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Discovery of Reversible Switching of Coloration of Passive Layers on Titanium

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Colored passive layers on Ti can be prepared by electrochemical means and their coloration can be switched reversibly between several colors by increasing or decreasing the AC voltage (V_{AC}) in a stepwise manner. The coloration, which originates from iridescence, is directly related to the passive layer's thickness (d) achieved at each V_{AC} value. Two concurrently occurring processes, the passive layer growth and passive layer dissolution, control the passive layer thickness. At a given AC voltage, the passive layer reaches a steady-state thickness at which the growth rate ($\upsilon_{\mathrm{growth}}$) equals the dissolution rate (υ_{diss}). An increase or decrease in V_{AC} modifies the values of $\upsilon_{\mathrm{growth}}$ and υ_{diss} until a new steady-state thickness, and new coloration, is achieved.

Introduction

Titanium (Ti) and other valve metals, such as zirconium (Zr), tantalum (Ta) and niobium (Nb), are known to develop colored passive layers upon oxidation at elevated temperatures (T = 800–2000 °C) in an O_2-containing atmosphere, or by applying a direct current (DC) or an alternating current (AC) in an aqueous electrolyte, such as $(NH_4)_2SO_4$, Na_3PO_4, and NH_4BF_4.[1–5] The coloration is known to originate from iridescence, i.e. constructive interference of light reflected at the outer air/oxide and the inner oxide/metal interfaces.[6,7] The electrochemical coloration of Ti in aqueous NH_4BF_4 that employs AC voltage yields a spectacularly wide spectrum of well-defined and bright colors that can be fine-tuned by adjusting the AC voltage (V_{AC}), temperature (T), electrolyte pH, and by choosing a suitable sample pretreatment, typically chemical etching, mechanical polishing or microsandblasting, as shown in Figure 1.[4,5] An XPS depth profile analysis showed that it is the incorporated fluorine (F) ions (originating from the NH_4BF_4 decomposition) that modify the refractive index and contribute to the richness of colors.[4] Such prepared colored passive layers on Ti are remarkably stable and the exposure to air even for years does not modify their visual properties. The Ti coloring that utilizes AC polarization yields a broad spectrum of colors that cannot be obtained using either DC polarization or thermal passivation. The electrochemical Ti coloring requires AC voltages as high as 80 V but the passivation time is up to 10 s, whereas the gas-phase coloration requires temperatures as high as 2000 °C and oxidation times as long as tens of hours. Apart from being lengthy, energy-consuming, and producing a narrower spectrum of colors, the gas-phase oxidation of Ti or other valve metals produces passive layers that reveal fractures that develop as the sample is cooled down from the high temperature to the room temperature, because the thermal expansion coefficient of the metal and the metal oxide are different.

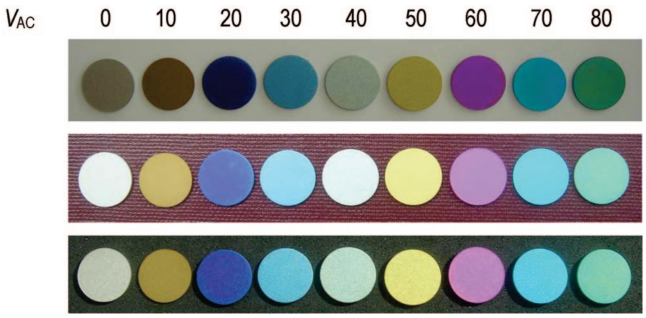

Figure 1. Coloration of passive layers on Ti prepared by the application of AC voltage (V_{AC}) in a 7.5% wt aqueous solution of NH_4BF_4; the passivation time is 10 s and the AC frequency is f = 60 Hz.

Some materials reveal the ability to switch reversibly between two colors when an electric charge is passed through; this phenomenon is referred to as electrochromism. For instance, a polyaniline film is either pale-yellow or dark-green depending on its redox state.[8] Anodically formed iridium oxides appear dark blue at a potential above 0.7 V and almost transparent below 0.7 V.[9,10] The electrochromic

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(1) William, W. D., Jr. *Materials Science and Engineering, An Introduction*; John Wiley & Sons: New York, 1991.
(2) Piontelli, R.; Pedeferri, P. *J. Electrochem. Soc.* **1968**, *115*, 1046.
(3) Gaul, E. *J. Chem. Educ.* **1993**, *70*, 176.
(4) Jerkiewicz, G.; Wieckowski, A.; Strzelecki, H. *Langmuir* **1996**, *12*, 1005.
(5) Hrapovic, S.; Luan, B. L.; D'Amours, M.; Vatankhah, G.; Jerkiewicz, G. *Langmuir* **2001**, *17*, 3051.
(6) Wyszecki, G.; Styles, W. S.; *Colour Science: Concepts and Methods, Quantitative Data and Formulae*; Wiley-Interscience: New York, 1982.
(7) Massau, K. *The Physics and Chemistry of Colours*; Wiley-Interscience: New York, 1983.
(8) Evans. G. P. In *Advances in Electrochemical Science and Engineering*; Gerischer, H., Tobias, C. W., Eds.; VCH: New York, 1990; Vol. 1.
(9) Buckley, D. N.; Burke, L. D. *J. Chem. Soc., Faraday Trans. I* **1975**, *71*, 1447.

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effect gives rise to a reversible transition between two states, where one or both reveal coloration.

So far there is not any known electrochemical system that possesses the ability to switch reversibly between more than two colors when an electric potential is applied or a current passes through. In this contribution, we present the first ever electrochemical system that reveals this ability and switches reversibly between several colors on the time scale of seconds.

Experimental Section

Titanium Electrode Preparation. Circular Ti samples that served as working electrodes were used in the course of research. They were made of Ti sheet (Johnson-Matthey, 99.6 wt % containing 0.12% Fe, 0.08% Si, 0.05% C, 0.10% O, and 0.04% N) and were 10 mm in diameter and 0.30 mm in thickness. They were spot-welded to a Ti wire (Aldrich, 99.7 wt %) for electrical contact and degreased in acetone under reflux in order to remove any organic impurities. Subsequently, they were etched for 1–2 min in a solution made from 30 cm^3 of concentrated HF and 50 cm^3 of concentrated HNO_3 diluted to 1000 cm^3 with demineralized H_2O. Following chemical etching, they were rinsed with demineralized water (Millipore Milli-Q Gradient).[11,12] The wire-shaped electrodes, which served as quasi-reference electrodes in open-circuit potential (E_{OC}) measurements, were made of Ti wire (Aldrich, 99.7 wt %) that was 0.81 mm in diameter. They were connected to a copper wire through an electric connector and sealed with epoxy resin (Struers); only the Ti wire was in contact with electrolyte. Upon the resin hardening, the Ti wire was cut to a length of 1.0 cm and the incision was polished with sandpaper (down to 4000 grade) using a mechanical polisher (Struers) to reach a nice, flat end. The wire-shaped Ti electrodes were degreased in acetone and rinsed with demineralized water. They were then treated in the etching solution described above, rinsed with demineralized water, and sonicated in an ultrasonic bath (Branson) for 1 min.

Electrochemical Formation of Colored Passive Layers on Ti. The formation of colored passive layers on Ti was accomplished in a single-compartment electrochemical cell using a 7.5 wt % aqueous solution of NH_4BF_4 (Aldrich, 97 wt %) as the working electrolyte. The temperature was maintained at 25 °C using a water bath (Haake); high-purity N_2 was passed through the electrochemical cell to expel any gas generated during the passive layer formation. The AC voltage was applied for 10 s using a variable AC power supply (3KVA AC Power Source Model 3001iM, $V_{AC} = 0$–300 V, $f = 16$–500 Hz, California Instruments); V_{AC} was monitored by means of a multimeter (Fluke 45). The counter electrode was made of Pt foil spot-welded to a Pt wire (Johnson-Matthey, 99.9 wt %); its real surface area was at least 10 times greater than that of the Ti electrode. The distance between the Ti working electrode and the Pt counter electrode one was 10–20 cm. This separation was sufficient to allow for effective circulation of the electrolyte between the electrodes and for removal of the gases generated during the AC polarization.

Electrochemical and Morphology Analysis. The analysis of E_{OC} as a function of time was performed using PAR model 263A potentiostat and PAR M353 corrosion software package. The instrumentation was very suitable to sample E_{OC} every second or less during the passive layer dissolution. The uniformity of surface coloration and the morphology of colored passive layers were examined using an optical microscope (SEIWA Optical, Correct Metallurgical Microscope, SDM-TR) equipped with a Pixera digital camera (Professional, 2.5 lux); the magnification was in the 100–400× range.

Results and Discussion

Preparation of Colored Passive Layers on Ti. Figure 1 shows colored passive layers on Ti that are formed upon the application of an AC voltage ($V_{AC} = 10$–80 V, $f = 60$ Hz) for 10 s in an aqueous NH_4BF_4 solution (7.5 wt %). Such formed colored passive layers are very stable and do not discolor upon prolonged exposure to air or dilute aqueous solutions of common inorganic acids (HCl, H_2SO_4), bases (NaOH, NH_4OH), or salts (NaCl, Na_2SO_4). In fact, their coloration does not fade even upon exposure to air for several years.[5] Elsewhere, we reported that the thickness (d) of colored passive layers on Ti increases with V_{AC} augmentation, and that its value is 50, 100, 155, 210, 270, and 320 nm for the passive layers formed at 10, 20, 30, 40, 50, and 60 V, respectively.[5] SEM analysis of their surface morphology showed that they are compact and do not reveal any surface defects (cracks, pits) that could develop during the colored passive layer growth.[13] Only in the case of application of very high V_{AC} that is close to or above the potential of electrical breakdown (V_{eb}), pits can develop initially at edges ($V_{AC} \leq V_{eb}$) and eventually over the entire surface ($V_{AC} \geq V_{eb}$) as the electrical breakdown sets in (accompanied by visible sparking) and the colored passive layers deteriorate.[13]

It is important to recognize that the application of an AC voltage that is 10 V or higher ($f = 60$ Hz) results in 60 cathodic and anodic cycles per second, thus in 600 cycles in the case of polarization for 10 s. Because the reversible potentials of H_2 and O_2 generation in aqueous electrolytes are 0.00 and 1.23 V (plus an overvoltage, η), respectively, the following processes occur during each anodic and cathodic cycle: anodic−passive layer growth, O_2 generation, H_2 oxidation, and anodic oxide dissolution (so-called trans-passive region in corrosion science); cathodic−partial passive layer reduction (reduction of Ti^{4+} to a lower oxidation state, Ti^{3+} or Ti^{2+}, as evidenced by an XPS analysis), H_2 generation, and O_2 reduction.[4] The presence of Ti ions in aqueous NH_4BF_4, which provided the evidence for the dissolution of passive layers, is easily detected by inductively coupled plasma-mass spectrometry (ICP-MS) or electrochemical techniques.[13] Clearly, the electrochemistry of AC polarization is much more complex than that of DC polarization and the quantification of charge associated with each process is practically impossible.

Reversible Color Switching. In a separate series of experiments, an AC voltage was first increased in a stepwise manner from 0 to 70 V and then decreases in the same manner from 70 to 0 V; the voltage step was 10 V and the time step (duration of passivation at a new voltage) was 10 s. Thus, the total passivation time is, for instance, 30 s when

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(10) Monk, P. M. S.; Mortimer, R. J.; Rosseinsky, D. R. *Electrochromism: Fundamentals and Applications*; John Wiley & Sons: New York, 1995.

(11) Parthasaradhy, N. V. *Practical Electroplating Handbook*; Prentice Hall: Englewood Cliffs, NJ, 1989.

(12) Angerstein-Kozlowska, H. In *Comprehensive Treatise of Electrochemistry*; Yeager, E., Bockris, J. O'M., Conway, B. E., Sarangapani, S., Eds.; Plenum Press: New York, 1984; Vol. 9.

(13) Zhao, B.; Jerkiewicz, G. *Can. J. Chem.* **2006**, *84*, 1132.

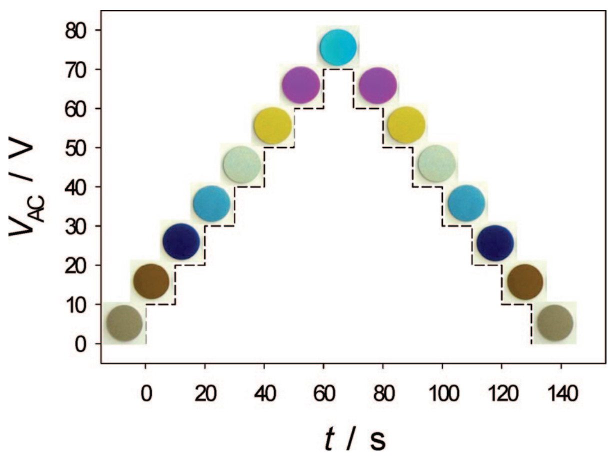

Figure 2. Variation of the coloration of passive layers on Ti achieved by a stepwise increase and decrease in the AC voltage (V_{AC}) in a 7.5 wt % aqueous solution of NH_4BF_4. The AC voltage step is $\Delta V_{AC} = \pm 10$ V and the time step is $\Delta t = 10$ s.

$V_{AC} = 30$ V is achieved in a stepwise manner or 60 s in the case of $V_{AC} = 60$ V. In our earlier work,[5] we explained that the coloration change past the initial 10 s of passivation are minor, because the growth rate of the passive layers decreases exponentially with time and a steady-state coloration (and thickness) is reached for each V_{AC} value within some 10 s. Figure 2 shows the coloration obtained at each AC voltage. As V_{AC} is increased and maintained at its new value for 10 s, a new color is obtained and maintained. Interestingly, once the highest V_{AC} is reached and the corresponding color is obtained, it is possible to reverse the coloration to that observed at lower V_{AC} values. For instance, the sky-blue color obtained at 30 V in the ascending voltage mode is also achieved at 30 V in the descending voltage mode. In order to obtain the best reproducibility of the color switching in AC polarization of Ti in aqueous NH_4BF_4, it is essential to maintain the distance between the electrodes some 10–20 cm. Such a distance ensures minimal mixing of the gases generated at both electrodes, as explained in our previous work.[4,5]

The color switching in the descending mode that we report here seems at first counterintuitive because it implies that a thicker layer becomes thinner as the applied AC voltage is lowered. Under typical DC anodization conditions, the oxide growth is expected to proceed at each voltage, although a high voltage stipulates a high growth rate whereas a low voltage a low growth rate. Even though the colored passive layers on Ti are remarkably stable in various media, they still undergo etching in F-containing aqueous solutions, such as HF or NH_4BF_4. In fact, aqueous solutions of HF are used to prepare oxide-free surfaces of valve metals, as in the case of our research. Kelly[14] demonstrated that F^- ions are instrumental in the etching of metallic Ti and that the process proceed through the dissolution of a surface oxide layer (TiO_2). He also observed that the TiO_2 dissolution rate is determined mainly by the F^- concentration. Thus, the existing results as well as the new date presented in this contribution clearly reveal that F-containing ions affect the interfacial behavior of Ti in aqueous electrolytes. As we explain it below, F-containing ions are instrumental in the color-switching phenomenon that we report here.

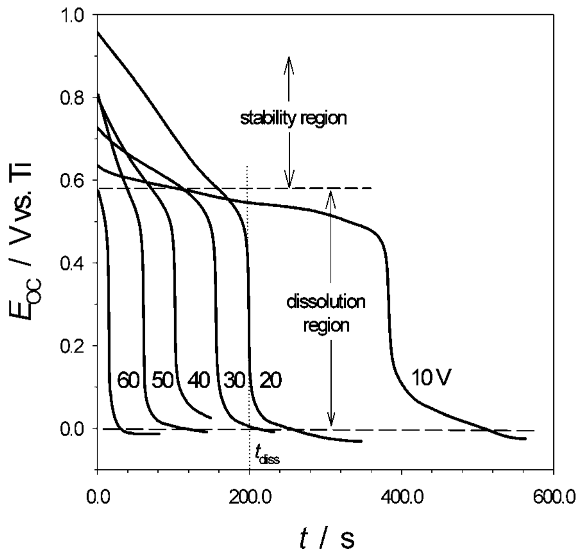

Figure 3. Open circuit potential (E_{OC}) versus time (t) transients measured in 7.5 wt % aqueous solution of NH_4BF_4 for six colored passive layers on Ti formed at 10 – 60 V. Extrapolation of the steep E_{OC} versus t part to $E_{OC} = 0$ V provides the passive layer dissolution time (t_{diss}).

Explanation of the Color Switching Phenomenon. Figure 3 presents a set of open circuit potential (E_{OC}) versus time (t) transients for six colored passive layers formed at 10–60 V immersed in 7.5 wt % aqueous NH_4BF_4 solution. The values of E_{OC} are measured versus a freshly etched Ti wire (free of any oxide; it serves as a quasi reference electrode) that is immersed in the same electrolyte. The colored passive layers on Ti have superior corrosion-protection properties with respect to untreated Ti and they have a value of E_{OC} (at $t = 0$ s) that is some 0.58 – 0.95 V higher than that observed for untreated Ti. However, they undergo gradual dissolution with simultaneous color disappearance in aqueous NH_4BF_4 under open circuit conditions.[14] As the passive layer dissolution progresses, the value of E_{OC} gradually drops and eventually reaches $E_{OC} = 0$ V; the latter value corresponds to the passive layer removal (values slightly lower than 0 V can be attributed to the development of a surface hydride layer).[5] The results presented in Figure 3 and the thickness of colored passive layers (d = 50–320 nm; see above) can be used to determine an average passive layer dissolution rate ($v_{diss} = d/t_{diss}$) under open circuit conditions. The time required to dissolve each passive layer (t_{diss}) is determined by extrapolating the steep dissolution part of each E_{OC} versus t plot to $E_{OC} = 0$ V (see the dotted line in Figure 3 for the curve for 20 V). Because the value of d for the colored passive layers is known, it is easy to calculate v_{diss}. Figure 4 presents the average v_{diss} values under open circuit conditions as a function of V_{AC} values required to grow the colored passive layers. It is important to observe that v_{diss} is the greatest (6.40 nm s^{-1}) for the thickest layer ($t_{diss} = 17$ s) and the smallest (0.13 nm s^{-1}) for the thinnest one ($t_{diss} = 395$). The results presented in Figures 3 and 4 allow us to propose a mechanism for the reversible color switching.

In the ascending mode (Figure 5), when V_{AC} is increased from a lower ($V_{AC,1}$, point A) to a higher value ($V_{AC,2}$), then

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(14) Kelly, J. J. *Electrochim. Acta* **1979**, *24*, 1273.

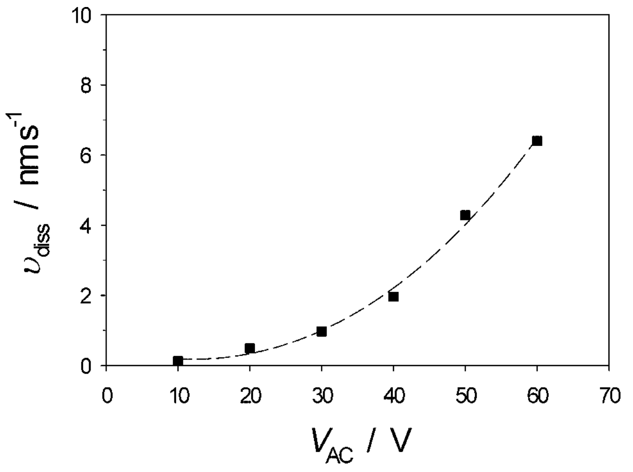

Figure 4. Passive layer dissolution rate (υ_{diss}) under open circuit condition versus the AC voltage (V_{AC}) for six colored passive layers formed at different V_{AC} values.

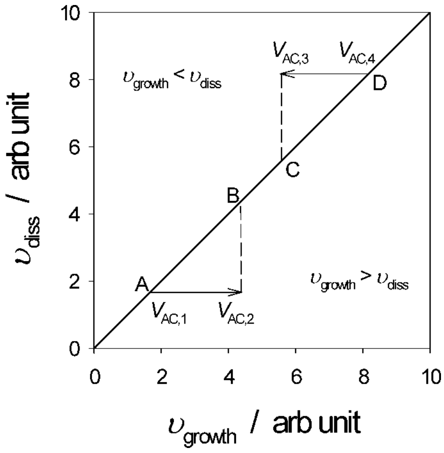

Figure 5. Schematic representation of the relationship between the passive layer growth rate ($\upsilon_{\mathrm{growth}}$) and the passive layer dissolution rate (υ_{diss}).

$\upsilon_{\mathrm{growth}}$ is greater than υ_{diss} and the passive layer thickness increases until a new steady-state thickness is reached (point B). In the descending mode (Figure 5), when V_{AC} is reduced from a higher ($V_{\mathrm{AC,4}}$, point D) to a lower value ($V_{\mathrm{AC,3}}$), then υ_{diss} is greater than $\upsilon_{\mathrm{growth}}$ and the passive layer thickness decreases until a new steady-state thickness is reached (point C). The color switching effect takes several seconds because this is the time required for a passive layer either to increase its thickness through passive layer growth or to decrease its thickness through chemical etching.[4,5,14]

A question arises as to whether the electrochemical color switching reported here for passive layer on Ti could be accomplished using other valve metals. The results and interpretation presented above specify that the passive layer must undergo simultaneous growth and dissolution upon the application of AC voltage. If the electrolyte composition does not facilitate etching, then there is no mechanism that can reduce the thickness of an existing passive layer. In addition, the composition and electronic nature of the passive layer must be such that no limiting thickness is reached at a given V_{AC}, a condition often encountered in the DC growth of insulating oxide layers.

Conclusions

Our results demonstrate that a broad spectrum of brightly colored passive layers on Ti can be prepared by the application of AC voltage in aqueous NH_4BF_4 electrolyte and that their coloration can be switched reversibly by either increasing or decreasing V_{AC}. To the best of our knowledge, this is the first such an electrochemical system. In addition, we are unaware of any other methodology that would allow one to reversibly tune the coloration of passive colored layers on Ti. We explain that the growth of passive layers and etching occur concurrently, and that the steady-state thickness achieved at a given V_{AC} determines the coloration. Thus, increase of decrease of V_{AC} creates new steady-state conditions, thus a new passive layer thickness and a unique coloration.

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