vs. *d*
Bottom: SEM backscatter image of the layer cross-section

References

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[2] E. Matthias, M. Reichling, J. Siegel, O.W. Kaeding, S. Petzoldt, H. Skurk, P. Bizenberger, E. Neske, (1994). "Influence of thermal diffusion on laser ablation of metal films." Appl. Physics A 58(2): 129-136.

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Results

The correlation traces shown in Fig. 2 demonstrate that the layer could be identified at all wavelengths. However, the ablation rate is significantly lower when using lasers in the UV regime, with the lowest *h* (and thus the best depth resolution) appearing at both 266 nm and 355 nm.

For 532 nm and 1064 nm, the low number of pulses before the layer breach (and thus, the high ablation rate) causes a high uncertainty in determining the actual ablation rate.

The relationship between ablation rate and fluence can be seen in Fig. 3. α_{eff} values are strongly dependent on the wavelength. This indicates that the pure heat diffusion model (Eq. 2) is insufficient to describe ablation behaviour. Evidently, the the simple approximation $L_{th} = 1/\alpha_{eff}$ is contradicting the observations. This finding requires a fundamentally new ablation model. In this context, effects such as plasma shielding and reflectivity may play a significant role.

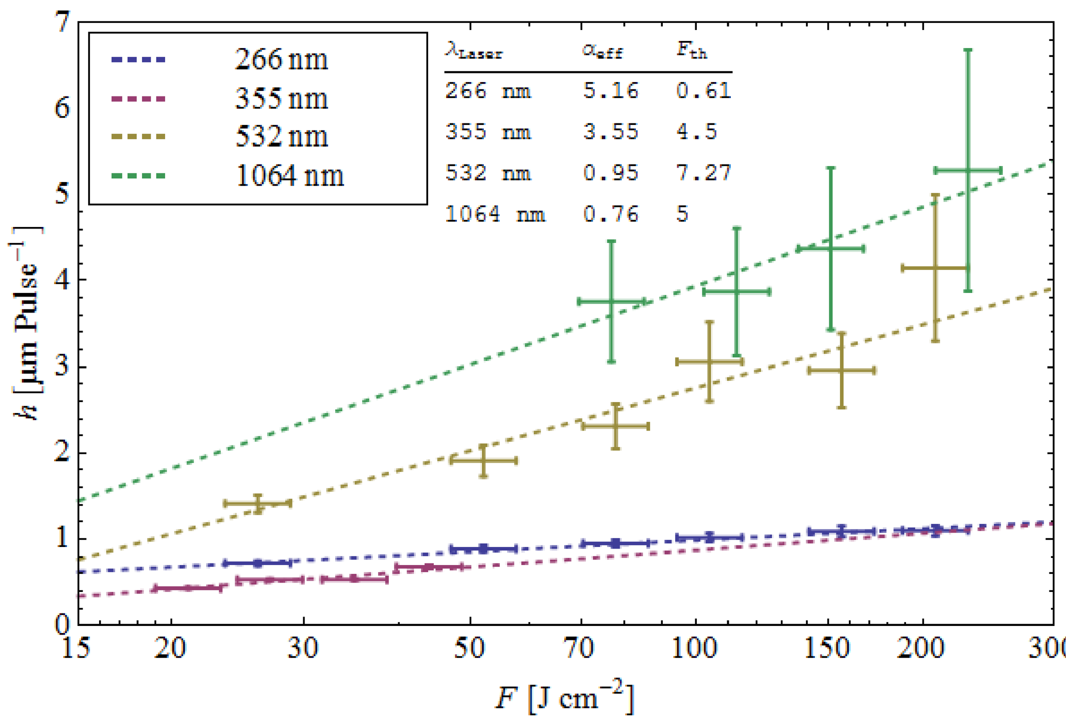

Fig. 3: Ablation rate *h* vs peak fluence F_0 for all laser wavelengths. The slope of the linear fits (dashed lines) corresponds to α_{eff}.

Conclusion

- Identification and observation of the layer was possible at all wavelengths.
- The model proposed in [1] holds for all wavelengths.
- The ablation rate decreases substantially from IR to the UV range.
- At optimal conditions, depth resolutions <0.5 µm can be achieved
- Neither optical absorption nor heat diffusion can completely explain the ablation process.
- This finding requires a fundamentally new ablation model.

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