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Innovative anodizing treatments to improve corrosion resistance of titanium

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Anodizing on titanium is a very versatile and economic surface treatment able to passivate the metal through the formation of an adherent oxide layer. Initially, only DC anodizing was used, thus making the final voltage and treatment time the control parameters, ruling color, structure and thickness of the oxide.

More recently, the effect of applying a pulsed current was proposed and exploited. When a unipolar signal was selected (anodic polarization only) the "recovery effect" established during the off-period allowed to avoid oxide burning, caused by overheating, and to reduce the porosity, favoring gas evacuation. In this direction, several duty cycles (intended as $(t_{on}-t_{off})/t_{on}$, where t_{on} is the duration of the anodic phase in a cycle, and t_{off} is the rest time) were proposed with the aim of optimizing the kinetics of growth and recovery, demonstrating generally an enhanced oxide thickness for percentage of anodic phase (t_{on}) larger than the rest period (t_{off}). In addition, frequency covers a fundamental role in oxide growth kinetics. Generally, it is a good practice to work with a frequency far from the relaxation constant of the electrical double layer (EDL) established at the metal-oxide interface, thus avoiding current damping with subsequent loss of efficiency.

A relatively recent modification of standard pulsed anodizing consists in the overcoming of a voltage threshold, universally recognized as the spark voltage, entering the so-called plasma electrolytic oxidation (PEO) technology. This made possible to exploit several advantages resulting from plasma-chemical reactions like enhanced growth rate and stabilization of rutile.

To decrease the detrimental effect of strong discharges, a bipolar duty cycle has been proposed, where an anodic pulse is followed by a cathodic polarization. This effect, generally called "soft spark regime", resides in the ability of the cathodic current to modify the local environment at the oxide interface, promoting the smoothing of a potential barrier at the EDL level responsible of the occurrence of anodic breakdown. This is generally verified for cathodic to anodic charge ratio greater than 1, thus the requirement of using a duty cycle able to promote the transfer of a higher amount of cathodic current with respect to the anodic one. Based on that the use of bipolar duty cycles can be considered as the ultimate frontier to improve thickness, uniformity and compactness, all properties allowing reaching a level of surface functionalization to improve corrosion resistance in harsh environments.

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