Microstructural Characterization of Thin Laser Bonded Coatings based on Transitional Metal Oxides Powder

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Abstract: The reliable marking of details, produced from stainless steel, plays a more significant role in the logistics as well as in wearing. The laser induced coatings must meet different conditions: it must have an excellent contrast to the substrate, be durable and wear-resistant.

Laser bonding is a process of preparing coatings of oxides powder, 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 with different optical and microstructure properties is produced.

The color change and adhesion of such coatings are a result of the chemical compound and microstructure changes during the laser processing. This processing is performed at very high temperature, so it can be characterized as a thermodynamic non-equilibrium.

In this work a coating of MoO_3 has been produced by laser bonding. Micro-Raman scattering and X-Ray Powder Diffraction (XRD) have been used to estimate the chemical compound of the produced coatings, as well as their microstructure phases.

It has been demonstrated that in addition the initial a-orthorhombic MoO_3 the monoclinic b-phase is observed. The chemical compound undergoes also changes – in both spectra (Raman and XRD) the presence of new less-stable oxide Mo_4O_{11} can be found as well as $Fe_2(MoO_4)_3$ (iron molzbdate), but no MoO_2 in every structural form.

The results obtained show, that except the microstructure phase change of the metal oxide new oxides appear. These new oxides lead to the assumption that complex catalytic and de- and re-oxidation processes between the oxides in the melt and substrate are performed and a stable chemical bond to the substrate is build.

Keywords: laser, laser bonding, transition metal oxide, catastrophic oxidation, Raman scattering, X-Ray diffraction

Introduction

The laser bonding is a technology that avoid some adverse effects of laser ablation, such as micro-cracks in the affected zone and sterilization difficulties of medical instrument, marked with ablation [1][2].

On other hand it is similar to the process of the laser coating and a possible application field is the wearing due to local change of tribological, mechanical and micro-structural properties of the substrate surface.

The transition metal oxides, especially MoO3, offer rich possibilities for characteristics change of the substrate surface. They are, in first line, very aggressive oxidants in liquid form, so that a hard oxide crust from the substrate metal can be built. On other hand, they acts oft as catalysts, so we can expect, that at the end of the process the initial, but some changed transitional metal oxide shall be found.

In another works [3] we show, that the coatings have excellent mechanical properties such as very good hardness (comparable with the steel) and wear-resistance.

This high adhesion points on a tight chemical bond with the substrate surface. During the laser processing the initial powder layer of transition metal oxide (MoO_3 in our case) is melted. MoO_3 in molten state is a very aggressive oxidant and a good catalyst as revealed by some researchers [4].

Other scientists studied the behavior of molybdenum alloys steels and found the so called *catastrophic oxidation.* The catastrophic oxidation is a process when the molybdenum oxide, build from the steel molybdenum and oxygen in the atmosphere

attacks very aggressive the substrate surface, so that can be seriously damaged [5]

The excellent mechanical properties of molybdenum trioxide and especially its good adhesion and wear-resistance need an explanation, because we couldn't find any researches about the possible oxidation processes during the laser bonding. The structural properties have not been an object of scientific investigations

The non-equilibrium of the laser induced transitions gives a new variety in the properties of the coating due to high temperature and short pulse duration, which does not allow that the materials take their equilibrium states and in this form new interesting behavior of the coating could be expected.

This work is an attempt to reveal phenomenologically the chemical and micro-structural behavior of molybdenum oxide layer/coatings on stainless steel substrate obtained by laser bonding.

As measuring methods X-Ray Diffraction (XRD) and micro-Raman spectroscopy have been involved.
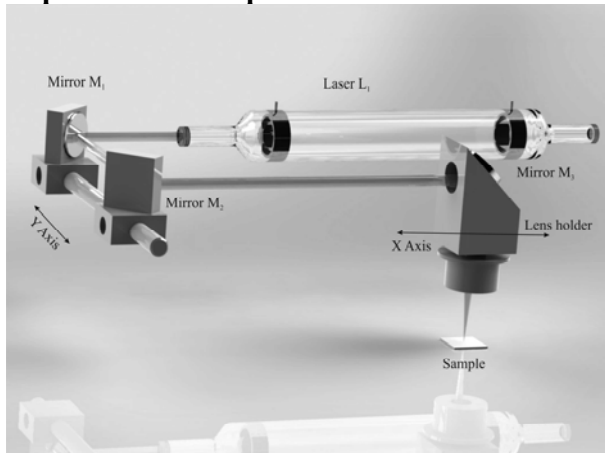
Experimental setup

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 (infrared, wavelength $\lambda = 10,6$ μm) L_1. The laser beam is being directed by two movable mirrors M_1 and M_2 (it can be moved with a high velocity up to 30 m/min parallel to the Y-axis) to the 50 mm focusing ZnSe lens. The sample of dimension 10x10x1 mm is being positioned in the focal plane of the lens.

The substrates of stainless steel of the Grade 304 were pre-coated with pure α-orthorhombic MoO_3 which has been sprayed to the surface.

Measuring methods

XRD

XRD is suitable for estimation of the lattice parameters of crystal materials.

It is well known [6] that if a crystal is exposed to a X-Ray beam, the beam is reflected from all crystal plane at the angle as the incident (Fig. 2).
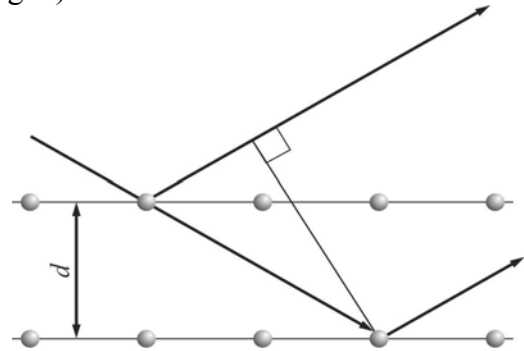

Fig. 2 Each plane has the behavior of a plane mirror, so both incident and diffraction angle are equal.

The reflected parallel rays are phase shifted, so that at certain angles peak intensities can be registered according to the Bragg equation:

$$n\lambda = 2d \sin \theta$$

Where n is an integer, called *diffraction order,* λ – the wavelength of radiation, d is the spacing of the crystal planes responsible for a particular diffracted beam, and θ is the diffraction angle.

If the function $I(2\theta)$ is graphically built, we can calculate the lattice parameters of the crystal from the positions of the peaks.

A diffractometer comprises a X_Ray source, a X_ray generator, diffractometer assembly and detector and a data collection system (Fig. 3).

The X-Rays are generated by acceleration of electrons into metal target in a vacuum tube. The high energy electrons cause emission of photon from the deeper levels of the metal nucleus during their refilling. If the electron energy is eV, the photo frequency can be

calculated from $eV = h\nu$. Therefore the minimum wavelength of the so called *Bremsstrahlung* should be $\lambda_{min} = 1,243/V$, where λ is nanometers, and V in kilovolts.
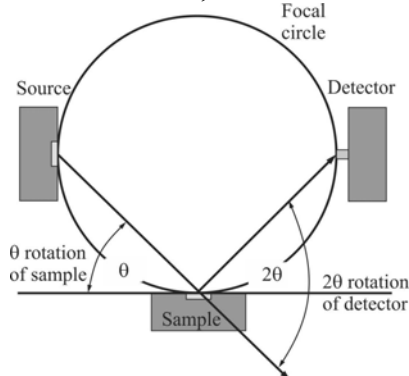

Fig. 3. Difractometer assembly and measuring procedure.

The radiation from the target consist of a continuous spectrum, superimposed by a very narrow and intensive *characteristic radiation* of the chemical element. The characteristic line obtained when an a hole from an excited K-shell electron is filled by a L-electron, contributes to the Kα – line, while the line, obtained by refilling with an M-electron, builds the Kβ line.

It must be noted that outgoing from the arguments, mentioned above, the selection of the wavelength is very important in order to avoid fluorescent radiation and to minimize the absorption. Thus Cu Kα line ($\lambda = 0,154$ nm) is appropriate for measurements of steel and other iron alloys ($K_{FeK} = 7,109$ keV, $\lambda = 0,1789$ nm).

The X-Ray spectrum is acquired, rotating the the detector about the sample (Fig 3). To use the full resolution of the method, the diffractometer must be accurately aligned and calibrated, usually better than 0,01°.

The X-ray method can be successfully implemented for study of *polycrystalline powder material*, like transition metal oxides.

The diffraction peaks are compared either graphically with specific lines for different material using diffraction lines databases (as examples JCPDS) or with calculated data, based on crystallographic data.

So, in this way the XRD gives reliable information about the presence of particular polycrystalline material or powder.

Micro-Raman spectroscopy

In addition the Raman spectroscopy gives information about the crystal modifications of both polycrystalline and amorphous materials. In Raman spectroscopy, the specimen is irradiated by a laser and the scatter light is observed in direction, perpendicular to the laser beam.

There are two type of scattered light: *Rayleigh* and *Raman scattering*.

The Rayleigh scattering has the same frequency as the incident light, while the Raman scattering is very weak with frequencies $\nu_0 \pm \nu_m$, where ν_m is the frequency of vibrational mode of the molecule. Both lines are called *Stokes and Anti-Stokes lines* [7]. That is the same, as if the material is excited by the incident light to virtual lines above and below the basic state. The incident light is scattered at different angle and with different energy, resp. frequency.

Because this scattering is independent on the subordination of the atoms, it can be applied also for amorphous materials.
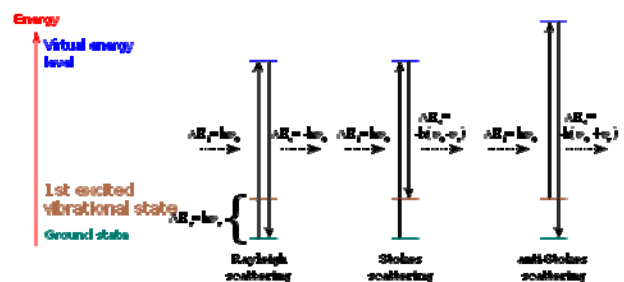

Fig 4 Explanation of Raman scattering. Picture from Wikipedia.org

Here must be noted, that the Raman spectroscopy is proper rather for estimation of *vibrational state of oscillators* the for exact identification of chemical elements or compounds, because many of them can have "elastic" properties of the chemical bond, very close to the attempted.

A combination with XRD, which gives information from the nuclei and in this sequence about the chemical contents, is more adequate for chemical identification. It has another adventage – many amorphous phases can be quantitative detected, what is impossible, if only XRD is used.

Experimental results and discussions

XRD

XRD was performed at Karlsruhe Institute of Technology, Institute of Applied Materials - IWP. The used diffractometer was Seifert PTS300 with a Cu-cathode with a resolution of 10^{-4} degrees with and beam diameter of 2 mm. For more intensity except the Cu-Kα (1,5418 nm) also the Cu-Kα1 (1,5405) was used.

10 specimens (dimensions 10x10x1 mm), prepared with laser bonding at different technological conditions (thickness and scanning velocity from 10 m/s up to 30 m/s, see Table 1) have been examined. Additionally, the spectrum of the stainless steel of Grade 304 has been acquired in order to distinguish the lines, coming from the substrate. Results are presented in Fig. 5 (substrate) and Fig. 6 (10 samples).
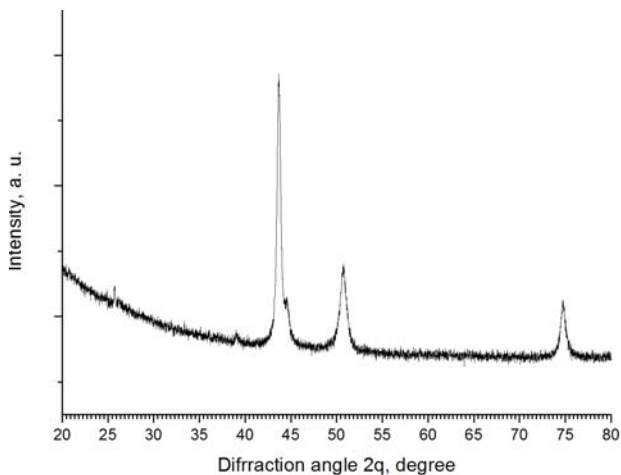

Fig. 5. XRD spectrum of the stainless steel

First, it must be noted, that no significant differences between the specimens can be observed. They have the same peaks, though wit different intensity, This can be a result of dispersion in the coating thickness.

Second, the graphs give information about the chemical compound of the coating.

The XRD spectra have been compared with the JCPDS data base [8] for powder materials. It was searched mainly for MoO_3 (α – JCPDS card No. 5-508 and β - JPCPDS card No. 87-1445 crystal phase), as well as for MoO_2 (JCPDS card No. 73-1249) and Mo_4O_{11}

(JCPDS 72-0447). Mo_4O_{11} is one of the metastabile non-stoihiometric molybdenum non-stiohiometric oxides. In [9] a model for producing of Mo_4O_{11} has been suggested. According to this mode, the oxide is a result of the interaction between melted MoO_3 and MoO_2. The MoO_2 in our opinion comes into being due to the thermal reduction of MoO_3.
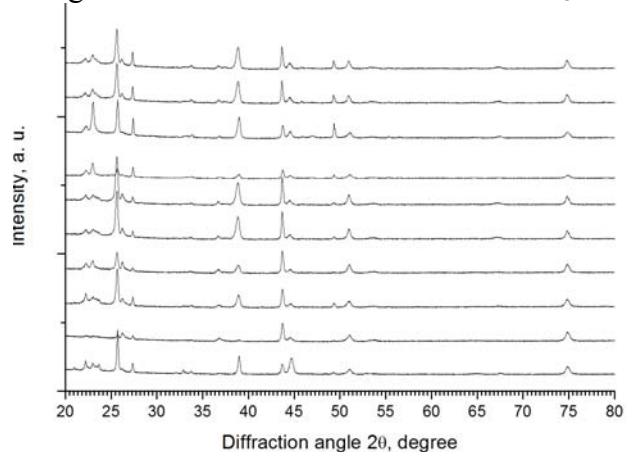

Fig. 6. XRD spectra of the specimens

According to the JCPDS 5-508 the orthorhombic MoO3 has a very intensive line at 27,335 degrees and adjacent sharp intensive lines at 23.329 and 25,704 degrees, which can be clear seen in Fig. 6. Additionally, other peaks of α-MoO3 can be found. Thus we can maintain, the final coating contains MoO3 in orthorhombic form.

Lines of MoO_3 in monoclinic form also can be found (JCPDS 37-1445 – 23,10, 25,014, 51,285 degrees).

Presence of Mo_4O_{11} has been detected in the spectra. The responsible lines lay at 20,935, 22,206, 22,491, 23,707 and 25.577, 32,090, 32,877, 33,627 degrees (JCPDS 5-337). The most of them are clear to be distinguished in the coatings spectra.

Contrary, the presence of MoO_2 in crystal form is very controversial. It most intensive lines could be expected at 26033, 37,025 at 53,512 degrees. No presence of the first peak, which is a results of the diffraction from the closest neighbors, were found. A weak maximum in the spectrum is observed at 37,025 and 53,512, what can point to small portion of un-reoxidized MoO_2, but it can lay in the region of the experimental uncertainty

and, for that reason, information from different measuring methods is needed.

Additionally, a check for iron molybdate oxide Fe(MoO4) and $Fe_2(MoO_4)_3$ has been performed. Diffraction pattern for this compounds are stored in JCDPS card No. 89-2367 and 89-2368. Only for $Fe_2(MoO_4)_3$ the two almost intensive line at 22.988 and 25.709 degrees have been found in all XRD pattern from all 10 samples. This can speak for a complex oxidation process, in which the MoO_3 plays a key role as an intensive oxidant and catalyst. We suppose that the initial powder pure MoO3 decomposes and the oxygen attacks the substrate. Because of the small processing time most of the chemical substance cannot arrive their equilibrium state. The MoO_2 is re-oxidized by the atmospheric oxygen into MoO again. Parts of them gets into a reaction with MoO_2 into Mo4O in the melt. The iron oxide binds with molybdenum oxides to $Fe_2(MoO_2)_3$. Additional experiments in oxygen free atmosphere can prove our supposition.

Raman spectroscopy

Micro-Raman spectroscopy has been performed using a Horiba Raman spectrometer with laser peak at 632,8 nm (He-Ne laser).

The confocal micro-Raman spectroscopy enhances the possibilities of the method due to gathering data from very small area. Optically, the coating surface is very irregular, bulbs and indents can be seen. Additionally, different structure behaviors are observed. For that reason 5 typical points have been chosen. Fig. 7 depicts these regions.

The Raman spectra from these points are shown in Fig. 8.

On first hand, the points show different structural characteristics.

While point 1 and 2 show more flatten scatter spectra, the other points have intensive more or less sharp peaks. This difference can be explained by the technologic conditions. Because the offset between the scanned rows has been 0,05 mm and the averaged focal point size app. 0,2 mm, some of the regions

have been exposed several times to laser irradiation. The high temperature molt the re-crystallized material during the exposure, so that the part of the polycrystal phase has been amorphized. The regions, that were not so long irradiated, a part of the MoO_3 remained crystal. But in these points traces of recrystalized material can be found (the weak peaks in the region 800-1000 cm^{-1} in the graphs below).
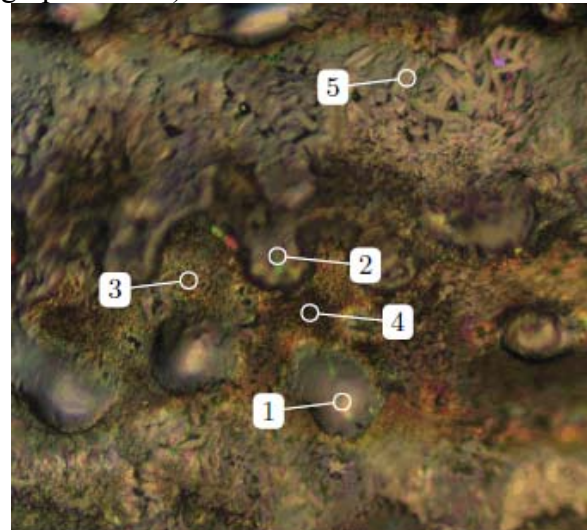

Fig. 7. Points from which Raman scattered light has been collected (50x maginification)

In [10] Camacho-Lopez et al.. reported following characteristic peaks of α-MoO_3: 152, 280, 660, 819, and 995 cm^{-1}, and 203, 208, 229, 346, 350, 365, 459, 469, 496, 569, 588, 744 cm^{-1} for MoO_2.

Dieterle [11] studied the Raman lines of Mo_4O_{11}: 183, 206, 229, 264, 306, 340, 380, 431, 452, 498, 568, 744, 790, 835, 843, 907 and 985 cm^{-1}.
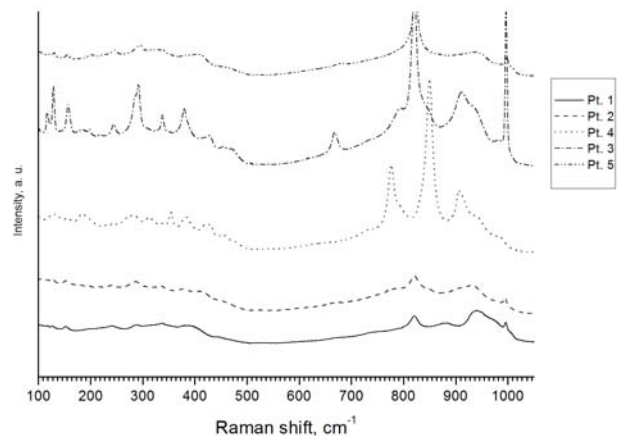

Fig. 8 Raman spectra of different points on the layer (magnification 50x).

The Raman spectra of different points have some features. First, the spectra from point 1 and do not show high intensive peaks. This leads us to the presumption, that in the bulbs the material consists of more amorphous phase with a content of α-MoO_3.

Point 3-5 depicts on crystal state. They have relatively sharp peaks, which have been identified by us as MoO_3 (α and β phase) and Mo_4O_{11} can be found also.

In all point no presence of MoO_2 has been detected. This is in agreement with the hypothesis that MoO_2 in the melt reacts with the atmospheric oxygen to MoO_3 and with MoO_3 to Mo_4O_{11} [6].

It must be noted that Raman scattering is a result of the interaction of the falling photon with chemical bond, which can be interpreted as an oscillator. The information acquired by Raman spectroscopy concerns mechanical vibration of the part of molecules. For that reason the method does not give an un-ambiguous identification of the chemical substances, so that is possible, that a Raman peak, which is described as pure element in other work, belong to a chemical bond of a more complex substance, which contains a Mo-O bond, as example iron molybdate.

Thus, Raman spectroscopy supports results of the XRD study.

Conclusions

Several samples of laser bonded MoO3 on stainless steel have been prepared.

The samples were studied with XRD and Raman spectroscopy to identify the chemical and phase content of the coating.

XRD and Raman spectroscopy find MoO_3, Mo_4O_{11} and $Fe_2(MoO_4)_3$ and no MoO_2.

The presence of these oxides is an indication of intensive oxidation. The MoO_3 serves as a catalyst and the oxygen, released by the oxide, attacks the substrate. Mo_4O_{11} can be a result of the reaction between MoO_3 and MoO_2 in the melt.

$Fe_2(MoO4)_3$ indicates to a chemical bond between the iron in the steel substrate and the laser bonded coating, which can explain the good adhesion of the layer.

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Характеризиране на микроструктурата на тънки лазерно бондирани покрития от прахообразни окиси на преходни метали

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Резюме: Надеждното маркиране на детайли от неръждаема стомана играе важна роля както в логистиката, така и за повишаване на износоустойчивостта. Лазерно бондираните слоеве трябва да отговарят на различни условия: да имат добър контраст с подложката, да имат дълъг живот и да са износоустойчиви.

Лазерното бондиране е процес на нанасяне на покрития от окиси, главно на преходни метали, които се облъчват с лазер. Оксидният прах претърпява различни физични и химични преобразования и върху подложката се образува слой с различни оптични и микроструктурни свойства.

Промяната на цвета и адхезията на такива покрития е резултат от промяната на химичния състав и микроструктурата по време на лазерната обработка. Тази обработка се извършва при много висока температура и процесът може да се характеризира като термодинамично неравновесен.

В тази работа с помощта на лазерно бондиране се създадоха слоеве от MoO_3. Използвани бяха микрораманова спектроскопия и рентгенова дифракция (XRD) за определяне на химичния състав на нанесените покрития, както и на техния фазов състав.

Демонстрирано е, че към първоначалния ◊-орторомбичен MoO3 се наблюдава и моноклинен β-MoO_3. Химичният състав също претърпява промени – в рамановите и рентгено-дифракционни спектри се наблюдава нов по-малко стабилен Mo_4O_{11}, както и $Fe_2(MoO_4)_3$ (железен молибдат), но не и MoO_2 в никоя структурна форма.

Получените резултати показват, че освен промяната във фазовия състава, се появяват нови окиси, тези окиси водят до предположението за сложни каталитични и де- и ре-оксидационни процеси между окисите в стопилката и подлжката и че се образува стабилна химична връзка със субстрата.

Ключови думи: лазер, лазерно бондиране, окиси на преходни метали, катастрофична оксидация, Раманово разсейване, рентгенова дифракция