High Performance Colorful PVD Coatings

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ABSTRACT

Colorful Nb based PVD coatings have been developed to serve decorative applications. Metallic Nb coatings have been deposited by the combined steered cathodic arc/unbalanced magnetron sputtering technique, and subsequently anodized in weak aqueous acidic solutions to form a wide pallet of colorful, hard oxides (HV 1500) by utilizing the optical interference effect. Tribological wear tests on anodized niobium surfaces carried out by oscillating an alumina containing abrasive pad under a 5N load have shown an estimated 10 times more abrasion resistance compared to powder decorative coatings used on stainless steel yachting knife handles. No change in color of the anodized coatings was observed after testing for 120 hours under UV radiation and 125 cycles in an industrial dishwasher using proprietary detergents and rinse aids. The potendynamic corrosion tests in 0.8M NaCl solution (pH 7) have shown that the anodized niobium coatings, when deposited on 316 stainless steel reduced the corrosion current density to the range of 10^{-8} to 10^{-9} A/cm^2 and increased the pitting potential to up to 1200 mV. Immersion tests according to DIN EN 1811 in artificial sweat have shown no discoloration and no dissolution of Nb from the anodized coatings, as well as elements from the substrate material, which proves the biocompatibility of these noble and colorful surfaces.

INTRODUCTION

There is an increasing demand for decorative quality in the coating industry incorporating anti-wear properties together with biocompatibility, alimentary, and chemical inertia. Typical examples include watch cases and bracelets, cutlery, jewelry and spectacle frames. The more traditional “wet” technologies such as painting, lacquering, powder coating, spraying, electrophoretic coatings, and electroplating, are being replaced by the more environmentally friendly PVD processes. PVD coatings such as TiN, TiCN, ZrN, TiZrN, CrN and TiAlN are routinely used as decorative finishes combining both aesthetic appearance and high wear resistance [1,2,3]. Among them the golden colored TiN is probably the oldest PVD deco-coating on the market, introduced in the mid 1980s in Europe, the Far East and USA. Combined with a flash of gold alloy top-coat, it has come out as a high quality replacement technology of electroplated gold [4]. Additionally, TiN benefits from its high chemical stability and is being accepted as a biocompatible material. However, most of the above mentioned coatings provide a very limited color range of yellow, red, and brown colors matching predominantly gold, brass, and chrome surfaces. TiAlN and C-based coatings expand this range by achieving black hued colors. Entering new market segments and addressing new applications, however, requires development of new coatings providing a much wider palette of colors, including blue, purple and green tones. This wider range, including all the rainbow colors, can be achieved by utilization of interference high refractive index Me-oxide layers such as Ta_2O_5 or Nb_2O_5 . These oxide layers can be grown either by anodic oxidation in acidic aqueous solutions [5], by heat treatment under the presence of oxygen, reactive deposition techniques [6], or anodic post-treatment of UBM deposited Ta or Nb metallic films in an oxygen ion containing plasma [7].

Spectacle frames manufactured in light weight titanium, where the aesthetic appearance is of utmost importance, present a typical example for a new market niche. Direct electroplating is not applicable and lacquering reduces the high tech claim inherent to the base material titanium. PVD technology has proven to be an adequate approach to ennoble their surfaces. The paper reports on the quality and the performance of Nb based decorative coatings deposited on Ti and SS substrates. The coatings have been deposited by the combined steered cathodic arc/unbalanced magnetron sputtering technique [8] and subsequently anodized in weak aqueous acidic solutions to form a colorful, hard oxide (HV 1500) by utilizing the optical interference effect.

COATING DEPOSITION TECHNIQUE

Nb, Ti, TiAl and TiAlV coatings have been deposited on various substrate materials such as Ti (b-Ti) alloy, SS316 and Al utilizing the combined steered cathodic arc/unbalanced magnetron sputtering technique, known also as ABS (Arc Bond Sputtering) [8]. Prior to the introduction of this coating, all substrates except Al were cleaned in an automated cleaning line comprised of a series of ultrasonically agitated aqueous alkali solutions, deionized water baths, and a vacuum drier. The Al substrates were cleaned in alcohol using ultrasonic agitation. An industrial HAUZER HTC 1000-4 system, with

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chamber volume of 1m^3, was used for coating deposition. Figure 1 schematically outlines the cross-section of the system with a typical target arrangement used for deposition of Nb coatings.

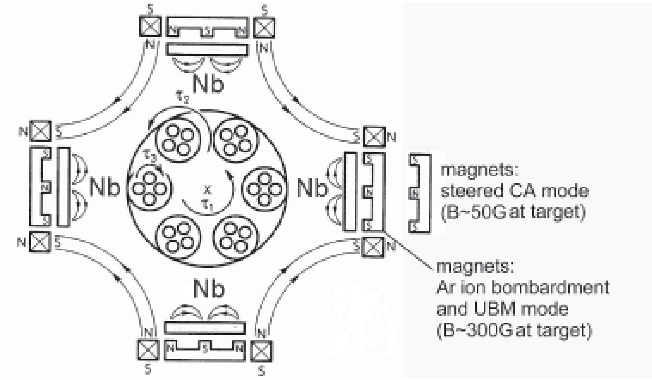


Figure 1: Schematic diagram of HTC 1000 ABS coater.

The HTC 1000-4 system comprises four dual-purpose cathodes, which can be operated either in steered arc or unbalanced magnetron sputtering mode. The key advantage of the ABS approach is the utilization of a metal ion pretreatment (metal ion etching) of the substrate material prior to the coating deposition step, which results in excellent coating adhesion [9,10]. In the surface pretreatment step, metal ions generated from an arc discharge sustained on one of the targets are accelerated towards the substrate due to the applied high bias voltage (Ub=-1200V), producing surface etching and implantation. The utilization of arc discharge, however, leads to contamination of the interface with macroparticles (droplets), which produce growth defects in the sequentially deposited coating by unbalanced magnetron sputtering [11]. These defects, if not considered, can deteriorate the uniformity of the colored anodization surface by formation of speckles and local discoloration. The number density of the defects depends on the melting point of the arc-evaporated material, therefore Nb etched surfaces are less contaminated compared to Ti and TiAl pre-treated ones [12]. To achieve high surface quality, the duration of the metal ion etching step was shortened to 4-5 min. only, which resulted in excellent uniformity of the surface colors. The subsequent coating, typically 1μm thick, was deposited by non-reactive unbalanced magnetron sputtering. The availability of four targets allows high productivity as all cathodes can be furnished with targets made of the same material giving high coating thickness uniformity. The coated spectacle frames, yachting knife handles, and tabletop matching cutlery sets were mounted on specially designed holders on the turntable in the center of the chamber, allowing for two and three-fold rotation, which further improves the coating uniformity on 3D parts. For the deposition of Nb and Ti, target materials with 99.9% purity were used. Ti-Al coatings have been deposited by sputtering of 50:50% alloy targets. TiAlV coatings have been produced by sputtering of 90:6:4 % alloy target. These coatings have been investigated as a more cost effective alternative of Nb. The coating deposition temperature has been maintained in the range of 250-300°C, which prevented softening of the cold drawn Ti alloy material used in some of the applications.

ANODIZATION PROCEDURE

Morphology of the Oxide Films

Anodizing is an established process in which a thin oxide film is formed on the surface of the anode in a galvanic cell as a result of electro chemical reactions (oxygen release on the anode). In this study, the anodization was carried out in a weak (1%) aqueous electrolyte of citric acid. A particular oxide film thickness may generate a bright distinctive interference color if the oxide is of high refractive index. These requirements are met best by the group of the “valve metals”, which includes Ta, Nb, Ti, Al, Zr, Hf and their alloys. The term “valve metal” refers to material, which will anodize only to a specific thickness, and depends on the magnitude of the voltage applied to the material and the material itself. Once the layer is anodized to that specific thickness, more current can pass through the material only by increasing the applied voltage (provided that the other anodization conditions, such as temperature and composition of the electrolyte are maintained). The following expression describes the relation between the thicknesses of the oxide layer, $D_{Ox.}$ (the color) and the applied voltage, U_A:

$$D_{Ox} = \alpha\, U_A \text{ (α is the voltage rate of the oxide growth,} \\ \alpha \sim 10 \text{ Å/V for niobium oxide).}$$

The color formation during the anodization step also strongly depends on the coating material. Figure 2 shows the voltage increase as a function of the duration of the anodization at constant current density of 5 mA cm^{-2} for the various coatings used in this study. This effect was investigated for a wide range (1- 5 mA cm^{-2}) of current densities. It can be seen that colors with high reproducibility can be achieved with Nb, TiAl and TiAlV. These three coatings reach the pre-selected maximum voltage of 100V, which indicates that all color variations within this voltage range are available. In contrast, Ti coatings show only a limited capacity for color formation by anodic oxidation in the current density range used in this experiment.

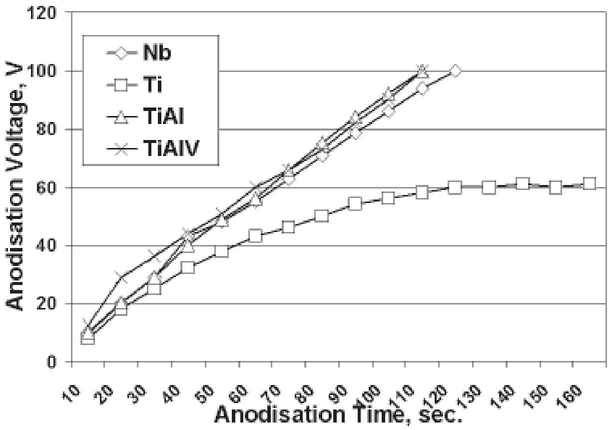
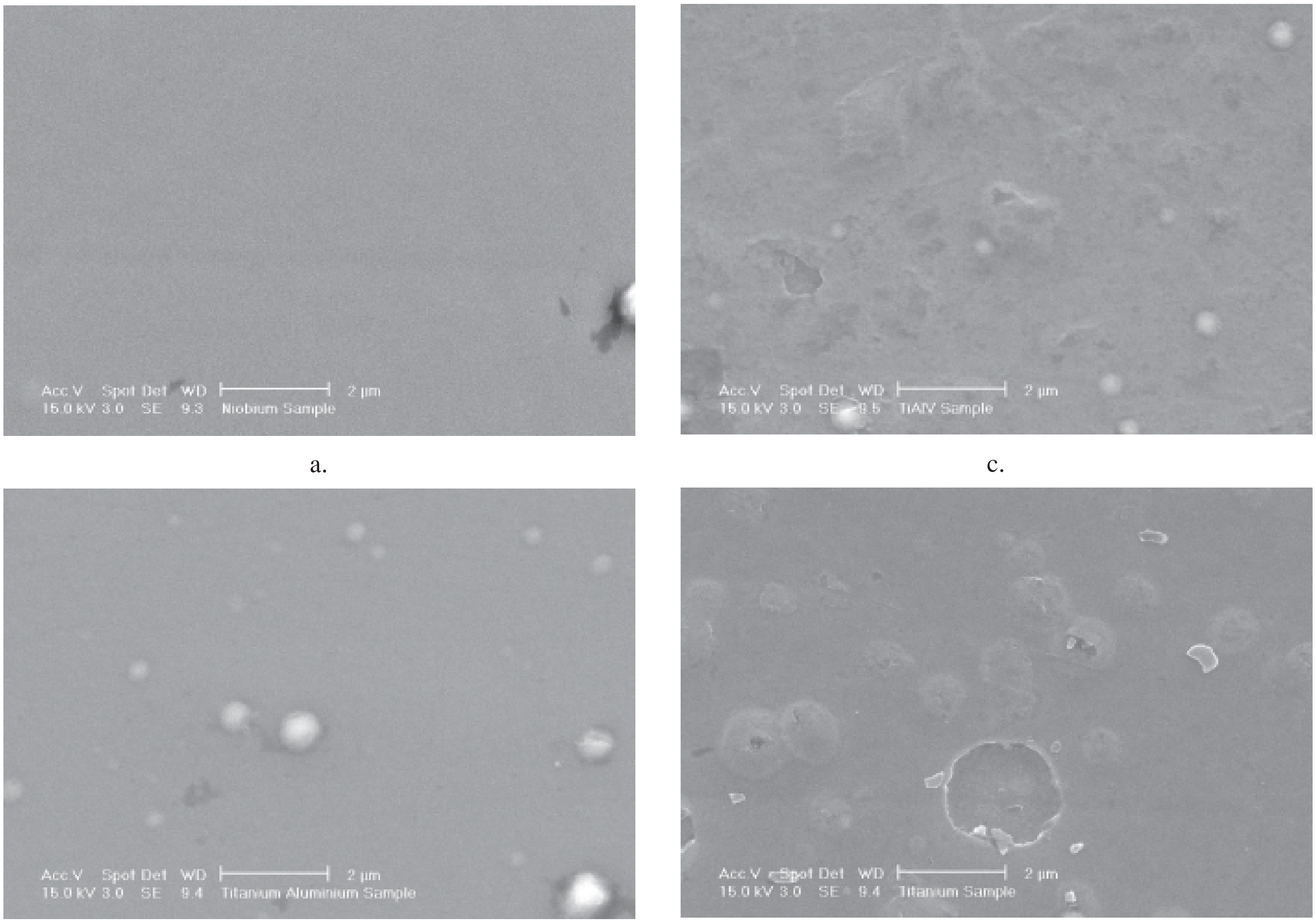


Figure 2: Voltage increase as a function of time for various PVD coatings anodized at constant current density of 5 mA cm^{-2}.

This behavior of the Ti is typical for materials, which tend to form porous oxide layers, when grown by anodic oxidation. The surface morphology of the oxide films grown on the different coatings was observed by SEM, using a Philips XL 40 analytical instrument. Nb, Ti, TiAl and TiAlV PVD coatings were deposited on mirror polished 316 stainless steel, substrates and anodized to achieve an oxide layer thickness of 500 Å, which corresponds to the antique gold color. The SEM micrographs of the anodized surfaces are shown in Figure 3. Two types of surface defects can be seen. The brighter, more globular shape defects are typical of the ABS technology growth defects, originating from droplets deposited on the substrate during the ion etching step. The number density of these defects (as mentioned above) is related to the melting point of the target material used for etching. Therefore, the surface of the Nb coating, where the surface was pretreated by Nb^{+} ions is almost defect free compared to the surfaces pretreated with lower melting point materials such as TiAl, TiAlV and Ti. Complete avoidance of the growth defects is possible if the metal ions are generated by filtered arc or by the novel High Power Impulse Magnetron Sputtering techniques [13].

The second type of the surface defects represent the morphology of the oxide films grown during the anodization process. Clearly, Nb forms a dense oxide layer, which provides a very smooth surface (Figure 3 a). In contrast, the Ti based alloys



a.

c.

b.

d.

Figure 3: SEM micrographs of the surface of anodized PVD coatings: a) Nb, b) TiAl, c) TiAlV and d) Ti.

and pure Ti coatings form rough surfaces due to the formation of the porous oxide films. In the case of the Ti coatings, the TiO_2 oxide easily spalls off, opening free access for the electrolyte to react with the substrate and terminate the voltage increase (color development) during the anodization treatment. Although both TiAl and TiAlV alloys similar to Nb allow generation of a wide palette of colors, when anodized in the voltage range up to 100V (Figure 2), the porosity of the oxide films has implications on the protective properties (both against corrosion and wear) of these layers. Ta and Nb obviously are the preferred metals for anodization. Both materials are capable of generating a wide range of deep interference colors due to the high density and more favorable optical properties such as high refractive index of the oxide films. On the practical side, Nb has an advantage for being more cost effective, due to having almost a factor of two lower material density compared to Ta. Table 1 demonstrates the availability of a large variety of interference colors produced by PVD Nb coatings anodized in the voltage range from 10-100V. The color coordinates have been determined using the MINOLTA COLORIMETRIC TECHNOLOGY for the CIE -L*, a* and b* color space.

Table 1: Color coordinates of anodized Nb coatings.

Voltage, V	L*	a*	b*	Color
10	65	0	+36	Champaign
20	70	+32	-46	Dark Blue
30	75	-9	-22	Light Blue
40	87	-5	+3	Colorless
50	71	-10	+45	Antique Gold
60	63	+6	+59	Pink
70	70	+67	-58	Purple
80	70	-33	-16	Turquoise
90	78	-36	+40	Green
100	75	-17	+58	Light Green

RESISTANCE OF THE ANODIZED FILMS AGAINST WEAR, CORROSION AND BIOLOGICAL ATTACK

In view of the fact that the actual color generated by the constructive interference effect relates to the thickness of the anodic oxide film, any thickness variations due to wear potentially could lead to color variations. One solution to this problem was seen in deposition of a wear resistant transparent top layer of Si_xAl_y-oxide for mechanical protection of the anodic oxide [7]. However, the proposed approach involves additional technological steps and is therefore regarded as high cost. In this study, various household items such as crockery, cutlery, and spectacle frames were coated with Nb and subsequently anodized to achieve different colors. Various tests relevant to these applications have been used to determine the degradation and the wear of the Nb oxide layers.

Adhesion test: Accurate evaluation of the adhesion of the anodized layers is difficult due to the very thin oxide film (200Å- 1000 Å). Qualitative adhesion tests, such as the bending test, combined with SEM observation of the coating surface at the region of the maximum deformation can provide sufficient information. A stainless steel knife handle, coated with Nb and anodized to achieve light blue color, which corresponds to oxide thickness of ~ 350 Å, was subjected to a severe bend test of 180°. No spallation of the coating or discoloration of the anodized surface at the apex of the bend was observed. SEM analysis showed only formation of parallel cracks in the oxide layer, which is expected from hard and brittle materials.

Dishwasher testing: Ceramic cups and saucers and martensitic stainless steel knife blades coated with Nb and anodized to various colors have been subjected to industrial dishwasher tests of 125 cycles using proprietary detergents and rinse aids. No adverse effects on niobium coated/oxidized inert layers were observed.

Ultraviolet radiation: Titanium based and stainless steel based niobium coated and oxidized samples have been subjected to intensive ultraviolet (UV) radiation at a distance from the source of 30 cm (HPR 125W HG III bulb). No discoloration of the anodized surfaces occurred after five days of exposure.

Edge testing – BS EN ISO 8442-5: 2001: Coated and anodized knives with different colors, i.e. a range of oxide thickness, were subjected to sharpness and wear performance tests in accordance with BS EN ISO 8442-5: 2001. Specification for sharpness and edge retention of cutlery developed at CATRA [14]. The knives were tested using a 50 N load, 25 mm stroke for 25 cycles, cutting into synthetic card containing 5% quartz. In this test, the depth of cut into the very abrasive media represents the cutting power and therefore the wear resistance of the sharp edge. Table 2 summarizes the edge test results.

Table 2: Edge test results for anodized knife blades.

Test Sample	Thickness of the oxide, Å	Depth of cut, mm
Uncoated		0.15
Nb coated only		0.15
Anodized at 25V	250	0.2
Anodized at 50 V	500	0.23
Anodized at 60 V	600	0.3

The edge test results show that the coated oxidized blades performed better than the uncoated and non-oxidized blades, and this was related to oxide thickness. The thicker the oxidized outer layer, the better the wear performance, which was doubled in the case of the 600 Å sample, thus demonstrating improved wear resistance that will help the blades keep their aesthetic appearance and performance longer.

Abrasion testing: The abrasion resistance of the oxidized niobium coatings was assessed in accordance with the BS 7069: 1988 – Abrasion Resistance of Cookware. A powder coating, which is currently available on the market for use on knife handles, was selected as a reference coating. The test was carried out using a specialized testing rig. The rig utilizes a downward load of 5 N on to a rigid plastic block (80 mm x 30 mm), to which a 3M Scotchbrite—an abrasive pad consisting of a random nylon web impregnated with phenolic resin and aluminium oxide—is attached. The pad pneumatically cycles back and forth across the test specimen, which is submerged in 5% soap solution. The number of cycles to wear away the coatings was recorded and is tabulated in Table 3 below.

Table 3: Abrasive wear results of various decorative coatings.

Test Sample	Number of Cycles	Thickness of the Coating
Powder coating on stainless steel	750	0.1 mm (100,000 Å)
Dark Blue Nb on stainless steel	15	250 Å
Yellow Nb on s/s	15	500 Å
Turquoise Nb coating on Ti	50	800 Å
Yellow Nb coating on Ti	25	500 Å

The powder coating is significantly thicker (200 times) than the average niobium oxide coating, but has only taken 50 times more cycles to erode away, which indicates that the oxidized coating is more scratch resistant and harder wearing.

Corrosion tests: The corrosion behavior of anodized Nb coatings deposited on various substrate materials, such as different grades of stainless steel (b-Ti alloy and Al) has been investigated by potentiodynamic polarisation and immersion tests. Detailed results are presented in a paper entitled, "Corrosion Performance of PrD-Coated and Anodized Materials for the Decoration Market" [15]. In this paper, the potential of anodized Nb coatings to protect stainless steel, SS316 and β-Ti alloy against corrosion is discussed.

Potentiodynamic polarisation tests were carried out on anodized Nb coatings deposited on SS316, using an EG&G potentiostat, Model 273. The samples were polarized from -1.0V to +2.0V at a potential ramp of 1 mV/s in a buffered 0.8M NaCl solution (pH 7). The values of the potential were referred to a standard calomel electrode (SCE). The polarization curves show a broad passivation range up to 1200mV and very low current densities in the range of 10^{-8} A.cm^{-2} (see Figure 4). The thickness of the anodized oxide layer obviously plays an important role. Thicker layers (~400Å) developed at anodization voltage of 40V achieved lower current densities (10^{-9} A.cm^{-2}) therefore provide better protection, compared to layers produced at 30V (see Figure 4).

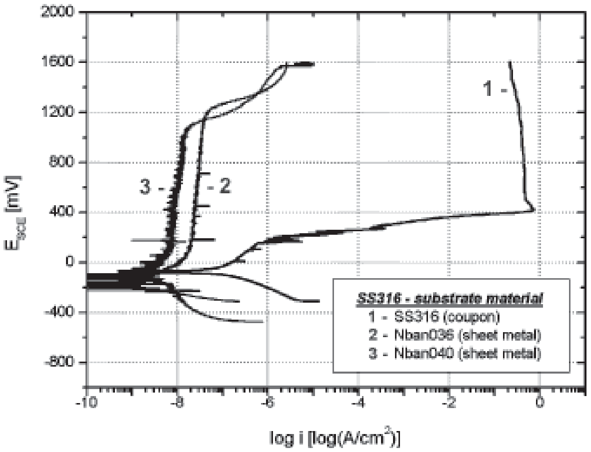


Figure 4: Potentiodynamic polarisation curves for bare and protected by anodized to various voltages Nb coatings 316 SS substrates.

Immersion tests: β-Ti and SS316 samples coated with Nb and anodized were tested in artificial sweat to study the effect of the biological attack when in contact with the human body. Discoloration as well as coating or substrate elements release was monitored. The immersion tests in artificial sweat were carried out according to DIN EN 1811. The test duration was one week and the test solution was kept at 30°C. After the test the solution was analysed with an ICP (inductive coupled plasma) spectrophotometer equipped with an Ulbricht sphere and a D65 light source. The color was measured with a d/8 geometry and analyzed with respect to a 2° observer before and after the immersion test. The color change DE value was calculated with the following formula:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Equation 1

The results from such measurements for three different samples (colors) are summarized in Table 4.

Table 4: Color change due to immersion test.

Color	Δ E	Before immersion			After immersion		
		L_1^*	a_1^*	b_1^*	L_2^*	a_2^*	b_2^*
Green	6.9	67.9	-34	+9.2	68.8	-39	+4.3
Pink	1.12	54.1	+47	-14	53.3	+46	-14
Yellow	1.19	71.9	-3.9	+55	72.5	-5.7	+55

The variations in the Δ E values for all of the samples was negligible or nearly not recognizable for the human eye, which demonstrates the high stability of the Nb oxide layers formed by anodization. After the immersion tests, the electrolytes were further analyzed using the ICP method for traces of Nb. The Nb content in the electrolyte in all three cases was lower than the detection limit of the analyzer, which further confirmed the extremely high electrochemical stability of the anodized layers. Similarly, the anodized layers provided very good protection for the SS316 samples in the conditions of the immersion test. In this case, the main interest was on detection of eventual nickel release from the stainless steel through pores in the PVD coating. For all three samples however, the nickel content in the electrolyte was £ 0.032 μg.cm^{-2} week^{-1}, far below the critical value of 0.5 μg.cm^{-2} week^{-1}, permitted by the DIN standard. The immersion tests revealed that the anodized Nb coatings can be classified as materials with high biocompatibility with reduced probability for nickel allergic reactions.

CONCLUSIONS

A wide pallet of colorful, hard oxides (HV 1500) utilizing the optical interference effect were developed to serve decorative applications by anodization of metallic Nb coatings deposited by the combined steered cathodic arc/unbalanced magnetron sputtering technique. A variety of mechanical and electrochemical tests proved the excellent wear and corrosion resistance as well as the high biocompatibility of the anodic oxide of Nb. The aesthetic appearance and durability opens perspective for successful implementation of the technology for applications in cutlery, jewelry, spectacle frames, surgical instruments, and many other sectors requiring decorative finishes.

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