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Improved multilayer coatings by combined use of electrochemical and ultra-short pulsed laser deposition techniques

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ABSTRACT

Electrochemical and ultra-short pulsed laser deposition (USPLD) methods were combined to produce multilayer coatings on various base materials that are challenging to be coated by using traditional electrochemical techniques. A thin and well-adherent metallic intermediate layer was coated on each base material by USPLD method before final nickel or nickel-trivalent chrome coating by electrochemical methods. In this way, the pretreatment steps for electrochemical deposition were simplified compared with traditional methods and hazardous chemicals were not used during the pretreatment process. The morphology, coating thickness and the elemental composition of the multilayer coatings were analyzed using scanning electron microscope (SEM) coupled with Energy Dispersive X-ray spectroscopy (EDS), and the adhesion strengths of each coating were tested by scratch and pull-off tests. The results show good adherence for all studied coatings on aluminum alloy (6082) and stainless acid-proof steel (SS316L), whereas obtaining a sufficient adhesion of coatings on glass (borosilicate) and polycarbonate (PC) requires a correct choice of coating materials and process steps. The critical loads in scratch test are approximately 20 N for coatings on aluminum and glass, at least 50 N for coatings on SS316L and approximately 5 N for coatings on PC. In pull-off tests, maximum adhesion strengths for coatings on aluminum and SS316L are approximately 25 MPa for electroless coatings and 10 MPa for electroplated coatings. Coatings on glass and PC reach adhesion strengths of approximately 4–9 MPa, which is sufficient for many applications.

1. Introduction

Electrochemical deposition is a well-established coating method and applied widely in different fields of industry. Each constitutive electrochemical deposition technique, electroplating and electroless plating, has its own advantages and parallel use of these methods provides a broad selection of feasible coating–substrate material combinations for various applications. However, direct electrochemical deposition on certain base materials is rather complicated and requires the use of hazardous chemicals. Thus, it is important to study alternative techniques, which could bring improvements to conventional coating processes.

The process of electroplating is driven by electric current and can be applied virtually for any electroconductive material, such as metals. However, direct electroplating of two very commonly used metals, aluminum and stainless steel, is complicated by passivating oxide layer, which must be removed before plating. On the other hand, electroless plating is based solely on chemical reactions and is feasible also for non-conductive base materials, such as glass and plastics. However, the overall range of usable materials for electroless plating processes is quite narrow. Moreover, electroless plating is a rather slow process and typically requires high temperatures and extensive use of highly toxic chemicals. Some essential alternative coating processes for above-mentioned base materials found in the research literature from the past two decades are listed in Table 1, whereas the following paragraphs briefly review the traditional methods for plating on these base materials.

Aluminum and its alloys are widely used in industry due to their beneficial properties, such as low density, high strength-to-weight ratio and high electrical and thermal conductivity [1]. However, coating of aluminum is difficult due to its high affinity for oxygen, which leads in formation of a persistent oxide layer destroying the adherence of the coating [2–3]. The most common industrial plating processes on aluminum start with zincation or stannation, which are immersion coating methods based on an exchange reaction between aluminum and zinc or tin, respectively [2–3]. Several studies show that double zincation, i.e. repeating zincation two times, provides the best adhesion, whereas further repetition leads to poorer results [4–7].

The high corrosion resistance of stainless steels is based on thick oxide layer and the removal of this layer is a key factor in plating of stainless steels [2–3]. The traditional steps of pretreatment processes for stainless steels include thorough cleaning, pickling with strong acids and, as the most important step, activation [2]. Activation must be done just before the actual plating and low pH nickel strike baths

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Table 1
Alternatives found in the literature for traditional coating methods used for plating the base materials studied in this article.

Base material	Alternative method	References
Aluminum	Nickel strike preplating	[20–22]
	Hypophosphite intermediate layer	[20–21]
	Porous anodic aluminum oxide intermediate layer	[23–24]
Stainless (acid-proof) steel	(Reviewed in Refs. [8–10])	
Glass	Silane/aminosilane intermediate layer	[11,25–29]
	Carbon/carbon nitride intermediate layer	[11,30]
	Polymer intermediate layer	[31–32]
	Zinc oxide intermediate layer and activation by UV illumination	[33]
	Spin-deposition of a palladium organometallic precursor layer and activation by laser	[34]
Plastic	Environmentally friendly etching processes	[14,35–36]
	Polymer intermediate layer	[37–39]
	Grafting nitrogenated groups by plasma to prepare the surface for the chemisorption of palladium	[15–16]
	Decomposing organometallic precursors by plasma/laser/UV irradiation	[18–19,40]

are often used for this purpose. Much of the research into plating on stainless steels deals with the development of proton exchange membrane fuel cells (PEMFC), because stainless steels are a promising material of the bipolar plate of PEMFCs (see Refs. [8–10] for a review).

Glass is a challenging material to be metal coated, not only due to its non-conductivity but also due to the smoothness of glass surface and the large difference between the mechanical and physical properties of glass and metals [11]. An especially problematic issue is the difference in coefficients of thermal expansion between glass and metals, which may result in interfacial tension gradient and detachment of the coating from the substrate if the temperature variation is large during the coating process or in service conditions. The traditional process for coating on glass consists of many steps, such as cleaning, roughening, sensitization and activation [3]. The purpose of sensitization and activation is to produce a thin conductive layer capable of catalyzing the subsequent metallization on the glass surface and these steps can be done either simultaneously or separately. Traditionally, stannous chloride is used as a sensitizing agent and palladium chloride as an activating agent.

Plating on plastics has many applications in industry since coupling the beneficial properties of plastic, such as lightness, toughness and ease of processing, with the advantageous properties of metallic materials, such as electrical conductivity, heat resistance, corrosion resistance and reflectivity as well as decorative appearance, has benefits in both functional and decorative application areas [3,12–13]. Plating processes of plastics share the same challenges as glass plating processes, although in lighter form, and the processes consist of almost identical steps [3,12–13]. Surface roughening of plastics is an important step and is most often done by wet chemical etching by using highly toxic chromic acid as the etchant. The most common plastic to be plated is acrylonitrile butadiene styrene (ABS), due to its advantageous mechanical properties and the efficiency of its etching process by chromic acid [12–13]. Thus, previous research has focused mainly on plating on ABS, but other common plastics, such as polypropylene (PP), polycarbonate (PC) and polybutyleneterephthalate (PBT), have been the target of several studies, too [14–19].

Ultra-short pulsed laser deposition (USPLD) is an emerging coating technique in which a high intensity pulsed laser beam vaporizes the target material in a plasma plume and the released molecules travel through vacuum at high speed to the substrate, where they form strong bonds with the substrate material. Unlike in the case with longer pulse durations, short pulsed lasers are more sensitive to adaption of materials. For ultra-short pulses, only a minor volume of material is heated and melted. The laser energy is deposited in outermost thin layer, which has beneficial effects since the film-thickness deposited with a single pulse is limited by the skin penetration depth. The ablation process becomes more precise with enhanced accuracy and reduction on macroparticles or droplets in comparison with longer laser pulses [41].

Due to the pulsed nature of the process, the energy is consumed almost completely in bond formation and the temperature rise inside the target or sample is negligible. Due to the high kinetic energy of atoms or ions, the adherence of the coating layer is excellent and the range of feasible materials covers virtually all solid materials. However, the method is constrained by relatively high cost of the equipment and limited penetration of material to areas which are not within the line of sight of the target [42].

In addition to metals, oxides and other compound, USPLD method can be utilized for amorphous diamond, AD films (also known as high quality hydrogen free DLC or tetrahedral amorphous carbon, ta-C). The structure of the film is known to be amorphous with high fraction of sp^3 type bonding [43]. Carbon existing in an amorphous state does not possess any long-range order. Micro- or nanocrystalline graphite domains may be observed in the amorphous matrix. This metastable material contains a mixture of sp^3- and sp^2-hybridized carbon atoms. These materials possess properties intermediate between those of graphite and diamond [42]. Detailed name variants and properties have been discussed previously in Refs. [43] and [44].

The hypothesis of this study is that combining USPLD and electrochemical methods is a feasible way to produce multilayer coatings with adequate adherence and performance on various base materials by the reduced use of chemicals. In this paper, the combination of the aforementioned coating methods is presented for producing well-adherent nickel and trivalent chrome coatings on base materials that are difficult to coat by traditional methods. The base materials chosen for the experiments were aluminum alloy (6082), stainless acid-proof steel (SS316L), glass (borosilicate) and polycarbonate plastic. First, USPLD method was used to produce a thin nickel adhesion layer on each substrate and, then, the coating process was continued by electrochemical nickel and chrome plating. Finally, the morphologies, coating thicknesses, elemental compositions and adhesion strengths of the coatings were determined.

2. Experimental

2.1. Sample preparation

Microscope slides (Thermo Scientific, Menzel, Braunschweig, Germany) of size 76 × 26 × 0.8 mm were used as glass samples and the lateral dimensions of all other samples were chosen to be the same size (Fig. 1). Aluminum samples were cut from a 10 mm thick aluminum plate (alloy 6082, supplied by Skandinavian Yhtyneet Metallintuojat, Helsinki, Finland) and ground and polished manually with different

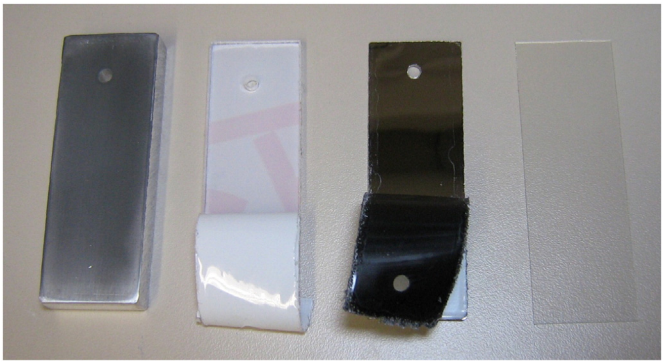

Fig. 1. Samples prepared from each substrate material under study. From left to right: aluminum, polycarbonate, stainless acid-proof steel and glass. Polycarbonate and stainless steel sheets had a protective plastic film which was removed after sample cutting.