A Comparison between Different Materials Based on Transition Metal Oxides as Additives for Laser Bonding on Stainless Steel

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Abstract

In this work, a new modification of the laser bonding is considered. Only one specific transition metal oxide is used to create an additive coating on a stainless surface. The following materials have been selected for comparative analysis: MoO_3, WO_3 and a commercial laser bond ink produced by TherMark. Temperatures over 2,000 K at the focal spot, with a very steep temperature increasing front of 10^7 K/s and spatial gradients of 10^7 K/m, have been evaluated. The mechanical properties of the coating have been studied by ramp scratch and Vickers hardness tests. The structural state and adhesive properties have been studied by X-ray diffraction (XRD) and Raman spectroscopy. A spectrophotometer has been used to estimate the contrast. The experimental results show a hard coating with excellent adhesion to the substrate with a thickness of several μm. The presence of intermediated oxides has been detected, which is an indication of oxidation processes. The good adhesion is explained by a chemical bond between the oxide and the substrate.

Keywords: *Lasers, laser machining, laser bonding, transition metal oxides.*

1. Introduction

The quality control and management are currently becoming more and more important due to the globalization of the world industry. In this relation, the correct marking and identification of details play a key role. This kind of visual notification does not change its properties during the whole product lifecycle (NASA 2002). The materials for the marking of the details must meet different requirements and must be durable over the whole lifecycle of the hardware. The usual inks do not adhere very well to metals, so the marking is not durable. Since 1997, a new method patented by TherMark, Irvine, CA, USA, and called "laser bonding" overcomes most of the disadvantages of other methods.

The modification of the laser bonding using only one transition metal oxide for preparation of a dark coloured film over a stainless steel substrate, which is well bonded to the metal, is reported in this work.

2. Experimental Results

The following materials have been selected for this comparative study: MoO_3, WO_3 and a commercial laser ink (TherMark 2012). In the proposed method, the initial materials in the form of a powder are sprayed onto the metal plate. Then the laser radiation melts locally the initial mixture by following a topological contour and a dark-coloured coating is being built up. A 30-W CO_2 laser has been used as a heat source. The experimental details have been presented by Christov *et al*. (2010).

2.1. Mechanical Properties

The study of the mechanical properties has been performed by a CSEM Revetest® tester at Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. The Vickers test has been carried out at a load of 50 mN. The ramp-load scratch test has been performed at a loading rate of 100 N/min with a speed of 5.7 mm/min.

Table 1. Hardness and critical load of the three materials.

Material	Hardness (HV)	Critical load (N)
MoO_3	250	No
WO_3	450	15
TherMark	Very hard	25

A comparison of the hardness and critical load of the three materials is presented in Table 1. The hardness of the stainless steel has also been measured as a reference. It has a Vickers number of HV250. The hardness against penetration of all materials is very high in comparison with the hardness of steel or beyond. They also reveal different adhesion to the substrate. The best results have been achieved by the processing of MoO_3 because no critical load has been found. Even at a load of 100 N, residuals of the coating in the form of traces have been microscopically observed which depicts the high wear-resistivity of MoO_3 coating. The other materials also have a good adhesion but they fail and crash at smaller loads. In this respect, they are less durable than MoO_3.

2.2. Structure Analysis

2.2.1. XRD patterns

The XRD spectroscopy of the materials has been performed by a Seifert 3003 HR diffractometer at Karlsruhe Institute of Technology, Karlsruhe, Germany. The angle resolution has been set to 0.01°. XRD patterns of the three materials are presented in Fig. 1. In the spectrum of MoO_3, sharp peaks of ferrymolibdite $Fe_2(MoO_4)_3$ (JCPDS card 83-1701) have been detected at 38.76° and 44.55° which indicate a crystal state of the ferrymolibdite. Different molybdenum oxides have been also observed: α-MoO_3 (orthorhombic), Mo_4O_{11}, Mo_8O_{23} (JCPDS cards 89-5108, 89-6725 and 84-1248). This supports the assumption of redox processes in the melt of MoO_3. No MoO_2 XRD lines have been recognized. Strong steel lines have also been found, which can be explained with the small thickness of the coating, so that the X-rays can reach the surface of the steel substrate. In the spectrum of WO_3, sharp peaks of steel have been detected using a reference spectrum from clean stainless steel of the same sheet as the samples. WO_3 at 23.811° and 41.24° (JCPDS card 89-4482) has been recognized, as well as the intermediate stoichiometric tungsten oxides W_4O_{11} (24.509°, 40.605°, JCPDS 02-0319), $W_{18}O_{49}$ (25.246°, 30.442°, 33.566°, 36.28°, 40.605°, JCPDS 84-1516). These broad peaks can be explained by their different orientation with respect to the incident radiation, which is an indication of a poly-crystal phase convolved with an amorphous phase. In the XRD pattern of the coating with the commercial laser marking spray of TherMark, except the peaks of steel, poly-crystal MoO_3 possibly mixed with amorphous (a broad base at nearly 35°) phase can be recognized, as well as peaks from the intermediate stoichiometric molybdenum oxides Mo_4O_{11} and Mo_8O_{23} (Rao *et al*. 2013). The presence of molybdenum oxides can be easily explained, because the manufacturer announces the presence of MoO_3 in this spray. Also, the broad peak of possibly amorphous FeO (the relatively weak peak at 26.22°, JCPDS cards 77-2355 and 75-1550) and Fe_3O_4 (30.37°, 37.13°, 56.99°, 62.9°) have been recognized. No peaks of Fe_2O_3 have been observed although a corresponding search has been done using JCPDS cards 76-1821, 73-2234 and 73-0603.

2.2.2. Raman spectra

The Raman spectroscopy has been performed using a Horiba Labram HR-800 Joubin Yvon confocal micro-Raman spectrometer (MoO_3) at Faculty of Physics, Sofia University "St. Kliment Ohridski", Sofia, Bulgaria, and a micro-Raman spectrometer at Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany. The Raman spectra are shown in Fig. 2.

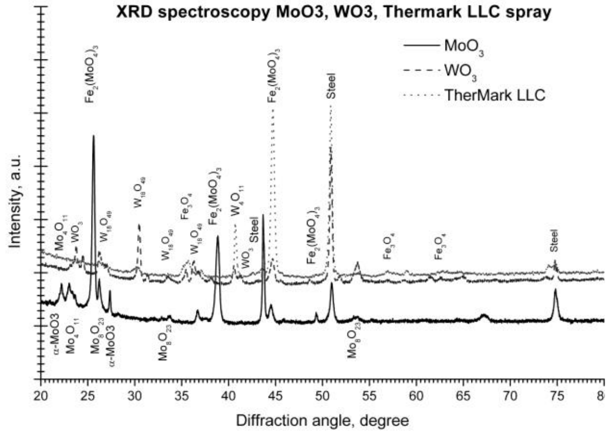

Fig. 1. XRD patterns of laser bonded MoO_3, WO_3 and TherMark spray.

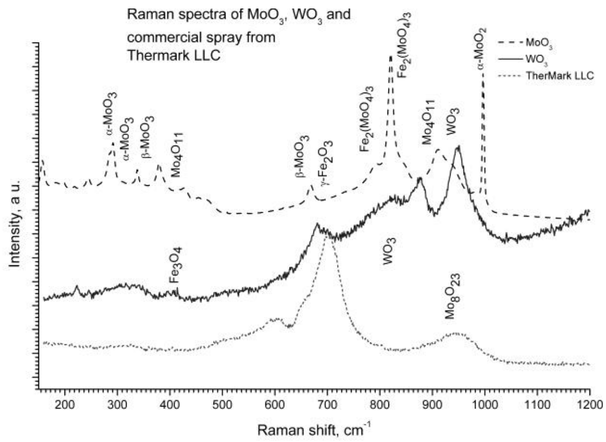

Fig. 2. Raman spectra of the three materials.

2.2.2.1 MoO_3

The characteristic MoO_3 lines at 996, 375, 291 and 244 cm^{-1} (Camacho-López *et al*. 2007; Dieterle *et al*. 2012; Dieterle and Mestl 2002) have been observed. Also, an additional line of Mo_4O_{11} at 130 cm^{-1} has been recognized. The observed slight differences in the positions and widths of the lines are explained with the peculiarities of the preparation techniques because the material is a manifold exposed to laser radiation. As a result, the crystal substances become more or less amorphous. A line of $Fe_2(MoO_4)_3$ (Xu *et al*. 2008) at 933 cm^{-1} has also been recognized. In regions with a drop shape (not shown in Fig. 2) the lines are wide broadened and this fact leads to the assumption of vaporization and subsequent condensation of an amorphous oxide.

2.2.2.2 WO_3

In the Raman scattering spectrum of the WO_3 coatings, very broad peaks of WO_3 (809, 950, 954, 809, 693 and 193 cm^{-1}) have been observed (Lee *et al*. 1999). A broad weak peak of Fe_2O_3 (Shim and Duffy 2002) at 406 cm^{-1} has also been observed.

2.2.2.3 TherMark

Molybdenum trioxide MoO_3 has been noticed at 196 and 336 cm^{-1}. The first line is ascribed to the twisting of terminal bonds O=M=O, but it can also depict a Mo(IV) oxide. The absence of MoO_2 in the XRD pattern is the reason to exclude this oxide. The presence of Mo_8O_{23}, according to Lalik (2011), is a result of the reduction of MoO_3 to MoO_2 with subsequent oxidation. The broad strong peak at 700 cm^{-1} is identified as γ-Fe_2O_3. Fe_2O_3 has also been found at 553 cm^{-1} (Shim and Duffy 2002). The absence of iron (III) oxide in the XRD pattern can be explained with the assumption that it is in an amorphous form.

3. Discussion

The good adhesion to the substrate is a result of the complex thermo-chemical reactions in the liquid phase. In particular, MoO_3 reveals very strong oxidation properties. It is acting as an acid (flux) in the liquid phase, like in "catastrophic oxidation" of molybdenum steels (DeVan 1961). WO_3 has similar properties but it needs more energy to become liquid. The oxide attacks the surface of the iron substrate and iron oxides are built. These iron oxides are disolved by the liquid and a process of building of iron salts from transition metal acids begins. As a result, ferrymolibdite $Fe_2(MoO_4)_3$ has been detected. Tungstenides have not been found, possibly because the temperature, needed for total melting of WO_3, has not been reached. The ferrymolibdite is strongly chemically bonded to the substrate and takes the role of an interface. The other components of the coating dissolve at the interface so that the oxide film is also well connected to the substrate. The situation is different with the TherMark spray. Since the quantity of MoO_3 in the spray is not large, the contained iron oxide promotes the formation of an interface. In turn, the oxides dissolve the melted silica so that a protective glass film is being built. This process is very similar to the enamelling of steel (ArcelorMittal Flat Carbon Europe 2008).

4. Conclusion

Technological samples have been investigated using three different materials: MoO_3, WO_3 and commercial laser bonding ink from TherMark. The study of the mechanical properties shows a good adhesion to the substrate of all materials. However, MoO_3 reveals a better wear-resistance and plasticity in comparison with WO_3 and TherMark ink. These two materials typically crash at much lower loads than MoO_3, especially the glass containing fragile coating from TherMark. Both XRD and Raman analyses reveal similar results with respect to the structural and phase states. Generally, intermediate stoichiometric oxides of Mo and W are observed. An important peculiarity of all spectra is the presence of iron-containing compounds such as ferrimolibdite $Fe_2(MoO_4)_3$ or different iron oxides. It is believed that these iron-containing compounds build an interface with the substrate which is responsible for the good adhesion. Correspondingly, they make a metallurgical bond with the intermediate oxides. In the future, a high temperature thermochemical model should be composed to explain more precisely the chemical evolution during processing times in the millisecond range, which should take into account the extreme temperature gradients. Such a model would contribute to a better understanding of the coating process and would inspire ideas for new technological properties and broader industrial applications.

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