Improving Surface Properties by Laser-based Drying, Gelation and Densification of Printed Sol-Gel Coatings

D. Hawelka*, J. Stollenwerk**, N. Pirch*, K. Wissenbach*

* Fraunhofer Institute for Laser Technology (ILT)
Steinbachstraße 15, 52074 Aachen, Germany

****** Chair for the Technology of Optical Systems (TOS)
RWTH Aachen University, Steinbachstraße 15, 52074 Aachen, Germany

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Introduction

Functional coatings are a powerful tool to improve properties and to widen the application range of various components. For this purpose industry highly demands low-cost and resource efficient coating processes that are easy to integrate into production lines. Wear protection coatings are required to increase the lifetime of highly-stressed mechanical components in many industrial sectors (e.g. automobile, alternative energy). In many cases, conventional expensive batch-based vacuum processes (e.g. PVD) are not applicable due to the required high throughput or huge dimensions of the components. Therefore inline-capable wet-chemical coating processes hold great potential to become an alternative. Major challenges of these innovative technologies are the application of the liquid coating material and the thermal post-treatment required for the transformation into a dried and densified layer with the desired properties. The developed inline coating process for the production of highly wear resistant coatings consists of three steps. In the first step a zirconia-based sol-gel coating material is applied to hardened steel substrates by a wet-chemical coating process (e.g. pipe-jet printing, spin-coating). In the second step a laser process is used to dry the wet thin film and remove the organic ingredients. Finally, a second laser process is used to generate adapted temperature-time-profiles in order to achieve peak temperatures > 1200 °C required for the functionalization of the films without reducing the hardness of the hardened steel substrate having a low thermal stability of 180 °C.

Experimental

Within previous investigations carried out in close collaboration with Merck KGaA Darmstadt, Schaeffler KG, Dilas GmbH and Biofluidix GmbH sol-gel coating applied by spin-coating have been dried and functionalized by a two-stage laser process [1, 2]. Organic ingredients were removed by the first laser treatment carried out with continuous diode laser radiation. Within the second laser treatment carried out with pulsed diode laser radiation it was possible to increase the coating hardness to more than 1000 HV. The investigations presented in this paper focus on the application of an inline-capable printing process in order to substitute the spin-coating process and on the laser-based drying of these printed coatings. The Biofluidix Biospot 600 device is used to print drops of the coating material with a diameter of (5± 0,5) mm onto the steel surface cleaned with alcohol. The drops are deposited in a honeycomp structure with a pitch of 3 mm in order to achieve a uniform and homogeneous thin film. The printed green films still contain solvents and uncondensed molecular precursors. Applying very high temperatures to the undried sol-gel coating (green film) leads to the decomposition of the applied green film. Therefore, the following aspects must be considered:

1. Solvents need to be removed (drying).
2. A high degree of network formation needs to be achieved (gelation) without exceeding the decomposition temperature of the molecular precursors.
3. Due to the single-layer thickness of ≤ 100 nm, multilayer systems with a thickness of ≥ 400 nm must be generated to enable an accurate measurement of the mechanical properties without any influence of the substrate.

The aim of the investigation presented in this paper is to develop a laser-based process to handle these tasks. Continuous diode laser radiation (wavelength $\lambda = 980$ nm) is used to generate temperatures < 800 °C. In order to achieve a two-dimensional treatment a 2D galvano scanner is used to guide the laser-spot across the coated surface in a meander-shaped track (Figure 1). The resulting laser process parameters are: laser output power P_L, beam diameter d_S, hatch spacing d_y, scanning velocity $v_{scan.}$

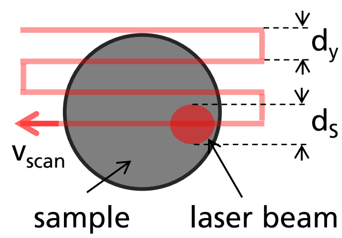

Figure 1: Schematic diagram of the laser treatment strategy (resulting process parameters: laser output power P_L, beam diameter d_S, hatch spacing d_y, scanning velocity v_{scan})

The peak temperature of the laser-induced temperature-time-profile is increased by increasing the laser output power starting at 50 W. In order to identify laser process parameters leading to a drying state similar to the state of a furnace-dried coating an iterative strategy consisting of systematical adaption of the process parameters and analysis of the laser-treated coatings is pursued (Figure 2).

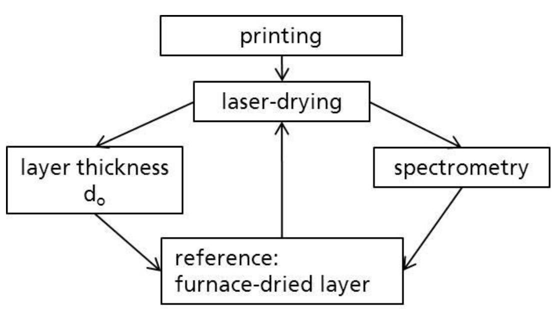

Figure 2: Experimental approach

The peak-temperature is not accessible by experimental measurements. Because of that FEM-simulations (Finite Element Method) of the laser-induced temperature-time-profiles are carried out based on a heat-conduction-model of the coated steel substrate. For this purpose the optical properties of the printed thin film need to be determined in order to develop an adequate model of the laser-induced heat sources (Figure 3).

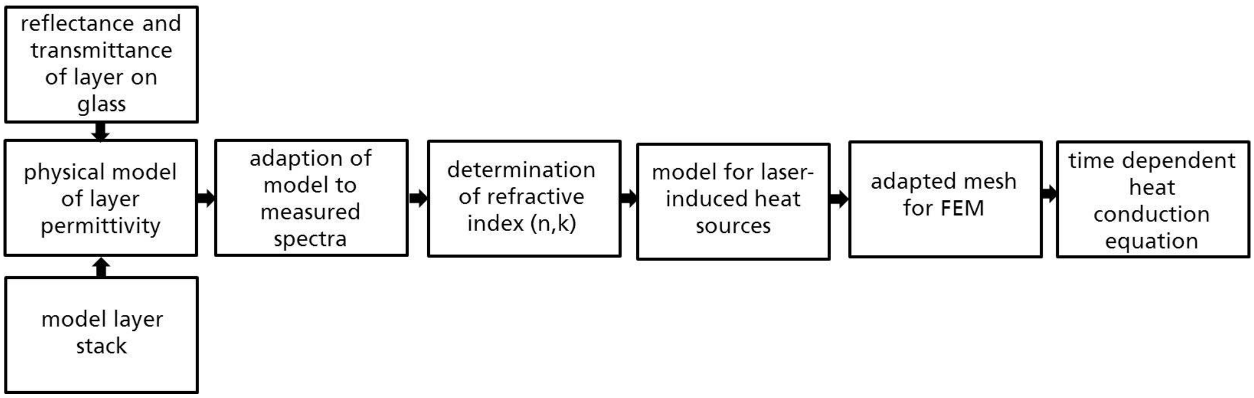

Figure 3: Schematic diagram of the model-based approach to simulate the laser-induced temperature-time-profiles

Keeping the scanning-velocity v_{scan} and the hatch spacing d_y constant, FEM-simulations with different values of the laser output power lead to a fundamental understanding of the correlation between the laser output power and the laser-induced temperature-time-profile. This model-based approach offers the possibility to investigate the coating properties as a function of the peak-temperature. The evolution of the layer thickness and the amount of uncondensed organic precursors is investigated by Fourier Transform Infrared Spectroscopy measurements (FTIR), UVVISNIR spectrometry and White Light Interferometry (WIM) as a function of the simulated peak-temperature. Finally, a furnace-dried thin film serves as a reference to obtain the optimal laser process parameters. The key issue of the presented investigation is, whether the laser-based drying-process allows for the same degree of network formation and solvent removal as the time-consuming furnace-process. Nanonindentation measurements are carried out on both furnace-dried and laser-dried multilayer systems with a coating thickness of ≈ 400 nm in order to investigate the Young's Modulus and Vickers hardness as a function of the type of the applied heat treatment. Within the laser-dried multilayer-system the laser-drying parameters are adjusted for every layer referring to the absorbance determined by UVVISNIR spectrometry in order to make sure that every layer is dried at the same temperature.

Results

A laser treatment with a simulated peak temperature of approximately $T_{max} \approx 400$ °C leads to a significant decrease of the FTIR-peaks associated with the organic ingredients (wave number 1500 - 1600 cm^{-1}) (Figure 4). At the same time the coating thickness is significantly reduced to (70 ± 15) nm. Further increase of the peak temperature to up to 700 °C does not have a significant effect on the amount of contained organic ingredients. On the contrary, the layer thickness is further decreased by increasing the peak temperature to ≥ 400 °C (Figure 4).

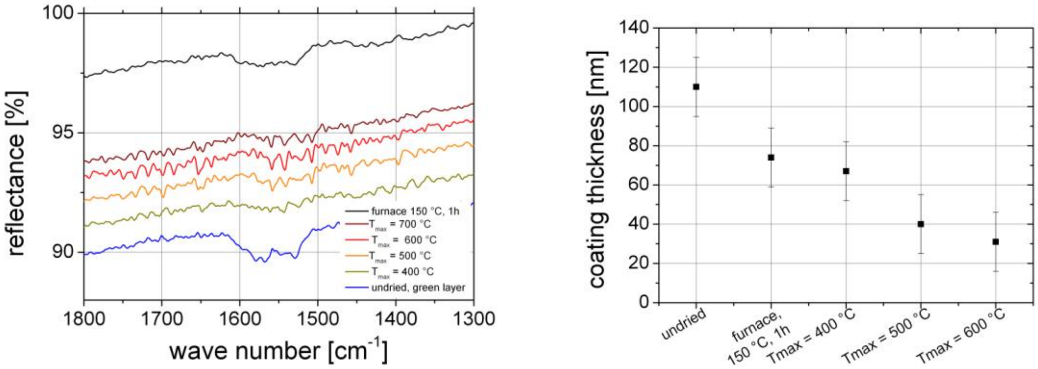

Figure 4: FTIR-spectra of laser treated layer (left) and the evolution of the layer thickness (right) as a function of the simulated peak temperature of the laser-induced temperature-time-profile (The vertical sequence of the spectra corresponds to the arrangement of the legend labels)

Referring to the FTIR-spectra and the coating thickness a drying-state comparable to furnace-dried films is successfully achieved byr a laser treatment with a simulated peak temperature of 400 °C (P = 50 W, v_{scan} = 2000 mm/s, d_y = 0,06 mm). The Vickers hardness and Young's Modulus of both a laser-dried and a furnace-dried multilayer-system (thickness 400 nm, number of layers 8 and 7 respectively) are summarized in table 1.

Table 1: Results of the nanoindentation measurements carried out on both a laser-dried and a furnace-dried multilayer system (test parameters: max. test load 0.1 mN, load time 20 s, hold time 30 s, Vickers Indenter)

drying process	Vickers hardness [HV]	Young's Modulus [GPa]	Indentation depth [nm]
laser	115 ± 20	21 ± 3	42 ± 4
furnace	160 ± 20	25 ± 3	35 ± 2

The higher hardness of the furnace-dried coating indicates a further advanced network formation which is due to the longer duration of the drying process (furnace: 1h, laser: 1 ms). The effect of this difference on the final coating properties achieved after the laser-based functionalization at significantly higher temperatures > 1200 °C will be investigated in further studies.

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