

# Real-time deformation monitoring of sol-gel-induced SiO<sub>2</sub>-TiO<sub>2</sub> films using laser-induced fluorescence microscopy for corrosion protection

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**Abstract**—Real-time analysis of the deformation of surface coatings using laser-induced fluorescence microscopy (LIFM) has been demonstrated. An SiO<sub>2</sub>-TiO<sub>2</sub> coating film doped with a fluorescent material by the sol-gel process was used, so that the changes in fluorescence intensity before and after corrosion could be monitored.

**Key words:** Corrosion, Sol-gel, Laser-induced Coating, Laser-induced Fluorescence Microscopy, Deformation Monitoring

## INTRODUCTION

Protective coatings are widely used in various fields such as the aerospace, oil, mining, and marine industries in order to increase the lifetime of essential components against corrosive environments [1-3]. Various coating techniques have been developed for numerous purposes, such as plasma vapor deposition (PVD), chemical vapor deposition (CVD), ion implantation for optical coating and sensor applications, and sol-gel and electrodeposition processes for appearance and corrosion resistance. Among these coating techniques, the sol-gel method is of unique interest because it starts with one or more organic precursors in their liquid state to build a solid inorganic structure on a substrate. This allows the preparation of a homogeneous, pure, film structure with molecular control in a process that is simpler and cheaper than any of the other techniques mentioned above [4,5].

The sol-gel process has been used to deposit films onto metallic substrates so as to increase their corrosion- and wear-resistance. It has been reported that an SiO<sub>2</sub>-TiO<sub>2</sub> sol-gel film was deposited on stainless steel (SS 316) by furnace heat treatment for sintering. However, furnace heating has the inherent disadvantages of size limitation and exposure to unnecessary oxidation during the heating process. Therefore, our group suggested laser heat treatment, which is considered as a possible substitute for the furnace heating method because the sample size is not strictly limited and the damage to the sample can be minimized by adjusting the laser output power and the absorbance of the targeted samples [6-10]. Moreover, the localized heat treatment provided by the laser can easily change the physicochemical properties of the substrate and make the substrate useful for further advanced applications. With the sol-gel method and laser treatment, fluorescent organic materials used as structure trackers can be easily immobilized in the gel structure because the starting materials are solvent-based materials in liquid form and the localized heat treatment can avoid the incineration of such organic compounds during the sintering process [11-14]. Therefore, such trackers can be used for in situ and real-time monitoring to observe

the deformation of the sol-gel-processed film structure in response to external effects such as temperature, pH, and chemical attack.

In this article, a new analytical method using laser-induced fluorescence microscopy (LIFM) for the detection of the deformation of coating materials is introduced. A fluorescent material was doped inside the SiO<sub>2</sub>-TiO<sub>2</sub> film coating. The fluorescence intensity change was monitored before and after laser sintering, and real-time monitoring of the film deformation in harsh environments was carried out.

## EXPERIMENTAL DETAILS

### 1. Preparation of Stainless Substrate and Sol-gel Solution

A 316L stainless steel was selected as the sample for coating. This steel has a high content of chromium (17 wt%), nickel (10 wt%), and molybdenum (2 wt%), and is commonly used for a range of engineering applications, in particular for marine equipment and electronic equipment. The samples were cut into sections (20×30 mm), polished using a clean cotton cloth, and cleaned in an ultrasound acetone bath for 30 min. Then, the samples were dried in air at room temperature before the coating process was carried out. A sol solution of titanium(IV) ethoxide and tetraethyl orthosilicate (TEOS) was prepared as a precursor for the SiO<sub>2</sub>-TiO<sub>2</sub> inorganic coating layer.

### 2. Dip-coating and Laser-induced Sintering

The sol solution was dip-coated on the surface of the stainless steel sample. The samples were dried at 50 °C for 2 min using a hot air gun to evaporate the solvent. An Nd : YAG laser (Intermark Elite Controllaser™) was used for the heating process. A coated sample was loaded on the center of a mechanical scanner to be scanned at a speed of 26 mm/s with a step distance of 0.1 mm (98% of laser beam overlapping). The laser delivers a Gaussian (TEM<sub>0,0</sub>) beam ( $\lambda_{peak}$ =1,064 nm, CW mode) with a maximum power of 85 W. In our experiments, the output power was adjusted in the range 6-60 W with a beam diameter of 5.5 mm.

### 3. Laser-induced Fluorescence Microscopy (LIFM)

A homemade laser-induced fluorescence microscope (LIFM) was built. An omnichrome 532AP tunable argon ion laser (488 nm, CW) was used as the excitation source for the fluorescence. The

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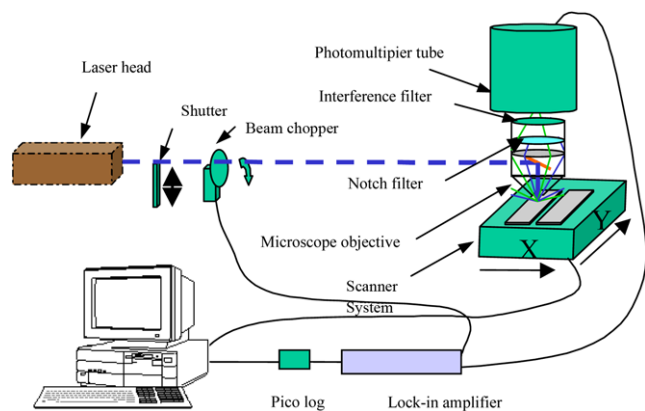


Fig. 1. Scheme of LIFM.

chopped beam was directed towards the microscope objective, where it was focused on the sample. The backscattered light (fluorescence and Raleigh) was collected through the microscope objective and passed through a one-inch 488-nm holographic notch filter (Kaiser Optical Systems Inc) and a 520-nm band pass interference filter with a full-width at half-maximum (FWHM) value of 10 nm (Comar Instruments). The 488-nm notch filter was used to stop the Raleigh light from reaching the detector, and the interference filter was used to collect the fluorescence from the sample only. The green light was then detected by a photomultiplier tube (PMT) with high sensitivity in the visible region (Thorn EMI electron tube, type 9558b). The signal was collected and amplified by a lock-in amplifier prior to conversion into a digital signal by a ten-bit analog-to-digital converter (Pico technology Ltd.). In this configuration, the microscope objective was fixed. The sample, usually the size of a microscope slide, was moved in the X- and Y-directions using a scanner (Hook & Tucker instruments Ltd). The resolution of the scanner was 125  $\mu\text{m}$  in both directions. The scanner and the data collection system were controlled by specially designed software via a personal computer (Fig. 1).

#### 4. Fluorescence Detection of Coating Layer Deformation

Two different sol solutions were prepared: one without fluorescein sodium, referred to as SO (sol-only) solution, and another with fluorescein sodium, referred to as SF (sol-with-fluorescein) solution. The solution of fluorescein sodium (M.W.: 376.128 g) was diluted to  $0.5 \times 10^{-4}$  M in ethyl alcohol.  $1 \times 10^{-8}$  mol of this solution was mixed into the S20 sol solutions. Prior to use, the mixtures were immersed in an ultrasound bath for 30 min until they exhibited a homogeneous, clear yellowish color. First, for the characterization of the fluorescence properties of the coating materials by LIFM, these two solutions were coated onto glass substrates as follows: (a) non-coated; (b) SF; (c) SF/SO; (d) SF/SO/SF/SO/SF. These samples were then scanned by LIFM to investigate the differences in fluorescence. The surface of each sample was scanned 32 times in four different areas, and then the gathered data were averaged for each position.

Subsequently, the SF solution was coated onto the metallic substrates for corrosion monitoring. The fluorescence change was monitored before and after heat treatment using LIFM. Two substrates were laser-treated with different laser powers. The Nd : YAG laser (60 W) was used to irradiate the surface of the coated stainless steel substrates with various scanning durations. Two samples, (a) non-

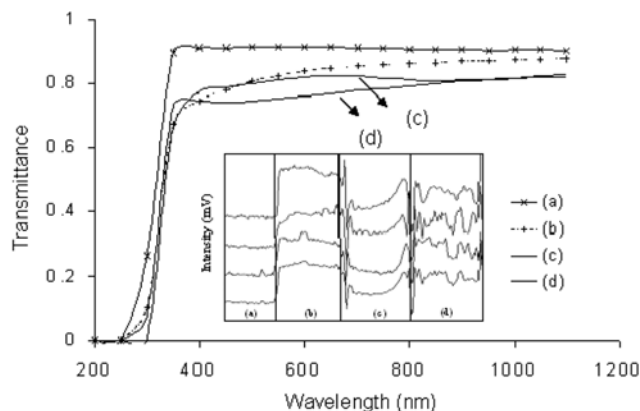


Fig. 2. Transmittance of samples (a), (b), (c), and (d), and the relative fluorescence intensities of samples (a) glass, (b) SF, (c) SF/SO, and (d) SF/SO/SF/SO/SF.

laser-treated and (b) laser-treated, were each immersed into 100 mL 5% (v/v) sulfuric acid to induce fast corrosion at the stainless steel surface. The fluorescence intensity of the acid solution was monitored every 2 to 3 min using fluorescence spectroscopy (Perkin Elmer LS 50B).

## RESULTS AND DISCUSSION

Fig. 2 indicates that the glass substrate showed more than 80% transmittance after the multicoating process was carried out. The data in the box show the relative fluorescence of the samples. Sample (a) is a baseline for the real-time scanning with LIFM. Sample (b) shows the increase in fluorescence after coating with the SF solution. Sample (c) shows an obvious decrease in intensity compared with sample (b). In the film coated five times with SO and SF solutions the data fluctuated, but indicated that the top layer included a fluorescent material.

Fig. 3 indicates that the fluorescence output before and after laser treatment did not differ for laser treatments up to 50 mV. However, from 80 mV, it shows significant difference. It might result from peel-off of coating film on the substrate and the demolition of organic materials during the laser treatment. The same sol solution with the fluorescein sodium was dip-coated onto the metallic substrates. The output voltages of the fluorescence were recorded before and after laser treatment, and it was found that the voltage differences increased in line with the increase in irradiation power.

Fig. 4 presents the fluorescence intensities of two acidic solutions in which the fluorescent coated samples were immersed for 30 min. The laser-heat-treated sample did not give rise to any significant difference in fluorescence intensity. However, for the non-treated sample a large increase in intensity was observed in the first 10 min. This intensity increase depends on the amount of fluorescent material in the acid solution. It is possible that the fluorescein sodium in the  $\text{TiO}_2\text{-SiO}_2$  network was extracted into the acidic solution when the coating film was destroyed after being attacked by the acid. This simple experiment verifies the acid durability and densification of the coating film, because a well-densified  $\text{TiO}_2\text{-SiO}_2$  sol-gel coating film would not be broken down in a mildly acidic solution. This technique would be useful for the continuous

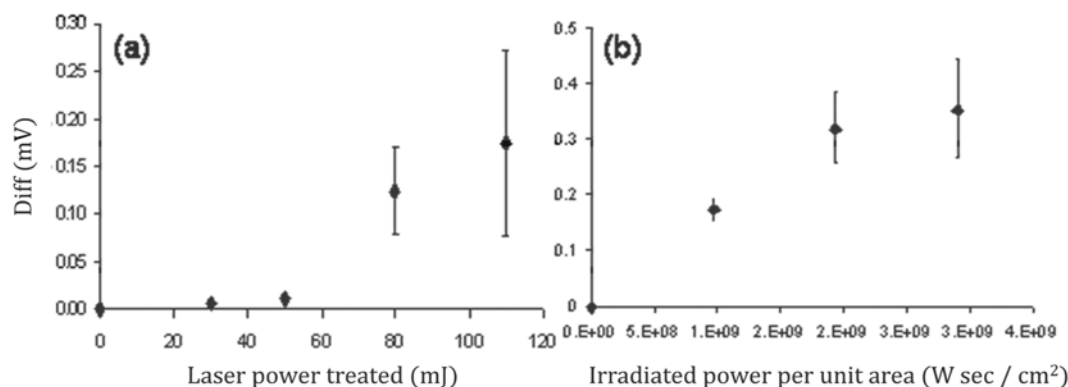


Fig. 3. The output voltage difference in fluorescence before and after laser treatment (mJ): (a) on glass substrates with dependence on output powers of the pulsed laser at 0, 30, 50, 80, and 110 mV; (b) on metallic substrates with dependence on 60-W Nd : YAG laser (CW) irradiation power.

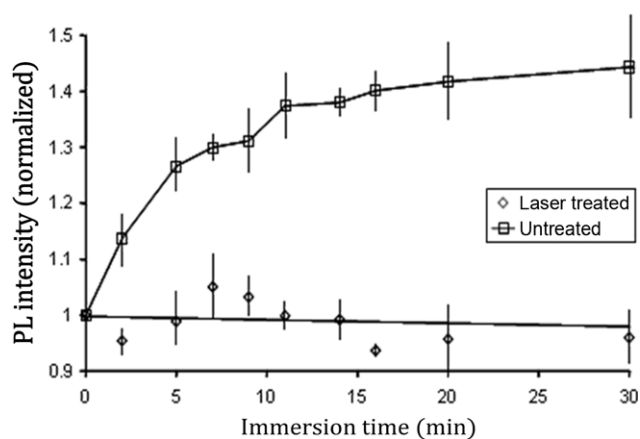


Fig. 4. Fluorescence change data for heat-treated and non-heat-treated samples immersed for different durations in acid.

monitoring of corrosion protection.

### CONCLUSION

We have carried out research on fluorescent materials in S20 coating films for use in sensors or other applications. The homemade LIFM showed adequate recognition of the existence of fluorescence in single-layer and various multi-layer film coatings. The fluorescence intensity was not affected in the limited range of laser powers for heat treatment and densification. In the initial experiment on corrosion detection using fluorescence, the fluorescence spectroscopy technique showed good recognition of densification or corrosion protection against the attack by an acid. However, it is necessary that more research be done on the relation between laser exposure and organic material degradation in terms of both qualitative and quantitative analyses, to allow the optimization and standardization

of these techniques for further development and application.

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