Plasma electrolytic oxidation of Ti - W surface alloys synthetized by PVD-LEHCEB

F Morini, S Franz, A Vicenzo and M Bestetti
1 Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering “G. Natta”, Via Luigi Mancinelli 7, Milano, 20131, Italy
2 Tomsk Polytechnic University, The Weinberg Research Center, 30 Lenin Ave., Tomsk, 634050, Russia
3 E-mail: federico.morini@polimi.it

Abstract. An innovative approach exploiting PVD-coupled Low-Energy High-Current Electron Beam (LEHCEB) and Plasma Electrolytic Oxidation (PEO) techniques were investigated to obtain photoactive TiO\textsubscript{2}-WO\textsubscript{3} mixed films. Ti-W surface alloys containing 14 at.% W were synthetized by PVD deposition of 185 nm thick W films onto Ti substrates, followed by LEHCEB alloying at 30 kV for 50 pulses. The obtained Ti-W surface alloys were treated by PEO in 1.5 M H\textsubscript{2}SO\textsubscript{4} at constant cell voltage ranging from 100 to 200 V. The resulting mixed oxide films were investigated by XRD, SEM and EDS analysis. Photoelectrochemical properties were determined by linear sweep voltammetry in dark and under UV-C and UV-VIS irradiation.

1. Introduction
Alloying Ti with refractory metals is a useful route to enhance its properties [1]. Ti-W alloys raised attention because W can induce higher hardness and wear resistance due to the possible formation of several metastable phases [2, 3]. Additionally, W alloying results in higher corrosion resistance and melting point, and low atomic diffusivity, which are fundamental properties for different applications [4]. Producing surface thin films allows to maintain Ti bulk properties, at the same time enhancing the features of the outermost micrometric layer of the material. Low-Energy High-Current Electron Beam (LEHCEB) is one of the promising ways to produce surface alloys with graded composition [5]. Indeed, LEHCEB has been proposed for surface modification and surface alloying, including grain refinement and the formation of metastable phases with enhanced mechanical and corrosion resistance properties compared to the substrate materials [6, 7].

Ti-W alloys attracted attention also for the possibility to produce mixed oxide systems for photocatalytic applications. TiO\textsubscript{2} is an extensively studied photocatalyst having a relatively large band-gap (~3.2 eV anatase and ~3.02 eV rutile) and has been widely applied in waste-water treatment and water splitting [8, 9]. WO\textsubscript{3} as well has been investigated as photocatalyst due to its small band gap (~2.8 eV) and higher light adsorption in the visible range [10, 11]. Mixtures of WO\textsubscript{3} and TiO\textsubscript{2} have been proved to outperform the individual oxides both in terms of photocatalytic activity [12-14]. Mixed TiO\textsubscript{2}-WO\textsubscript{3} films were obtained by reactive magnetron co-sputtering [15], thermal oxidation [12], electrospinning [13] and anodization of Ti in electrolytes containing W precursors [16]. An attractive alternative is plasma electrolytic oxidation (PEO) of Ti. This process promotes the
instantaneous formation of crystalline oxides [17-20] and has attracted attention as a promising route to produce large area photodelectodes for water treatment and solar-assisted hydrogen production [21-24]. Despite these promising features, PEO has been hardly investigated for the synthesis of mixed TiO$_2$ and WO$_3$ films [25, 26]. In this work mixed TiO$_2$ and WO$_3$ films were obtained by PVD-coupled LEHCEB followed by PEO. Crystallographic, morphological and photoactivity of alloys and oxides were investigated.

2. Materials and methods

2.1. Sample preparation
Commercially pure (c.p.) Ti (O ≤ 0.08%, C ≤ 0.08 and Fe < 0.07) was used as substrate material. Coupons (3×7×0.1 cm) were degreased in a 50/50 vol solution of acetone and ethanol and chemically etched in an aqueous solution of 2 M HF and 1.44 M HNO$_3$ for 2 min, then rinsed in deionized water and dried in air. RITM-SP facility (Microsplav OOO, Tomsk, Russia) was used for LEHCEB pretreatment and alloy synthesis. All samples were firstly pretreated with LEHCEB at 25 kV and 10 pulses to smoothen the surface and remove contaminants from the surface. After the pretreatment, a 185 nm thick W layer was deposited on the Ti substrate by PVD magnetron sputtering. A W (99.95%) target of 75 mm in diameter was used and a constant current (1.5 A and 380 V) was applied for 5 min. The deposition was followed by LEHCEB alloying treatment at 30 kV and 50 pulses. PEO of the Ti-W surface alloys was carried out in 1.5 M H$_2$SO$_4$ at 0°C for 5 min at constant cell voltage (from 100 to 200 V). The electrolyte temperature was controlled by means of a cryostat and an insulated jacketed cell. The cathode was a c.p. Ti grid. The anodized area during PEO was 2 cm$^2$. For comparison, PEO was also carried out on c.p. Ti samples. Table 1 reports the list of PEO treatments done on different samples.

| Sample | PEO voltage (V) |
|--------|-----------------|
| Ti_1; TiW_1 | 100 |
| Ti_2; TiW_2 | 120 |
| Ti_3; TiW_3 | 140 |
| Ti_4; TiW_4 | 160 |
| Ti_5; TiW_5 | 180 |
| Ti_6; TiW_6 | 200 |

2.2. Sample Characterization
Crystal phase composition was assessed by X-Ray diffraction (XRD) using an EMPYREAN PW1830 diffractometer (PANalytical Ltd.) in grazing incidence configuration (1°, Cu Kα1, λ = 0.15406 nm). Identified peaks were fitted and deconvoluted by Pearson VII fitting function (Origin Pro 2018). Surface morphology and elemental maps were determined by Scanning Electron Microscopy (SEM, ZEISSL EVO50VP, Carl Zeiss Jena GmbH) and Energy-Dispersive X-ray Spectroscopy (EDS) (Bruker Quantax 200 6/30 spectrometer, Bruker Corp.), respectively. Linear sweep voltammetry (LSV) was done in a 4 mM KCl aqueous solution in a three-electrode electrochemical cell by using an AMEL 2549 potentiostat (AMEL S.r.l.). Saturated calomel electrode (SCE) was used as reference electrode and a Pt foil as counter electrode. The exposed area for photoelectrochemical measurements was 1 cm$^2$. LSV was carried out in dark and under UV-C and VIS irradiation (Helios Italquartz S.r.l. and Hamamatsu Photonics K.K., respectively).
3. Results and discussion

3.1. Characterization of Ti-W alloys

The XRD patterns of the sample obtained by PVD-LEHCEB treatment show the presence of Ti-W alloys (figure 1). In particular, in addition to the reflections at $2\theta \approx 35.1^\circ$, 38.39° and 40.16° corresponding to the hcp structure of the Ti substrate, peaks at 39.19°, 57.08° and 71.21° were observed, which can be attributed to Ti-W bcc $\beta$ alloys. Based the least-mean square method, a lattice constant of 3.241 Å and a W content of around 14 at.% were calculated.

![Figure 1](image1.png)  
**Figure 1.** XRD patterns of etched Ti substrate and Ti-W surface alloys.

3.2. Plasma electrolytic oxidation of Ti-W alloys

Figure 2 shows the XRD patterns of the samples after PEO at different cell voltages. A mixture of TiO$_2$ and WO$_3$ was observed. The presence of a monoclinic WO$_3$ phase can be inferred on the basis of the peaks occurring at 35.10° and 40.30° and corresponding to the (220) and (103) reflection planes, respectively. The WO$_3$ reflections are more intense at lower PEO voltages. According to literature [17], by tuning the cell voltage the anatase-to-rutile relative content was modified. At low voltage (100-120 V), TiO$_2$ consisted in pure anatase ($2\theta \approx 25.2^\circ$). By increasing the cell voltage, a mixture of anatase and rutile (140 V) and pure rutile (160 - 180 - 200 V) was obtained.

![Figure 2](image2.png)  
**Figure 2.** XRD spectra of TiO$_2$-WO$_3$ films obtained by PEO in H$_2$SO$_4$ solution at different cell voltages. Solid lines represent rutile, dashed lines anatase phase and dot lines WO$_3$.

The anatase and rutile reflections were shifted with respect to the literature values, indicating a distortion of the TiO$_2$ lattice. This lattice distortion occurred both along the $a$ and the $c$ directions (table 2) and overall corresponded to an increase of the unit cell volume. Compared to pure TiO$_2$ films obtained in the same operating conditions, a stabilization of the rutile phase was observed. Indeed, in
TiO$_2$-WO$_3$ films rutile is the prevailing phase at cell voltages (140-160 V) where usually almost equimolar mixtures of anatase and rutile are obtained [18]. This could have a beneficial effect in view of applications in solar assisted energy conversion and catalysis, given the lower energy band-gap of rutile with respect to anatase.

**Table 2.** Lattice parameter and cell volume of anatase and rutile in TiO$_2$-WO$_3$ films. (Anatase: $a = 3.785$ Å, $c = 9.514$ Å, $V = 136.300$ Å$^3$; Rutile: $a = 4.653$ Å, $c = 2.969$ Å, $V = 64.280$ Å$^3$).

| Sample | Anatase | Rutile |
|--------|---------|---------|
|        | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $a$ (Å) | $c$ (Å) | $V$ (Å$^3$) |
| TiW_1  | 3.794   | 9.499   | 136.767     | 4.628   | 2.969   | 63.596     |
| TiW_2  | 3.806   | 9.491   | 137.459     | 4.618   | 2.969   | 63.322     |
| TiW_3  | 3.794   | 9.485   | 136.532     | 4.607   | 2.954   | 62.691     |
| TiW_4  | 3.791   | 9.515   | 136.750     | 4.592   | 2.956   | 62.339     |
| TiW_5  | 3.718   | 9.862   | 140.756     | 4.600   | 2.961   | 62.663     |
| TiW_6  | -       | -       | -           | -       | 4.598   | 2.960      | 62.579     |

According to SEM micrographs (figure 3), the surface morphology was porous and sponge-like. At 120 V the surface morphology strongly resembled that of pure TiO$_2$ [18]. On the other hand, at higher cell voltages the surface morphology differentiated from that of pure TiO$_2$ films, showing coarser and less homogeneous features. Correspondingly, EDS analysis and the related elemental maps demonstrate an higher content (from 3.2 at.% at 120 V to 0.3 at.% at 200 V) and more homogenous distribution of W at lower cell voltages (table 3). This is in agreement with XRD spectra, where the most intense WO$_3$ peaks were observed in samples synthetized at lower cell voltages.

**Figure 3.** SEM micrographs and corresponding elemental maps of Ti-W oxide obtained at 120 (a), 140 (b), 160 (c) and 200 V (d).
Table 3. EDS W content evaluated in Ti-W samples.

| Sample  | TiW_1 | TiW_2 | TiW_3 | TiW_4 | TiW_5 | TiW_6 |
|---------|-------|-------|-------|-------|-------|-------|
| W content (at.%) | 3.5   | 3.2   | 1.4   | 0.6   | 0.4   | 0.3   |

3.3. Photoactivity of oxides
In figure 4, the photocurrent of pure TiO$_2$ films (figure 4 (a)) and TiO$_2$-WO$_3$ films (figure 4 (b)) are showed.

Figure 4. Photocurrent density of TiO$_2$ (a) and Ti-W oxide (b) samples under UV-C irradiation.

Table 4. Photocurrent values of TiO$_2$ and Ti-W oxide samples during LSV at 0.5 and 1.5 V under UV-C irradiation.

| Sample  | Photocurrent at 0.5 V ($\mu$A/cm$^2$) | Photocurrent at 1.5 V ($\mu$A/cm$^2$) |
|---------|-------------------------------------|-------------------------------------|
| Ti_1    | 123.3                               | 117.2                               |
| Ti_2    | 153.6                               | 117.4                               |
| Ti_3    | 230.3                               | 238.6                               |
| Ti_4    | 228.4                               | 218.1                               |
| Ti_5    | 0.2                                 | -                                   |
| Ti_6    | 4.0                                 | -                                   |
| TiW_1   | 54.7                                | 95.8                                |
| TiW_2   | 13.4                                | 33.9                                |
| TiW_3   | 14.6                                | 43.7                                |
| TiW_4   | 94.6                                | 118.9                               |
| TiW_5   | 79.3                                | 116.4                               |
| TiW_6   | 135.5                               | 141.5                               |

As for the pure TiO$_2$ films, in agreement the literature [24], samples oxidized at intermediate voltages (140 and 160 V) showed the highest photocurrent, 238.6 $\mu$A/cm$^2$ at 1.5 V and 228.4 $\mu$A/cm$^2$
at 0.5 V, respectively. Oppositely, TiO$_2$-WO$_3$ films best performed at 200 V (141.5 $\mu$A/cm$^2$ at 1.5 V) and showed lower photocurrent values at lower cell voltages. Photocurrent values of TiO$_2$ and TiO$_2$-WO$_3$ films obtained at the different cell voltages are reported in table 4. Photocurrent values are considered both at 0.5 and 1.5 V because a well-defined plateau is not always present.

![Figure 5. Photocurrent density of TiO$_2$ (a) and Ti-W oxide (b) samples under UV-VIS irradiation.](image)

| Table 5. Photocurrent values of TiO$_2$ and Ti-W oxide samples during LSV at 0.5 and 1.5 V under UV-VIS irradiation. |
|-----------------|-----------------|-----------------|
| Sample         | Photocurrent at 0.5 V ($\mu$A/cm$^2$) | Photocurrent at 1.5 V ($\mu$A/cm$^2$) |
| Ti_1           | 6.8             | 10.9            |
| Ti_2           | 44.2            | 64.5            |
| Ti_3           | 115.3           | 172.8           |
| Ti_4           | 49.3            | 48.7            |
| Ti_5           | 46.5            | 30.8            |
| Ti_6           | 12.9            | 4.2             |
| TiW_1          | 17.9            | 35.4            |
| TiW_2          | 1.8             | 15.9            |
| TiW_3          | 50.8            | 165.8           |
| TiW_4          | 152.6           | 316.9           |
| TiW_5          | 118.9           | 181.6           |
| TiW_6          | 146.7           | 186.5           |

Photocurrent measurement under UV-VIS irradiation were also carried out for both TiO$_2$ and TiO$_2$-WO$_3$ films (figure 5). The most photoactive TiO$_2$ sample was obtained at 140 V, reaching 172.8 $\mu$A/cm$^2$ at 1.5 V. The highest photocurrent of TiO$_2$-WO$_3$ films was obtained at 160 V, with a value of 316.9 $\mu$A/cm$^2$ at 1.5 V. On average, TiO$_2$-WO$_3$ films outperformed pure TiO$_2$. This might be attributed to both the lower energy band-gap of the WO$_3$ phase and to the formation of favorable semiconductor heterojunctions [14]. Photocurrent values of TiO$_2$ and TiO$_2$-WO$_3$ films measured at 0.5 and 1.5 V are reported in table 5.
4. Conclusions

Photoactive mixed TiO$_2$-WO$_3$ films were synthetized by PEO of Ti-W surface alloys obtained by PVD-LEHCEB. The oxide films were crystalline in structure. TiO$_2$ consisted in a mixture of anatase and rutile phases at 100-120 V, and in almost pure rutile at higher voltages. The monoclinic crystal phase of WO$_3$ was also detected in all the synthetized sample. SEM surface micrographs showed a porous morphology characterized by coarser and inhomogeneous surface features with respect to pure TiO$_2$ films. According to EDS spectra, the average W content varied from 3.2 to 0.3 at.%. Photoelectrochemical characterization under VIS irradiation revealed that on average TiO$_2$-WO$_3$ films outperform pure TiO$_2$ films, demonstrating that the presence of the WO$_3$ phase red-shifted the light adsorption of the photoactive films compared to pure TiO$_2$.

References

[1] Kolli R P and Devaraj A 2018 Metals 8 1–41
[2] Dobromyslov A V and Elkin V A 2001 Scripta Mater. 44 905–10
[3] Callisti M, Tichelaar F D and Polcar T 2018 J. Alloy. Compd. 749 1000–8
[4] Opalrowski J M, Sisson R D and Biederman R R 1987 Thin Solid Films 153 313–28
[5] Ozur G E 2012 25th International Symposium on Discharges and Electrical Insulation in Vacuum (Tomsk: IEEE) pp 580–3
[6] Zhang X D, Hao S Z, Li X N, Dong C and Grosdidier T 2011 Appl. Surf. Sci. 257 5899–902
[7] Rotshein V P, Proskurovsky D I, Ozur G E, Ivanov Y F and Markov A B 2004 Surf. Coat. Tech. 180–181 377–81
[8] Fujishima A, Zhang X and Tryk D A 2008 Surf. Sci. Rep. 63 515–82
[9] Ochiai T and Fujishima A 2012 J. Photoch. Photobio. C 13 247–62
[10] Pancielejko A, Rzepnikowska M, Zaleska-Medynska A, Łuczak J and Mazierski P 2020 Materials 13 3506
[11] Chiarello G L, Bernareggi M, Pedroni M, Magni M, Pietralunga S M, Tagliaferri A, Vassallo E and Selli E 2017 J. Mater. Chem. C 5 12977–89
[12] Siol S, Ott N, Beall C, Stiefel M, Unutulmazsoy Y, Döbeli M, Tilley S D, Schmutz P, Jeurgens L P H and Cancellieri C 2020 Acta Mater. 186 95–104
[13] Soares L and Alves A 2018 Mater. Lett. 211 339–42
[14] Dozzi M V, Marzorati S, Longhi M, Coduri M, Artiglia L and Selli E 2016 Appl. Catal. B – Environ. 186 157–65
[15] Sliozberg K, Schäfer D, Erichsen T, Meyer R, Khare C, Ludwig A and Schuhmann W 2015 ChemSusChem 8 1270–8
[16] Nah Y-C, Ghicov A, Kim D, Berger S and Schmuki P 2008 J. Am. Chem. Soc. 130 16154–5
[17] Franz S, Perego D, Marchese O, Lucotti A, Castiglioni C, Vicenzo A, Morini F and Bestetti M 2016 Appl. Surf. Sci. 385 498–505
[18] Franz S, Arab H, Lucotti A, Castiglioni C, Vicenzo A, Morini F and Bestetti M 2020 Catalysts 10 325
[19] Mirelman L K, Curran J A and Clyne T W 2012 Surf. Coat. Tech. 207 66–71
[20] Quintero D, Galvis O, Calderón J A, Castaño J G and Echeverría F 2014 Surf. Coat. Tech. 258 1223–31
[21] Murgolo S, Franz S, Arab H, Bestetti M, Falletta E and Mascolo G 2019 Water Res. 164 114920
[22] Collivignarelli M C, Abbà A, Miino M C, Arab H, Bestetti M and Franz S 2020 J. Hazard. Mater. 387 121668
[23] Collivignarelli M C, Abbà A, Miino M C, Bertanza G, Sorlini S, Damiani S, Arab H, Bestetti M and Franz S 2021 Environ. Sci. Pollut. R. 28 1–10
[24] Franz S, Arab H, Chiarello G L, Bestetti M and Selli E 2020 Adv. Energy Mater. 10 2000652
[25] Bayati M R, Golestani-Fard F, Moshfegh A Z and Molaei R 2011 Mater. Chem. Phys. 128 427–32
[26] He J, Luo Q, Cai Q Z, Li X W and Zhang D Q 2011 Mater. Chem. Phys. 129 242–8