A Study of Hardness and Adhesion of Laser Bonded MoO_3 Layers on Stainless Steel

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Abstract: The reliable marking of detail, produced from stainless steel, plays a more significant role in the logistics. The marking must answer to different conditions: it must have an excellent contrast to the substrate, durable and wear-resistant.

Laser bonding is a process of preparing coatings of oxides, mainly from transition metals, which are irradiated by a power laser. The oxide powder undergoes different physical and chemical transitions and a layer over the substrate is produced.

The long life-time and the hardness of the marking coatings are results of the adhesion to the stainless steel surface.

In this work a coating of MoO3 has been produced by laser bonding. The geometrical and mechanical properties have been studied by a scratch test. A scratch test consists in scratching of the coating by a Rockwell-shape indenter with linear growing load, while the sample is moved with constant velocity.

The thickness of the coating has been evaluated. The Rockwell hardness has been calculated and values, comparable with these of the stainless steel have been obtained. These data and the behavior of the coating during the test point to a very good adhesion to the metal surface.

Keywords: laser, laser bonding, transition metal oxide, catastrophic oxidation, hardness, scratch test, Vickers hardening test

Introduction

Laser marking is a technology that encounters numerous industrial applications because of its flexibility, fastness and versatility. One of the great challenges is the marking of metals because of their high thermal conductivity. Up to now the most effective and implement method of laser marking the direct laser ablation. By this method a fast moving powerful laser beam provokes local sublimation of the material. However this technology reveals two serious disadvantages [1][2]. The first one is connected with existence of grooves and micro-cracks in the region that is marked. The micro-cracks worsen the local mechanical properties of the material thus this method is not desirable for details, working at higher loading (as example in the aero-space industry).

This kind of marking is proved as un-proper for medical tools due to complicated sterilization as result of keeping of microorganims.

The second adverse effect is connected with the need of pulse laser mode along with large peak power. This imposes implementation of specific lasers (solid state with Q-switching).

A new marking method known since 1997 overcomes these disadvantages, consisting of local laser sintering of proper powder material, initially deposited on the substrate, thus forming a layer with an assigned graphical and topological design. The layer thickness is of order of 1-2 μm, so that the relief can be ignored and the mechanical properties remain unchanged. This method is known as "laser bonding". Laser bonded coatings are prepared by laser irradiation of transition metal oxides like MoO_3 powder on stainless steel substrate.

Marking plays a significant role in many applications, one of which is the logistics. For the needs of the logistics the inscription must be reliable readable long time, i.e. it is undesirable, if the coating disappears from the substrate.

The marked area must meet different requirements: the coating must be durable and robust against adverse environmental influences and must have a long life-time. This long life-time is strongly dependent on the adhesion of the coating to the stainless steel substrate.

In this work we would represent the results of the study of some of the most important mechanical properties of the coatings: thickness, the hardness and the adhesion to the substrate.

The thickness of the coating can be measured removing a part of the layer by different methods: either optical or fine-mechanical devices [3].

Hardness is the property of a material that enables it to resist plastic deformation, usually by penetration. However, the term hardness may also refer to resistance to bending, scratching, abrasion or cutting [4].

The principal purpose of the hardness test is to determine the suitability of a material for a given application, or the particular treatment to which the material has been subjected.

The hardness tests do not provide accurate numeric data for modern materials, especially for thin oxide layers. The usual measuring method is to study the depth or area of an indentation left by an indenter of a specific shape, with a specific force applied for a specific time. There are three principal standard test methods for expressing the relationship between hardness and the size of the impression - Brinell, Vickers and Rockwell. For practical and calibration reasons, each of these methods is divided into a range of scales, defined by a combination of applied load and indenter geometry.

Because of small layer depth, typical loads used in a hardness test of metals (> 1000 N) cannot be applied. The loads used in such measurements are in most cases under 10 N [4].

The study of the hardness of the oxide layers/coatings has been performed by a Vickers hardness test, while a Rockwell hardness or scratch test seem to be more appropriate for study of adhesion of such chemically and physically complex coatings for laser marking [3]. These measuring methods and the corresponding results shall be discussed in the section **Measuring methods and results**.

Up to our knowledge there is no information about the mechanical and tribological properties of laser bonded coatings for marking, based on transition metal oxides, so that this work is an attempt to reveal phenomenologically the mechanical behavior of molybdenum oxide layer/coatings on stainless steel substrate: hardness and adhesion to the substrate.

Experimental setup

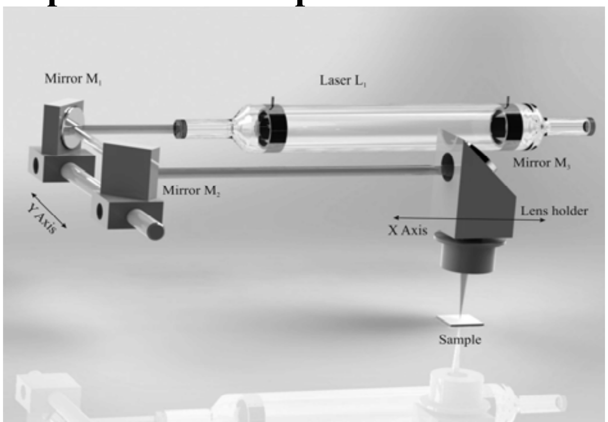


Fig. 1. Experimental setup for laser bonding

The equipment for laser bonding is shown in Fig. 1. It consists of a 50 W continuous working sealed CO_2 laser (wavelength 10,6 μm) L_1. The laser beam is being directed by two movable mirrors M_1 and M_2 (it can be moved parallel to the Y-axis) to the 50 mm focusing ZnSe lens. The holder with the deflecting mirror M_3 and the lens moves along the X-axis. This type of laser scanning system is called “fly-optics”, because the lens holder is of very low weight, enabling high scanning speeds (up to 30 m/min). The sample is being positioned in the focal plane of the lens.

Measuring methods and results

Thickness

Usually, the thickness is measured with an abrasive sphere, which removes part of the coating and substrate (Fig. 1).

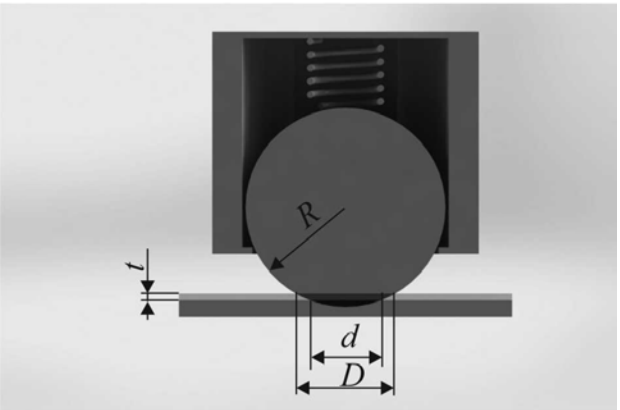


Fig. 1. Thickness measurement with an abrasive sphere

After performing the test, a calotte in the coating and substrate is build. It cross-section diameter with the coating and substrate have to measured under microscope. If R is the sphere diameter, d – diameter of the pattern, build on the coating, D – diameter on the substrate, the thickness t can be calculated from:

$$t = \sqrt{R^2 - \frac{d^2}{4}} - \sqrt{R^2 - \frac{D^2}{4}}$$

If D, $d \ll R$

$$t = \frac{D^2 - d^2}{8R}$$

This kind of thickness test is appropriate for smooth planar surfaces and sharp border of both imprints are presented.

Although, laser bonded MoO_3 coatings show a very rough surface, so a clear cross-section cannot be seen in the microscope.

We used two other optical methods for estimation of the thickness. The first one consist in focusing on the substrate and on different points of the coating (Fig. 2). The path that is needed for re-focusing on the other plane, shall distribution of the bulbs and indents, many measurements are needed to average the thickness.

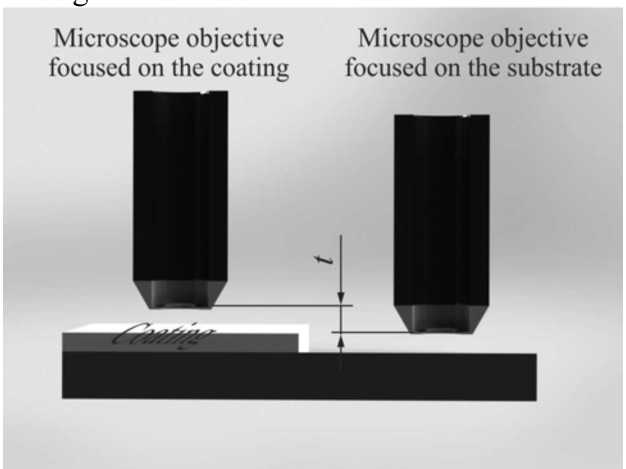
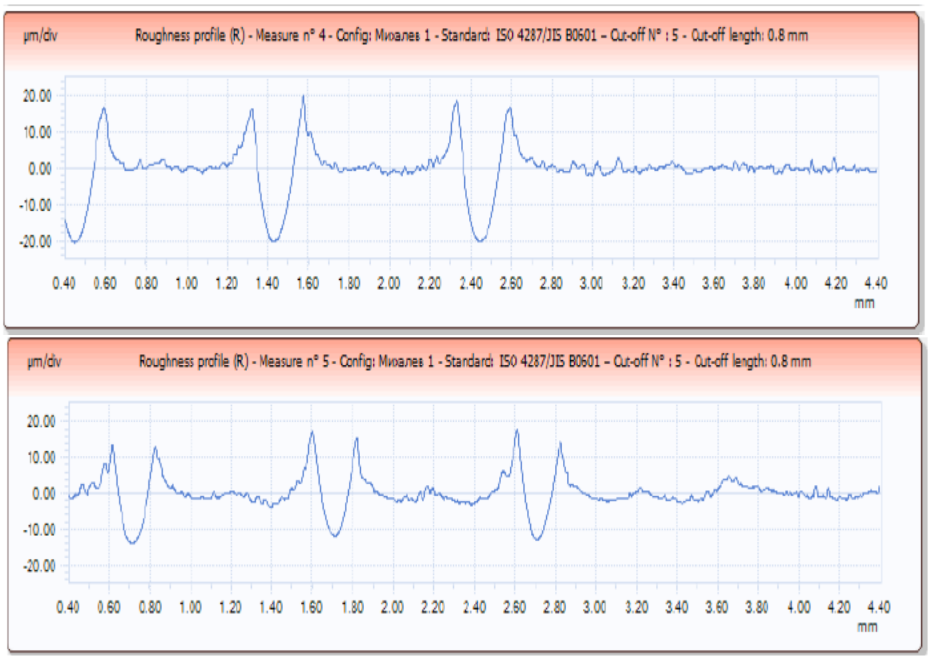


Fig. 2. Optical measuring of coating thickness t

The second method used was to trace the profile of the scratch line. The difference between the regular surface and substrate must be equal to the thickness of the coating (Fig. 3). The parameter Rv (ca. 10 µm) can



Par.	Value	Tol +	Tol -
Ra	3.682 µm	100,000	0,000
Rq	5.59 µm	100,000	0,000
Rt	40.416 µm	100,000	0,000
Rp	12.222 µm	100,000	0,000
Rv	12.862 µm	100,000	0,000
Rz	25.084 µm	100,000	0,000
Rc	14.228 µm	100,000	0,000
RSm	186 µm	10,000	0
Rδc	40.416 µm	100,000	0,000
RPc	88 /cm	1,000	0

Par.	Value	Tol +	Tol -
Ra	3.068 µm	100,000	0,000
Rq	4.495 µm	100,000	0,000
Rt	31.756 µm	100,000	0,000
Rp	13.541 µm	100,000	0,000
Rv	8.661 µm	100,000	0,000
Rz	22.202 µm	100,000	0,000
Rc	11.845 µm	100,000	0,000
RSm	248 µm	10,000	0
Rδc	31.756 µm	100,000	0,000
RPc	54 /cm	1,000	0

Fig. 3. Profile perpendicular to scratch lines (sample 9). Top: at the end of the test, bottom – in the middle of the line. Profilometer TESA, ISO 4287/JIS B0601, $\lambda_{cutoff} = 0.8$ mm.

be interpreted as the thickness height. Obtained results are in agreement with the data, acquired by other method (Table 1).
As result more relevant results have been obtained for the second set of samples, with a considerable thicker pre-processed sprayed coating. The averaged thicknesses are presented in Table 1.

Table 1

Coatings ticknes in µm	
Sample 1	1.5
Sample 2	1
Sample 3	1.9
Sample 4	1.8
Sample 5	1.5
Sample 6	5.7
Sample 7	2.5
Sample 8	> 10
Sample 9	> 8
Sample 10	1

Vickers hardness test
The Vickers hardness test was developed in the 20th years of previous century as an alternative to the Brinel method.
The setup is shown in Fig. 4.

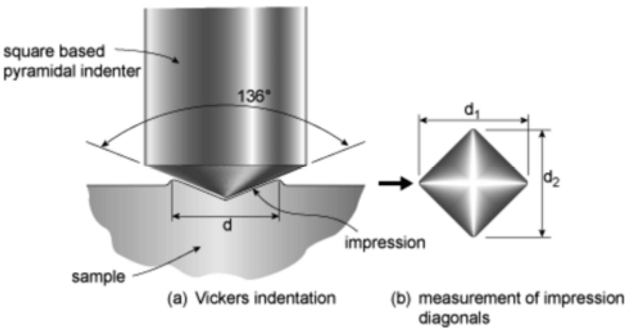


Fig. 4. Vickers hardness test equipment

This method is easier in application, since the calculations are independent on the size of indenter. The units given by test are known as Vickers Pyramid Number (HV). This units can be also recalculated in Pascals.
The indenter is in the form of a square-based pyramid with the angle of 136°, which gives an angle of 22° with the horizontal line.
The Vickers Number (HV) is given by the ratio of the force applied F to the area of the indentation A. This area can be calculated using the formula:

$$A = \frac{d^2}{2\sin(136°/2)},$$

where d is the averaged length of diagonals.
Finally:

$$HV = \frac{F}{A} \approx \frac{1.8544F}{d^2}$$

with F in kilogram-forces, and d in millimeters.

Adhesion and scratch test

The endurance of a marking coating is an important property, especially in the logistics, enabling long time errorless machine recognition of the parts. The endurance is strongly dependent on the adhesion to substrate, on first hand.
Up to our knowledge there is no method that gives an unambiguously quantitative evaluation of the adhesion. All the methods describe more or less phenomenologically the process of the coating failure.
In a ramp-load scratch test, a Rockwell-shape-tip is brought in contact with the coating, the tip is loaded with a constant load rate and the sample is translated simultaneously with a constant velocity (Fig. 5).

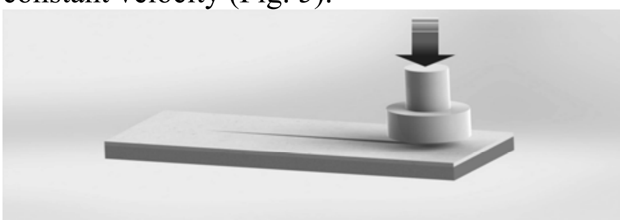


Fig. 5. Scratch test

The Rockwell-shape-tip is standardized to be a 120° conical diamond indenter with 0,2 mm curvature radius of the tip [5], [6] (Fig. 5).

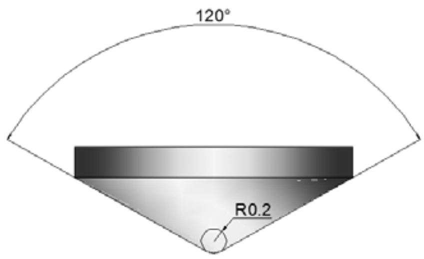


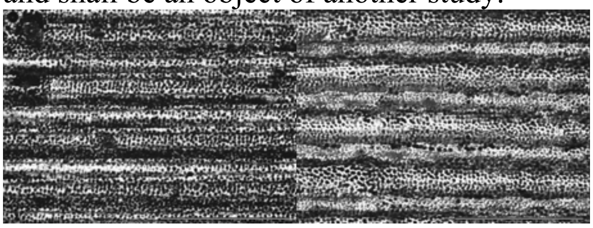
Fig. 6. Scratch test: Rockwell-shape tip

Our experiments have been performed at Karlsruhe Institute of Technology – Campus Nord using a CSEM Revetest scratch tester. More technical information about the device can be found at [7].
The test is performed until a coating failure occurs – the coating is broken or strong deformed. This load is called *a critical load.*
10 samples of laser bonded MoO_3 on stainless steel, prepared at different technological conditions (Table 1), have been examined.

Table 1

Sample	Laser power, %	Scanning speed, m/s	Initial powder thickness
1	100	30	Thin
2	100	25	Thin
3	100	20	Thin
4	100	15	Thin
5	100	10	Thin
6	100	30	Thick
7	100	25	Thick
8	100	20	Thick
9	100	15	Thick
10	100	10	Thick
Scanning row offset: 0,05 mm			

Fig. 7 presents an overview or the laser bonded surface. For simplicity only two samples are being shown, because that all samples show the typical scanning lines and a rough structure, consisting of bulbs. The origin of these swelling has been not cleared and shall be an object of another study.



Sample 1 Sample 2

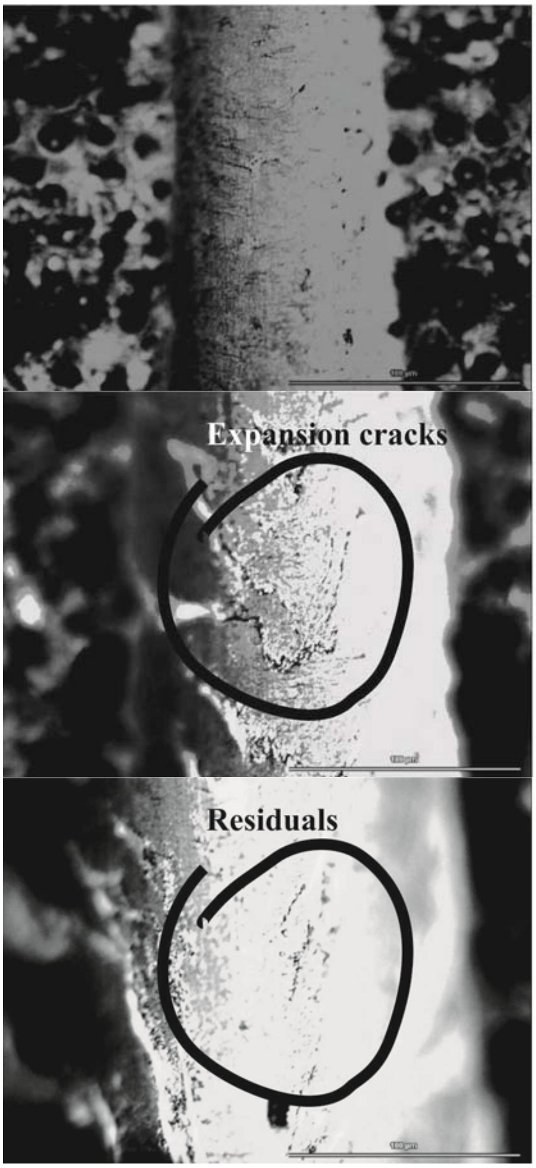
Fig. 7 Overview of the MoO_3 coating, viewed at 50x magnification

Then a scratch test has been applied. The normal load has been changed from 0 to 100 N. All the samples have nearly the same behavior. For simplicity typical scratch lines are shown in Fig. 8 in 500x magnification. It can be seen that no coating failure occurs and the coating is not strong deformed, even at 100 N.

In the middle (Fig 8 b) and c)) of the scratch line expansion cracks can be observed, due to plastic deformations in the coating, but no ruptures reveal in all samples.
The micrograph shows the substrate surface in the trace at the end (Fig 8 d)), but the coating remains unviolated and so no critical load is arrived. It must be noted, that in the final phase of the test, when the tip is so deep penetrated, so that it scratches the steel surface, residual portion from the coating can be observed.
This can be observed also in the surface profile graph, shown in Fig. 6.
Although no quantitative evaluation of the adhesion can be given, the results depict to very good binding to the surface. Even a load of 100 N (≈10 kgf) is not enough to separate the coating from the substrate, the plastic deformations are moderate, with no respect to the endurance. Such a strong adhesion can be explained by a chemical bond of the MoO_3 to the substrate during the laser bonding process and plasticity of the coating.

Conclusions

Samples of MoO_3 coatings on stainless steel under different technological conditions have been prepared. Mechanical properties of the coatings have been studied.
The thickness of the coatings has been measured and has been qualified as very thin (several micrometers).
The samples are very hard qualified. The microindentation gives a Vickers hardness number in order of this of the steel.
The scratch test reveals a very high adhesion to substrate Even at 100 N the coatings have not been damaged. The coatings have very high plasticity.



b)

c)

d)

Fig 8. Optical images at different phases of the scratch test: a) at the beginning, b), c) in the middle, d) at the end of test. Observation performed with an objective 500x, maximal load 100 N.

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Изследване на твърдостта и адхезията на лазерно бондирани слоеве от MoO3 върху неръждаема стомана

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Резюме

Надеждната маркировка на детайли от неръждаема стомана играе все по-голяма роля в логистиката. Маркировката трябва да отговаря на различни условия: да има добър контраст спрямо подложката, да е издръжлива и да е надеждна спрямо външни въздействия.

Лазерното бондиране е процес на изработване на покрития от окиси, предимно на преходни метали, облъчени с мощен лазер. Окисният прах претърпява различни физични и химични преобразования и върху подложката се отлага окисен слой.

Дългият живот и твърдостта на маркиращите покрития са резултат от адхезията към повърхността на неръждаемата стомана.

В тази работа са създадени слоеве от MoO_3 върху стомана посредством лазерно бондиране. Изследвани са геометрични и механични свойства на слоя посредством тест на надраскване. Той се състои в надраскване на слоя посредством индентор с рокуелова форма с линейно нарастващо натоварване, докато образецът се движи с постоянна скорост спрямо индентора.

Оценени са дебелините на слоевете. Твърдостта по Рокуел е изчислена и са получени стойности, близки до тези на стоманата. Данните и поведението на покритието по време на теста сочат за много добра адхезия на материала към повърхността на метала