Lasers in Manufacturing Conference 2021

Corrosion resistant blackmarking via numerical modeling and simulation

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Abstract

Classical Laser Blackmarking with USP laser sources is a well-established process that is commercially available nowadays since a few years. This is especially true for its wide use on stainless steel supplies of the medical industry. Surprisingly, other industries (like household and consumer products industries) have even higher requirements on wear behavior (like corrosion resistance) than the medical industry with its strict approval procedures.

With the help of mathematical modeling and numerical simulation we wanted to understand the in-depth reasons for the limitations of classical blackmarking and develop a new laser marking process that could also fulfill the demands for acid resistance on products like white goods, sanitary fittings or automotive accessories which have not yet been opened up for this kind of laser process. We describe our success in modeling and simulation as well as process development in that field which is then evaluated by corrosion testing procedures.

Keywords: modeling; simulation; blackmarking; corrosion-resistance

1. Myth-Busting Laser Black Marking

In a way, this publication is breaking a myth on Standard Laser Black Marking; the myth being that it is ubiquitously thought and advertised to work by the apparent nano-structure observed on the workpiece surface after processing with ultra-short laser pulses. People therefore tend to think that laser black marking relies on similar physics like the famous VANTA-black (Surrey-NanoSystems, 2014), which is a surface that is made from very fragile carbon nano-tubes and traps light by its nano-structure.

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We took a systematic look on the mechanisms that the classical laser black marking process is based on and at the same time developed a modified process that exhibits advantages over the classical process with respect to corrosion-resistance. Corrosion-resistance mainly means acid-resistance in this publication, describing the ability of a marking to withstand the exposure to acids and be still readable for a long time. At the same time the focus is on blackmarking of steel, though everything proposed is applicable to aluminum and other metals or metallic layers as well.

1.1. Process Mechanisms

The process of laser black marking of metals (e.g. described in Wang, 2018) works by two different mechanisms (shown in Fig. 1), meaning that there are (at least) two physical mechanisms that lead to a blackening effect. One of those is the blackening by the oxidation products of the chemical reaction taking place in the presence of oxygen (e.g. in the surrounding air as the process is usually done in an ambient atmosphere). These oxidation products can be seen as a sort of dye as in the case of iron or steel they are mostly of a sort of blackish color and are produced (more or less deliberately) during the heating of the metal material within an oxygen-containing atmosphere. In Fig. 1 it is shown that with an increasing thickness of the oxidation layer, the reflection degree of the coated surface goes down (to the level of a gray or black surface of less than 10% reflection degree).

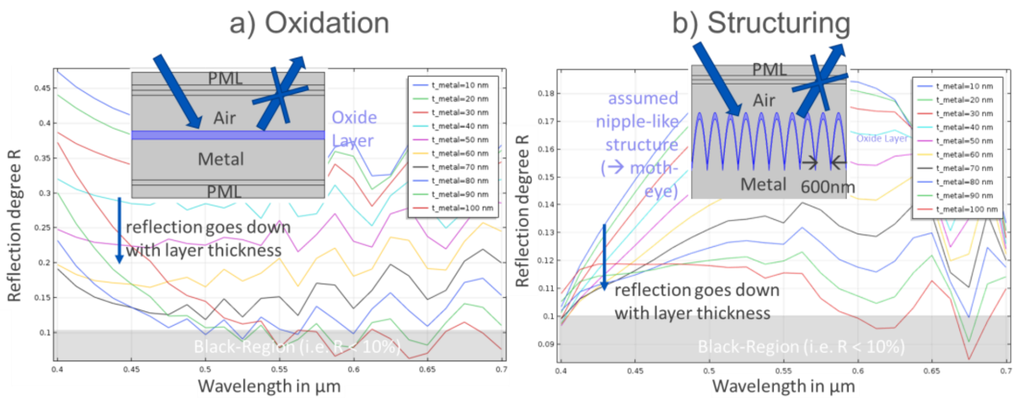

Fig. 1. There are two different mechanisms (analyzed on the left and right), by which the blackening effect in black marking is achieved: (a) oxidation and (b) structuring; for both mechanisms the basic (functional) simulation setup is shown in the graph inset, where the computational domain with different materials occupying different areas as well as a Perfectly-Matched-Layer (PML, see Taflove, 2005) for numerical absorption of the transmitted or reflected wave is illustrated; the effect itself is shown by the reflection spectra of each surface for different oxide layer thicknesses; note that the max. reflection degree in (b) is smaller than the maximum reflection degree in (a) proving that the additional structure in (b) decreases the reflection degree further

The other mechanism is blackening by structure, i.e. the reduction of the reflection degree by sub-micron structures that are proven to disguise a reflection (e.g. like a moth-eye, thus called moth-eye effect).

The effect of both mechanisms on the reflection degree of a surface can be calculated in a so-called functional simulation (see chapter 1.2), in which the propagation of a plane wave onto a black-marked surface under different angles and with different wavelengths is modelled.

As the structuring mechanism for blackening does not rely on oxides (which are mostly soluble in acids) this is the preferred mechanism for black marking. Unfortunately, not any sub-micron structure is doing the job of preventing any reflection. To find out, if the typical surface structure (i.e. laser-induced periodic surface structure, LIPSS, see Sipe et al. , 1983) that results from an ultra-short pulse ablation process is doing that, both numerical and experimental evidence is collected (see chapter 1.2 and 2).

1.2. Modeling

The mathematical modeling and numerical simulation used here involves two parts, i.e. the electromagnetic beam propagation and its consequence on the matter side, which is the ablation of solid material and formation of a nano-structured surface.

The first one is governed by the Helmholtz-equation in the following form

$$\nabla \times \mu_r^{-1}(\nabla \times \vec{E}) - k_0^{\,2}(\varepsilon - \frac{i\sigma}{\omega\varepsilon_0})\vec{E} = 0, \qquad \varepsilon = (n - ik)^2, \sigma = 0, \mu_r = 1 \tag{1}$$

with the electric field $\vec{E}$, the wave number k_0 and the real part n and imaginary part k of the refractive index.

This equation is then solved in frequency domain and can

a) predict the surface reflection of a visible light spectrum from any incident direction, which is the part of the **functional simulation** and
b) determine the absorption of mono-chromatic laser light inside the material domain of the simulation and thereby the local, inhomogeneous deposition of energy in order to ablate the material, which is the part of the **process simulation** producing the nano-structures to be seen on the workpiece surface.

Both purposes can be achieved with one principal model applied in different numerical setups. For the second purpose of simulating the feedback between the mechanisms of radiation propagation and ablation a simple iteration scheme for a volume-fraction variable α can be used

$$\alpha_i = \begin{cases} \alpha_{i-1} & ; \quad Q_{abs} < Q_{thres} \\ 0 & ; \quad Q_{abs} \geq Q_{thres} \end{cases}, \quad \alpha_0 = \begin{cases} 1 & ; \quad \text{where solid} \\ 0 & ; \quad \text{where void} \end{cases} \tag{2}$$

where i is the index of the iteration, Q_{abs} is the absorbed radiation energy received by equation (1) and Q_{thres} a material-specific ablation threshold for the absorbed energy. The initial value for the volume fraction is chosen to be 1 for areas/volumes with solid material and 0 for void areas/volumes. For a comprehensive model on nano-structure formation the equation (1) is solved iteratively and alternately with equation (2).

This method is actually quite similar to that described in Skolski, 2014.

1.3. Results

It was found, that it is possible to numerically predict the reflection spectrum of a given or simulated rough surface (see Fig. 1) as well as the formation of nano-structures due to the feedback of radiation and ablation (see Fig. 2) leading to Nano-Ripples.

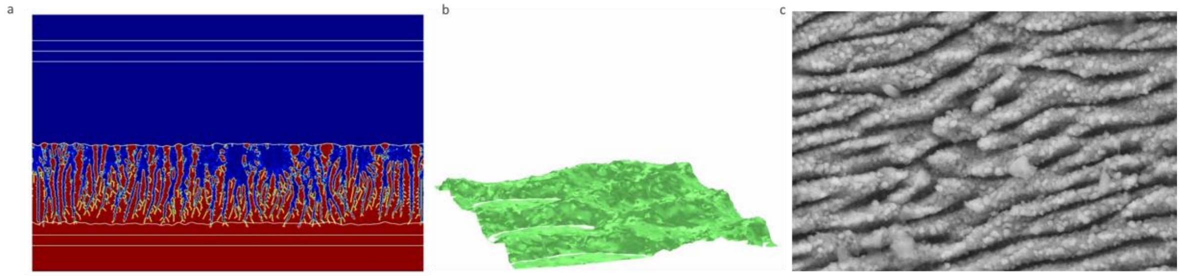

Fig. 2. (a) Simulation result of ripple formation in a 2D computational domain, in red color the bulk material that was not ablated, in blue the void area, white lines show different locations in the simulation domain (initial surface, PML area, sender line); (b) Simulation result of ripple formation in a spatially 3D computational domain; (c) Actual ripple structures in photographic measurement (from Zhu Liu, 2019)

As the numerical model was able to trace the reason for the blackening effect back to two potential candidates it was then possible to propose cross-checking experiments that could reveal the true nature of classical black marking (see chapter 2).

It was found, that the typical nano-ripple structure that evolves from an ultrashort pulsed black marking application is not performing well with respect to reflection prevention. So, it is actually the first mechanism of oxide layers that (for the conventional black marking processes) is taking a greater part in blackening, although the nano-ripples may be more prominent to the eye.

2. Proof of Concept

Cross-checking experiments were conducted, which prove that the classical black marking process, that is also producing Nano-ripples, is heavily relying on oxidation. This can easily be proven, if the same process is done under a protecting atmosphere with an inert gas like Argon. Compared to the process in ambient air, the processing result is actually not black any more but light-gray (see Fig. 3 (a) right-hand side).

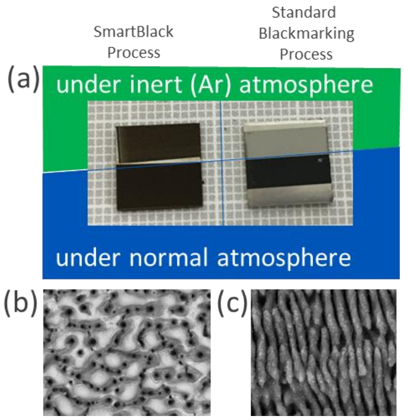

Fig. 3. (a) New SmartBlack (left) and Standard Blackmarking (right) Process Results under different atmospheres; (b) Micro-Structures (i.e. Cone-like Protrusions in this case) for SmartBlack; (c) Nano-Ripples for Standard Blackmarking

So, the blackening effect is gone in an inert atmosphere while the nano-structure is actually still present, which is proven in Fig. 4, which compares SEM-images of processing results in different atmospheres. It proves that the nano-structure does not change under different atmospheric conditions and is also not degenerated via acid treatment.

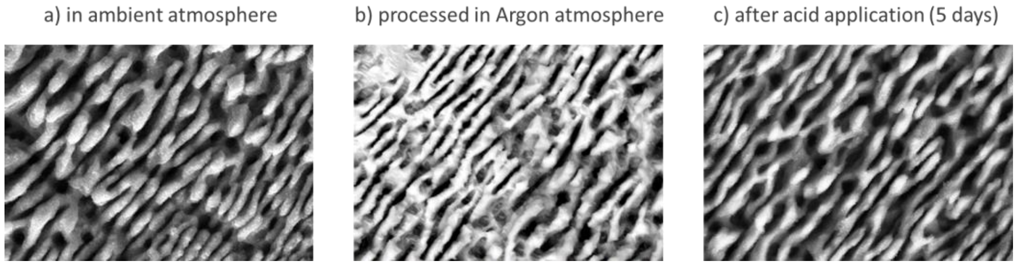

Fig. 4. Process results of the standard classical black marking in the form of SEM-pictures from processing (a) in an atmosphere containing oxygen, (b) in an atmosphere containing no oxygen and (c) after an acid resistance testing treatment for 5 days; the slight difference in picture (b) just results from a slight over-illumination in SEM

As the typical iron oxides like wustite (FeO), hematite (Fe_2O_3) and even magnetite (Fe_3O_4) as well as iron chrome oxides like chromite ($Fe_2+Cr_2O_4$) tend to be soluble in acids, the final result after acid treatment is the same as in the case of processing in an inert atmosphere. The latter one prevents the formation of any oxide layer (because the sample is kept under this inert atmosphere even in the cooling down phase after the laser process in order to exclude significant oxidation), while the acid treatment removes a significant amount of the oxide layer, thus canceling the blackening effect as well.

After these findings the interesting question was, if there actually is any laser induced periodic surface structure (LIPSS) that could do the job of blackening all by itself while not relying on any oxidation layer that would be gone after an acid treatment. Simulation tells us (see Fig. 1b) that there is such a structure, which is actually resembling the so-called cone-like protrusions (CLPs) which are also known as quasi-periodic laser-induced surface structures (see Schille et al., 2020).

By tweaking the marking process via parameter optimization into the direction of the more suitable nano-structures (like CLPs) for back-reflection suppression it was possible to achieve a major improvement on the robustness and resistance of a black marking against household acids (see Fig. 5), which we call SmartBlack (Fig. 3a left-hand side). This sort of black marking is especially suitable for the marking of household-goods (Fig. 6b), which may at some point in their product life cycle come into contact with household acids e.g. contained in cleaning agents or food.

The SmartBlack marking is more strongly based on and designed around the nano-structuring mechanism for the blackening of surfaces than the standard black marking actually is which is offered in the market today. In order to get an ideal processing result suitable laser sources with sufficient ultra-short pulsed output power and beam shaping equipment is necessary, as otherwise it would result in a local mixture of the Nano-ripple structures of standard black marking and the CLP-structures necessary for acid-resistant marking presented here.

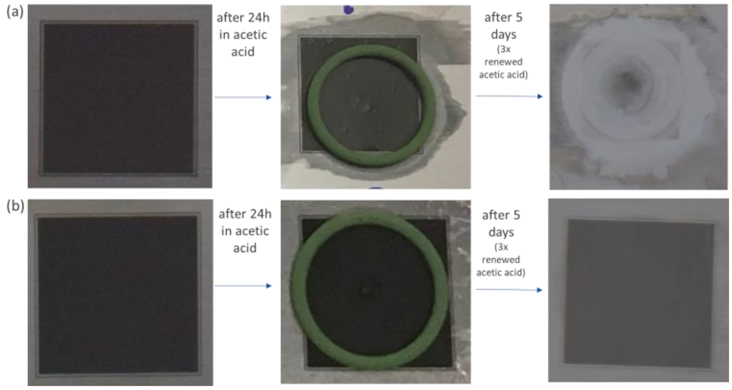

Fig. 5. From left to right: black-marked area directly after processing; acid treatment result after 24 hours; the same marking after a heavy acid treatment of 5 days, where the standard black marking (a) shown in the top row has already gone and the new SmartBlack processing result is still visible

3. Conclusion

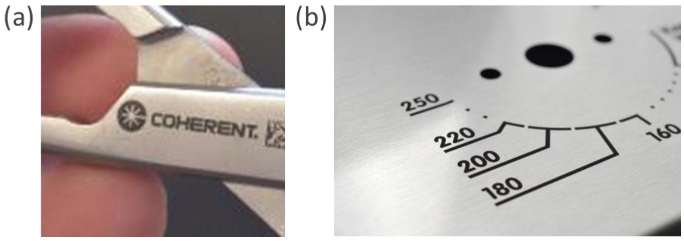

Fig. 6. (a) Black Marking on medical equipment like scissors; (b) Black Marking on white goods like your household stove

The Standard Black Marking offered in the market today is not relying on the nano-structures formed by the laser treatment. The laser induced periodic surface structure is more of a marginal than main effect. Instead it is based on the formation of oxides and oxide layers, which do the major part in blackening of the marked area but unfortunately are not completely acid-proof. This is still perfectly suitable for the marking of medical instruments (Fig. 6a) which do not experience environments with significantly low or high pH-values, as most biological and esp. human tissues expect an almost pH-neutral environment.

As Fig. 5 shows, by analyzing the underlying physical mechanism via numerical modeling and experimental observations we have achieved a major progress in making a laser black marking more acid resistant than before. This is the sort of progress necessary to address new markets for this technology such as black marking of automotive parts or household/white goods (Fig. 6b), which have much stronger requirements on acid resistance.

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