Electrochemical coating based on tin-nickel alloy with antibacterial properties

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Hygiene/antimicrobial issues in public places eg. hospitals, schools, hotels, public transportation etc. are of a crucial importance as its ignorance could lead to spread of viral diseases or epidemics and consequently to deaths. A typical example of that are hospital acquired infections (HAI). According to The European Centre for Disease Prevention and Control (ECDC) in the EU, about 3 million people are infected annually with HAI and about 25,000 patients die from HAI-related reasons. Such infections also arise extra healthcare costs and result in annual productivity losses of at least €1.5 billion. It is estimated that 15% of these infections are due to the transmission through inanimate objects. Although sanitization and disinfection of surfaces using chemical liquids such as chloride or alcohol-based detergents is a common practice to prevent transmission of diseases, frequently such procedures are skipped, skimped or in the case of public transportation not practically feasible.

Since 1985, when Matsunaga et al. [1] reported about photochemical sterilization of Saccharomyces cerevisiae (yeast), Lactobacillus acidophilus and Escherichia coli (bacteria), and Chlorella vulgaris in water using Pt-TiO_2 photocatalyst under metal halide lamp irradiation, much research has been performed on the photocatalytic antimicrobial effect of TiO_2 [2].

A lot of studies [6-12] have demonstrated that TiO_2-mediated photooxidation shows much promise for the elimination of microorganisms in many applications especially in the areas where the use of chemical cleaning agents or biocides has proven to be ineffective or is restricted by regulations, e.g., in the pharmaceutical or food industry. The photobiocide properties of TiO_2 also open the possibility of developing highly effective self-cleaning and selfsterilizing materials.

In this work, bactericidal activities of samples Sn-Ni films modified TiO_2, are investigated in killing of both gram-positive and gram-negative bacteria with the special reference on the role of the photoproduced reactive oxygen species of different types in the cell inactivation.

1. Experimental

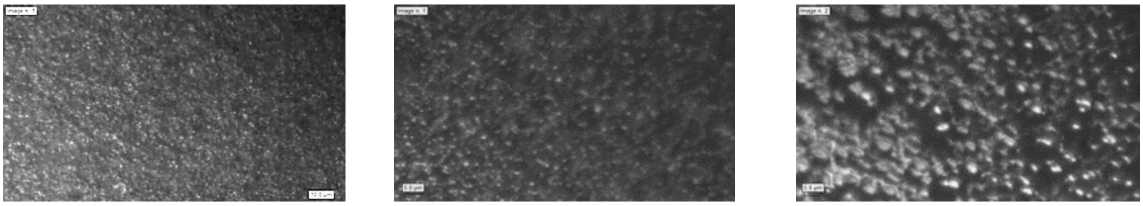
The most suitable matrix for antibacterial composite electrochemical coatings is a tin-nickel alloy containing 65% of tin and 35% of nickel. This coating has enhanced decorative properties, microhardness, corrosion- and wear resistance. Electrolytes for the electrodeposition of the tin-nickel alloy are aqueous solutions of nickel and tin salts. The concentration of tin salt determines the range of permissible cathode current densities [3].

Such composite coatings consist of Sn-Ni matrix and are doped with TiO_2 nanoparticles as a reinforcing mean. Doped-TiO_2 nanoparticles, having the ability to absorb visible light, can be activated indoors and thus present enhanced photocatalytic activity. The incorporation of such doped-TiO_2 nanoparticles in the Sn-Ni matrix will provide its self-cleaning and antibacterial properties. The percentage of the incorporated nanoparticles is of crucial importance. In order to increase the co-deposition rate and consequently the photocatalytic activity, pulse current plating could be utilized. By this method, higher co-deposition rate of nanoparticles can be achieved compared to the conventional direct current plating. These kind of coating is able to be operated under indoor light irradiation and can be applied to common touched objects (knobs, taps, handles) reducing the risk of infection's transmission by 50-100%.

Nanodisperse titanium dioxide, obtained by sol-gel technology, has the ability to absorb visible light and has increased photocatalytic properties [5]. The technology provides a stable particle size of the hydrosol in the range of 10-20 nm. As a peptizing acid, it is possible to use strong mono-basic inorganic acids: nitric and hydrochloric acids. The content of the solid phase can vary for the hydrosol from 1.5 to 6% by weight (in terms of TiO_2), for xerogels derived from this hydrosol - up to 70% by weight, while xerogels retain the ability to peptize in aqueous solutions without addition additional components. Titanium dioxide, which is part of the xerogel, contains up to 70-75% of the crystalline phase. These properties can be used to create antibacterial metal coatings. Nanoparticles of the sol TiO_2 are introduced in the tin-nickel alloy electrolyte.

2. Results and discussion

In the course of this research work, the composition and characteristics of the process were optimized. The optimal range of current densities for alloy electrodeposition was defined using the Hull cell (Fig. 1). It is recommended to use low current values (0.5 A/dm^2) to obtain a Sn-Ni-TiO_2 composite coating.



a) 1 A/dm^2 b) 0,8 A/dm^2 c) 0,5 A/dm2

Fig. 1. Microphotographs of the surface of metal coatings obtained at different current densities

At high current densities dark, opaque coatings are deposited, current density of 0,8 A/dm^2 allows to form – semimatous alloys and, at low current densities coatings are shiny.

Figure 2 shows potentiostatic anodic polarization curve of the tin-nickel alloy with titanium dioxide deposition onto copper.

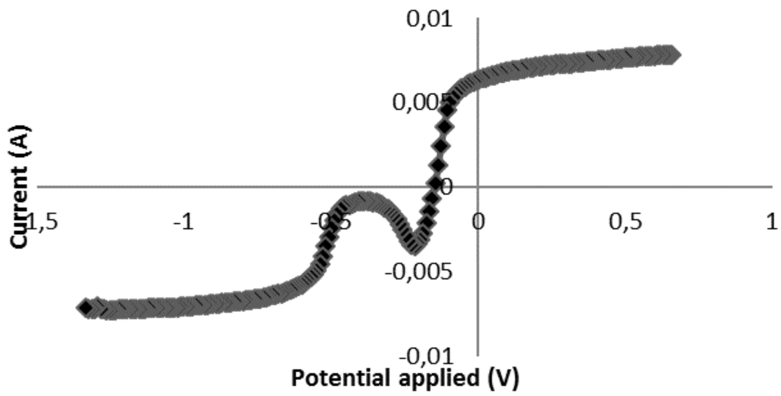


Fig. 2. Potentiostatic anodic polarization curve of the tin-nickel alloy with titanium dioxide deposition process

From the anodic polarization curve it is seen that at a potential values from -0.60 to -0.20 V a peak appears. This peak is characteristic for the process of electrodeposition of titanium dioxide. Therefore, during the electrochemical deposition of the composite coating, a co-precipitation of Sn-Ni-TiO_2. The chemical modification (doping) of TiO_2 nanoparticles aims to achieve lower band gap and thus become capable of operating in indoor light.

Development of pulse plating process in order to achieve high incorporation rate and uniform distribution of reinforcing nanoparticles on the surface of metal/alloy matrix leads to an effective immobilization of photocalalytic particles. Optimization of the pulse plating process in order to be sustainable in terms of saving energy, time and raw materials.

The antimicrobial activity of the samples was determined using gram-negative bacterium Escherichia coli and grampositive bacterium Staphylococcus aureus as the testcultures. The overnight cultures in the nutrient broth were diluted with sterile physiological solution (0.15 M NaCl), then 100ml of bacteria suspension was placed on the samples; the control samples have no photocatalyst coating. All samples were exposed to UV light for 60 min (Fig. 3).

Fig. 3. Samples after the antibacterial test: 1 - control sample (Sn-Ni), 2 – Sn-Ni-0,5g/l TiO_2, 3 – Sn-Ni-1g/l TiO_2, 4 – Sn-Ni-2g/l TiO_2

From the results in control sample (Fig. 3, 1) and in sample with Sn-Ni-1g/l TiO_2 (Fig. 3, 3) electrochemical coating, when UV light was not applied, no inactivation of microorganisms was observed. It is means that the bacteria on the surface of the samples could be distributed unevenly, and the recommended concentration of titanium dioxide synthesized from the sol is 1 g/l in the composition of the coating. Samples 2 and 4 (Fig. 3) also have antibacterial properties, but they are less active (50%).

3. Discussion and Conclusion

The result of the work is the development of a sol-gel mass production method of doped-TiO2 nanoparticles, realization of robust process parameters, enhancement of functional properties of obtained coating exhibiting high adhesion with the substrate, testing the antibacterial character of the coating under different relevant light conditions. Such coatings will be able to work with room lighting and can be applied to general facilities (pens, cranes, handrails and etc.), which will reduce the risk of transmission of infection in 50-100%.

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