

# Special Issue “Surface Modification of Metals and Alloys”

Oriol Rius-Ayra \*  and Nuria Llorca-Isern 

CPCM, Department of Materials Science and Physical Chemistry, Faculty of Chemistry, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain; nullorca@ub.edu

\* Correspondence: oriolriusayra@ub.edu

Recently surface modification has become necessary for the scientific community because of surface properties of new materials are usually inadequate in terms of wettability, adhesion, corrosion resistance or even drag reduction. In order to modify solid surfaces such as metals and alloys different treatments have been used to obtain a desired surface finish such as chemical vapor deposition, physical vapor deposition, chemical etching, electrodeposition or the application of non-equilibrium gaseous media, especially gaseous plasma. These treatments promote changes in roughness, hydrophobicity, biocompatibility or reactivity. Although such treatments have been studied extensively in past decades and actually commercialized, the exact mechanisms of interaction between reactive gaseous species and solid materials are still inadequately understood.

Moreover, for various reasons, it is difficult to find an alloy with a different surface behaviour from that of the bulk. A greater or more specific to extreme environments: resistance to corrosion and to wear, higher mechanical or fatigue resistance, hydrophobicity, oleophilicity, thermal (for low or high temperature exposure), magnetic, electrical or specific optic or light exposure behavior or to create biocompatibility or (bio)fouling or even their combined effect. In order to achieve and improve these properties in metals and alloys, we have to apply the strategy of surface modification based on a direct action on the metal or incorporating a coating that will provide these properties or functionalize its surface for complex requirements.

In general, the topics of interest range from newer approaches of conventional coatings technologies and thermomechanical processes, biocoatings, and surface modification for energy applications, catalysis, and nanomaterials to functionalization of metallic powder and additive manufactured metallic surfaces. All these improvements will be focused on developing successful engineering products and parts; some new strategies will also contribute to solving environmental issues.

This special issue provides recent trends in nanostructuring and functionalization of solid materials such as metals and alloys with the goal of improving their functional properties. Many different and innovative approaches that can be used to transform the metallic surface by means of physical, chemical, mechanical or biological characteristics providing different properties from the ones originally found on these surfaces allowing functionality for a given application and also for improving their properties.

Garfias Bulnes, Albaladejo Fuentes, Garcia Cano and Dosta [1] showed an analysis of the differences found in hard metal coatings produced by two high velocity thermal spray techniques, namely high velocity oxy-fuel (HVOF) and high velocity air-fuel (HVOF). Additionally, the effect of the metallic matrix and ceramic composition and the original carbide grain size on coating properties is compared to the most studied standard reference material sprayed by HVOF, WC-Co. For this evaluation, the physical properties of the coatings, including feedstock characteristics, porosity, thickness, roughness, hardness, and phase composition were investigated. Several characterization methods were used for this purpose: optical microscopy (OM), scanning electronic microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), and X-ray Diffraction (XRD), among others. The final performance (abrasive wear and corrosion resistance) shown by the coatings obtained



**Citation:** Rius-Ayra, O.; Llorca-Isern, N. Special Issue “Surface Modification of Metals and Alloys”. *Coatings* **2021**, *11*, 260. <https://doi.org/10.3390/coatings11020260>

Received: 17 February 2021

Accepted: 22 February 2021

Published: 23 February 2021

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by these two methodologies was also analyzed. Thus, the abrasive wear resistance was analyzed by the rubber-wheel test, while the corrosion resistance was characterized with electrochemical methods. The characterization results obtained clearly showed that the coatings exhibit different microstructures according to feedstock powder characteristics (carbide grain size and/or composition) and the thermal spray process used for its deposition. Thus, the incorporation of WB to the cermet composition led to a high hardness coating, and the complementary hardness and toughness of the WC-Co coatings justify its better abrasion resistance. The presence of Ni on the metal matrix increases the free corrosion potential of the coating to nobler region.

Sendino, Gardon, Lartategui, Martínez and Lamikiz [2] showed the manufacture of multiple parts in the Laser Powder Bed Fusion (L-PBF) process. The main advantage is that the entire working volume of the machine is used and a greater number of parts is obtained, thus reducing inert gas volume, raw powder consumption, and manufacturing time. However, one of the main disadvantages of this method is the possible differences in quality and surface finish of the different parts manufactured on the same platform depending on their orientation and location, even if they are manufactured with the same process parameters and raw powder material. Throughout this study, these surface quality differences were studied, focusing on the variation of the surface roughness with the angle of incidence of the laser with respect to the platform. First, a characterization test was carried out to understand the behavior of the laser in the different areas of the platform. Then, the surface roughness, microstructure, and minimum thickness of vertical walls were analyzed in the different areas of the platform. These results were related to the angle of incidence of the laser. As it was observed, the laser is completely perpendicular only in the center of the platform, whilst at the border of the platform, due to the incidence angle; it melts an elliptical area, which affects the roughness and thickness of the manufactured part. The roughness increases from values of  $S_a = 5.489 \mu\text{m}$  in the central part of the platform to  $27.473 \mu\text{m}$  at the outer borders while the thickness of the manufactured thin walls increases around  $40 \mu\text{m}$ .

Pezzato, Settimi, Cerchier, Gennari, Dabalà and Brunelli [3] reported a Plasma Electrolytic Oxidation (PEO) as a surface treatment and produced a thick oxide films on the surface of metals. In their work, PEO coatings were obtained on zinc-aluminized (ZA) carbon steel using a solution containing sodium silicate and potassium hydroxide as electrolyte, and working with high current densities and short treatment times in Direct Current (DC) mode. The thickness of the coating, as well as the surface morphology, were strongly influenced by the process parameters, with different dissolution grades of the ZA layer depending on the current density and treatment time. A compromise between thickness and porosity of the coating was found with low current density/long treatment time or high current density/short treatment time. The PEO layer was mainly composed of aluminum oxides and silicon compounds. The corrosion resistance increased remarkably in the samples with the PEO coating. These PEO coated samples are suitable for sealing treatments that further increase their corrosion properties. They will be also an ideal substrate for commercial painting, assuring improved mechanical adhesion and protection even in the presence of damages

Li, Cui, Zhu, Narasimalu and Dong [4] presented a fluoropolyurethane-encapsulated process that was designed to rapidly fabricate low-flow resistance surfaces on the zinc substrate. For the further enhancement of the drag-reduction effect,  $\text{Cu}^{2+}$ -assisted chemical etching was introduced during the fabrication process. The resulting surface morphology, wettability and flow-resistance properties in a microchannel were also studied. Zinc substrate with a micro-nanoscale roughness obtained by  $\text{Cu}^{2+}$ -assisted nitric acid etching showed superhydrophilic characteristics. However, after the etched zinc substrate was encapsulated with fluoropolyurethane, the superhydrophobic wettability can be obtained with a contact angle of  $154.8^\circ \pm 2.5^\circ$  and a rolling angle of less than  $10^\circ$ . As this newly fabricated surface was placed into a non-standard design microchannel, it was found that with the increase of Reynolds number, the drag-reduction rate of the superhydrophobic

surface remained almost unchanged at 4.0% compared with the original zinc substrate. Furthermore, the prepared superhydrophobic surfaces exhibited outstanding reliability in most liquids.

Rius-Ayra, Fiestas-Paradela and Llorca-Isern [5] reported a straightforward method for water-harvesting based on modifications of the surface wettability by using the electrodeposition process of magnesium chloride, lauric acid revealing a superhydrophobic surface ( $155^\circ$ ). Morphological characterization techniques showed the characteristic flower-like microstructures combined with close packed nanoarrays that were vertically aligned in a non-linear cone morphology formed by dynamic templating of hydrogen bubbles. From a chemical point of view, magnesium laurate is responsible for the surface tension decrease. To determine the durability an abrasive paper test was carried out revealing high durability against this severe condition. The water-harvesting ability of the superhydrophobic surface was studied at  $45^\circ$  and  $90^\circ$  tilted samples. The capacity of the water to be efficiently harvested was found to be at  $90^\circ$  tilt under fog conditions. The use of green reactants associated with this hierarchical structure broadens a new scope for sustainable freshwater collection and it becomes an excellent example of a green solution.

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