TRUMPF

White paper

Corrosion-resistant black marking on surgical steels

Contents

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Summary

Due to the introduction of the UDI standard (unique device identification) in the US and the EU, the medical technology sector is faced with higher requirements when it comes to the traceability of their products. For surgical steels, this means creating clear and legible, as well as corrosion-resistant markings which retain their level of quality in the subsequent clinical daily routine, even after numerous cleaning and disinfection cycles. Due to its physical characteristics, so-called "black marking" using an ultrashort pulse laser is very good suited to creating matt black, corrosion-free markings which retain a consistent level of quality for a particularly long time under clinical conditions. The correct laser parameters are essential for the desired results, and suitable refinishing can achieve further positive effects.

Situation

Marking using short-pulse lasers is an established process within the field of medical technology. The markings on surgical and medical devices (endoscopes, implants, etc.) have to remain durable and legible after numerous cleaning and disinfection cycles, however.

Markings using an ultrashort pulse laser (pulse duration in the range of pico- and femtoseconds) have a large process window and good corrosion resistance. This process is therefore an option for markings on medical instruments and components made from surgical steel as well as for other comparable critical markings. The process is called "black marking". The main advantage is the low heat input achieved through the extremely short interactions of the ultrashort pulses with the material. A further advantage is the generation of surface structures, so-called laser-induced periodic surface structures (LIPSS) or nanoripples, which create a particularly high contrast and very good legibility due to their effect on incident light. Both advantages are discussed in more detail below.

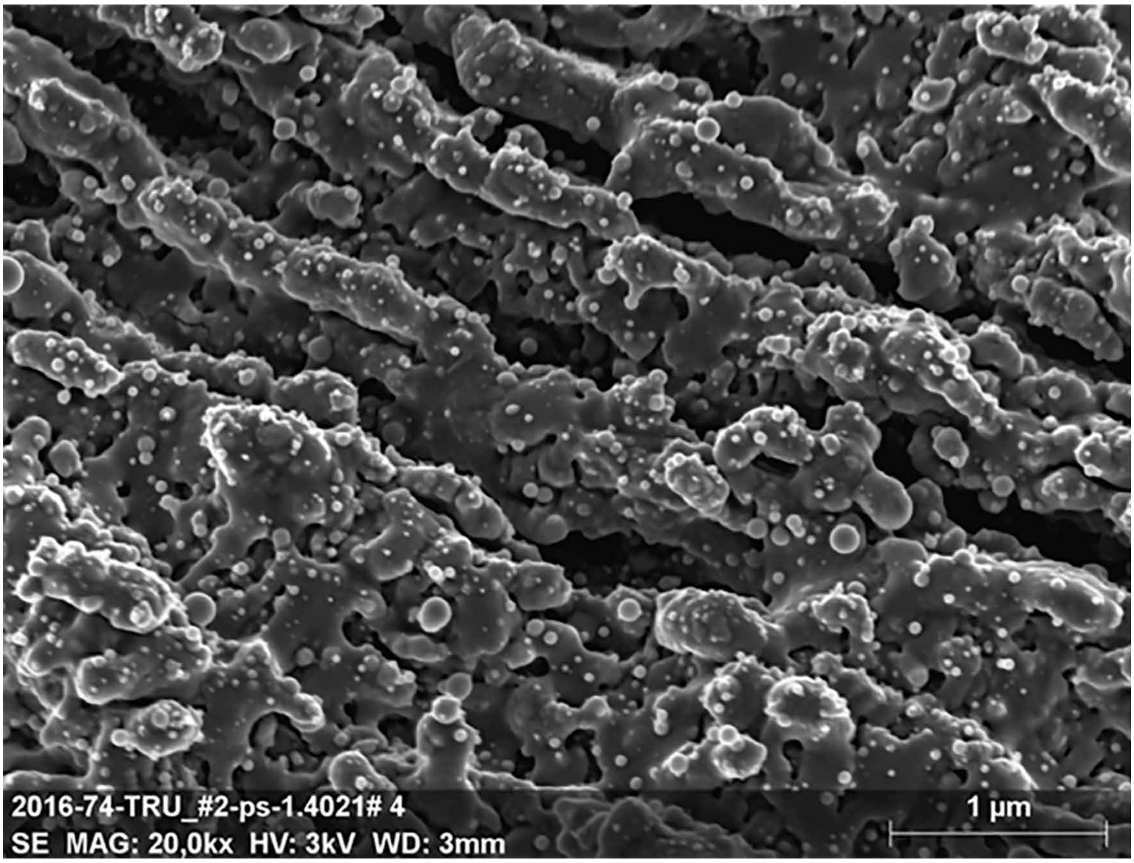


Figure 1: The LIPSS can be clearly seen in this figure. They minimize the direct reflection (light trapping effect) and scatter the light, thus ensuring a matt, high-contrast marking.

Material

In the field of medical technology, alloyed stainless steels are predominantly used. By definition, they contain a minimum of 10.5% chromium and protect their surface with a natural passivation layer, which makes them corrosion-resistant in a normal environmental atmosphere; it can lead to corrosion in some media, however. A higher percentage of chromium than that specified, and alloy components such as nickel or molybdenum have a positive effect on the resistance to corrosion and acids. Laser markings which are created on stainless steels with a high chromium alloy percentage also have better resistance to corrosion and acids. Polishing has also proven to be successful as a pretreatment as this wears and evens the surface structure, thus additionally protecting against corrosion.

Figure 2: UDI-compliant black marking on surgical forceps (stainless steel 1.4021).

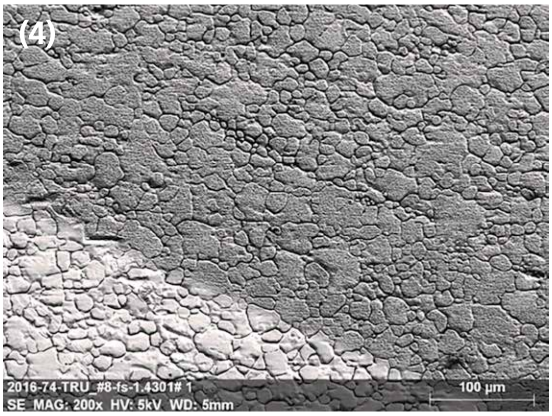
Figure 3: The same marking following a 24-hour salt spray test and 30-minute passivation in citric acid.

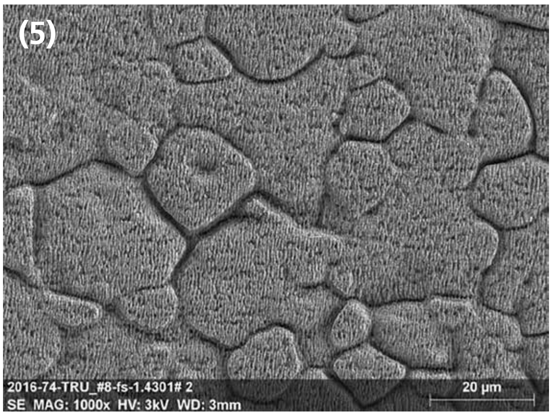
Surface changes with black marking

Matt markings with a high contrast are created on the surfaces using ultrashort pulse lasers. Unlike laser markings created with short-pulse lasers, the markings remain clearly legible from any angle, irrespective of the incidence of light. This is caused by the combination of two effects.

Firstly, a thin oxide film forms on the marked surface. Marking using ultrashort laser pulses leaves behind sufficient chromium in the surface, however (approx. 5 to 50 atomic layers), for the oxide film to be replaced with chromium ("it heals itself"), meaning that it retains its corrosion resistance, for example in the form of chromite ($Fe^{2+}Cr_2O_4$) or an iron-chromium spinel ($FeFe_{2-x}Cr_xO_4$). Black markings therefore do not demonstrate any impairment due to corrosion even after more than 1,000 corrosion tests, and remain clearly legible.

Secondly, investigations with a scanning electron microscope show a fine, periodically homogeneous ripple structure. These nanostructures (LIPSS) minimize the direct reflection (light trapping effect) and scatter the light. The LIPSS therefore ensure a particularly high-contrast, matt marking.





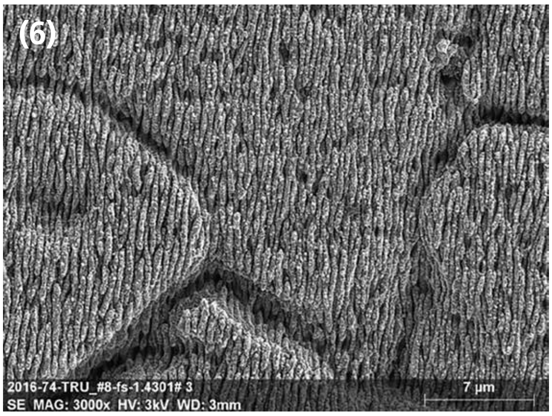


Figure 4–6: (4) Black marking with ultra-short laser pulses on austenite stainless steel 1.4301 under the scanning electron microscope (200x magnification). The dark, marked area can be seen clearly.
(5) 1000x magnification.
(6) 3000x magnification: Here the homogeneous structure of the nanoripples becomes clear.

Laser parameters

In order to create a resistant and durable result, a homogeneous marking layer growth should be aimed for. At high temperatures (above 570°C), thick oxide films may be formed on the surface of the material, but these lose their percentage of chromium, however, and are therefore more susceptible to corrosion and lose their passivation capacity due to their crystalline structure and composition (FeO and Fe_2O_3).

Ultrashort laser pulses, created for example with the TruMicro Mark, transfer very little heat into the material during processing due to their physical characteristics. If the pulse repetition frequency is additionally reduced, the heat input is also reduced. In tests at TRUMPF, it was discovered that the ideal result is achieved in the focus position (where there are the highest intensities) with just one pass. Here it is also recommended – as in general with laser marking – to perform the hatching before the outer contour of the marking for optimum contour definition, as the vector approaches of the hatching are smoothed in the process.

To obtain a dark, matt result, the scan speed velocity should be between 100 and 150 mm/s, at a pulse energy of typically 3 to 5 µJ (with optics with a focal length of 160 mm).

Refinishing

Figure 7: UDI-compliant marking following a 25-hour salt spray test.

Medical technology components are generally thoroughly cleaned following marking. Long treatment times, aggressive cleaning agents, or high temperatures may negatively influence the legibility and durability of the laser marking in the process.

A targeted passivation process using nitric or citric acid is recommended for refinishing. Tests at TRUMPF have demonstrated that citric acid is particularly suitable for stainless steel. Through the acid bath, highly reactive components of the surface such as free iron ions are removed, supporting the formation of a new, closed passivation layer. This increases the corrosion protection additionally. The components are cleaned by this at the same time.

In experiments, it can be observed that, under certain circumstances, the passivation can cause the quality of the marking to deteriorate. It has been shown, however, that a shorter treatment time as usual is sufficient to passivize components, whilst also retaining the quality of the marking.

Tests on the surgical stainless steel 1.4021, a martensitic steel, which is particularly critical for laser markings, have shown that the optimum is passivation using citric acid, with a concentration of 40% citric acid. At a temperature between 50 and 55°C and a treatment time of 10 min with a subsequent pure water cleaning bath, we were unable to determine any negative effects on the legibility of the marking.

The result of very good legibility with a high level of corrosion resistance was also proven to be valid following a boiling test in accordance with DIN EN ISO 13402 (30 min of being boiled in deionized water, then remaining in the same water for 60 min more, and then being air-dried for 2 h) and following a 24-hour bath in Ringer’s solution (hydrochloric acid with 0.9% sodium chloride).

Conclusion

Markings created by ultrashort pulse lasers appear to be a very good method to meet the criteria of UDI markings in an industrial environment with a large process window. They are characterized by a high level of corrosion resistance and good legibility. Suitable treatment after the marking process is important for a lasting high level of quality of the marking. In specific cases, TRUMPF recommends optimizing the laser parameters for the geometry and material of the component through tests.

Further information on beam sources and marking processes can be found at: www.trumpf.com/s/markinglasers

TRUMPF

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