Downstream analytics quantification of ion release during high-voltage anodisation of niobium

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Abstract

In operando quantification of field-assisted ion release during high-voltage anodisation (up to 100 V SHE) of Nb in 0.1 M sulphuric acid was performed. Electrochemical high-field oxide formation under both potential and current control was studied separately. The quantification of in situ ion release via ICP-MS revealed an increase of the oxide dissolution factor (from 337 to 422 fm V⁻¹) when decreasing the potential scan rate from 200 to 100 mV s⁻¹. Dissolution rates measured during galvanostatic oxide formation allowed measuring oxide dissolution factors of 719 and 837 fm V⁻¹ for current densities of 1.0 and 0.5 mA cm⁻², respectively. As compared to the potentiodynamic case, higher dissolution rates and oxide dissolution factors were measured for galvanostatic anodisation. The overall fraction of the charge used for generation of soluble Nb species was below 0.4% for all oxide growth regimes. Cross-sectional SEM imaging proofs an oxide formation factor of 2.1 nm V⁻¹. The surface of anodised films was extremely smooth and featureless without any cracks or voids. Based on X-ray diffraction, the films were found to be amorphous, indicating that no field crystallisation is occurring under the applied oxide growth conditions even at higher voltages.

Keywords High-field regime · Anodisation · Valve metals · Inductively coupled plasma mass spectrometry

Introduction

Anodic oxide growth occurs when valve metals such as Al, Hf, Nb, Ta, Ti and Zr are anodically polarised in suitable electrolytes [1]. The final thickness of the electrochemically grown oxide layer is mainly determined by the final applied voltage and the film formation factor. The film formation factor is a material-specific constant which typically depends on the used electrolyte. The charge transport necessary for completing the anodisation process occurs via a thermally activated and field-supported hopping of ions through the already present oxide layer [2]. Typically, extremely high electric field strengths in the order of 10⁶ V cm⁻¹ are required for

anodisation. Disregarding Ti, the current is typically only carried by ionic species [3]. Moreover, the oxide grows at both interfaces, the metal/oxide interface and the oxide/electrolyte interface, as dictated by anionic and cationic transport numbers. An exception is found for Zr and Hf which have very low transport numbers [4]. The thin oxide layers formed during anodisation are transparent and the phenomenon of optical interference is responsible for the apparent colours of the films on Hf, Nb, Ta, Ti and Zr [5].

Anodic oxide films on Nb have generated considerable scientific interest due to their wide range of possible technological applications. These Nb₂O₅ films can be used as a dielectric material in capacitors, as an alternative to Ta₂O₅ [6, 7], for electrochromic devices [8], generation of solar fuels [9, 10], gas sensing [11, 12], solar cells [13] and production of biocompatible interfaces [14–16].

Depending on the electrolyte that is used for anodisation, different types of anodic oxides on Nb can be formed. When using non-aggressive aqueous electrolytes like organic acids, phosphoric acid and sulphuric acid porous free barrier-type layers can be grown [17, 18]. These layers can be grown up to thicknesses of a few hundred nanometre using voltages up to hundreds of volts [19]. When using voltages beyond the

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dielectric breakdown, so-called plasma electrolytic oxidation (PEO) occurs which is leading to different surface morphologies [16, 20]. When using electrolytes which are chemically dissolving the forming niobium oxide layer during anodisation (e.g. containing fluorine), nanoporous anodic oxide layers can be grown. Depending on the used conditions, different types of nanostructured oxide layers can be grown ranging from porous layers [21] up to well-defined nanostructures [22, 23].

Many properties of Nb anodic oxide films during and after anodisation have been investigated in the past. This includes electronic properties [24], optical properties [25], anodic luminescence [19], photoelectrochemical properties [25, 26], composition changes [27, 28], growth kinetics [17, 29], corrosion properties [30, 31] and evolution of internal stress [32]. During all these studies, the question of Nb dissolution during anodisation itself was overlooked. Therefore, in the current work, an in situ investigation of the dissolution rate of Nb during high-voltage anodisation up to 100 V is presented. The Nb dissolution rate was measured by using a combination of an electrochemical flow-through cell and an inductively coupled plasma mass spectrometer (ICP-MS) [33]. Investigations were performed using different oxide growth rates under potentiodynamic and galvanostatic anodisation conditions.

Experimental details

In situ monitoring of the dissolution rate of Nb during anodisation was performed using an ICP-MS (I-CAP Q, Thermo Fisher) that was coupled to an electrochemical flow cell [34]. The downstream electrolyte was analysed for ^{93}Nb with a sample rate of 10 Hz using ^{89}Y as an internal standard for drift compensation. As electrolyte, a naturally aerated 0.1 M solution of ultrahigh-purity sulphuric acid (Ultrapur®, Merck) in analytical grade water (18.2 M Ω cm) was used for all electrochemical experiments.

As sample material, 3-mm in diameter rods of polycrystalline Nb (99.9% purity, Alfa Aesar) were used. The rods with an individual length of 10 mm were glued into precisely machined cylinders made from PEEK polymer (similar to RDE tips) using a two-component epoxy glue. The Nb was mechanically polished down to 0.04- μm silica suspension and afterwards electropolished in a $\text{HF}/\text{H}_2\text{SO}_4$ mixture [35]. The round opening of the used flow cell had a diameter of 5 mm. This experimental configuration ensures that no oxide film growth occurs under the sealing of the flow cell at high voltages. Additionally, Nb thin films were deposited by magnetron sputtering on borosilicate float-glass substrates. The base pressure in the sputtering chamber was 1×10^{-6} Pa and the sputtering process was carried out in Ar at 5×10^{-1} Pa. The power density used for sputtering the Nb target (99.95%

purity, MaTeck Material-Technologie & Kristalle GmbH, Germany) was 4 W cm^{-2} . This resulted in a sputtering rate of 3 nm min^{-1} , and the final thickness of the metallic film was approximately 550 nm.

All electrochemical experiments were performed using a Compactstat potentiostat (Ivium Technologies, The Netherlands) in three-electrode configuration using a 3-M Ag/AgCl reference electrode. The anodisation of Nb was performed at two different scan rates (100 and 200 mV s^{-1}) and current densities (0.5 and 1.0 mA cm^{-2}). The surface microstructure of Nb thin films was characterised before and after anodisation by scanning electron microscopy (SEM, Zeiss Gemini 1540 $\times$). Crystallographic properties were assessed by X-ray diffractometry (Philips X'Pert Pro). The radiation used for this purpose was CuK_α ($\lambda = 1.5406 \text{ \AA}$) and the system was operated in grazing incidence mode (GIXRD), with a fixed incident angle $\omega = 1^\circ$, in order to minimise the substrate influence on the measurements.

Results and discussion

Potentiodynamic oxide growth on Nb was continuously performed between 0 and 100 V vs. standard hydrogen electrode (SHE) using two different rates of potential increase. This anodisation was coupled to downstream analytics in order to investigate possible dissolution effects triggered by different electrical/mechanical stresses corresponding to each potential gradient. The use of the downstream analytics, providing a live quantification of the amount of dissolved Nb, allowed characterising the Nb concentration in respect to the anodising potential. In Fig. 1, these data are summarised for comparison and discussion. The current-voltage characteristics recorded during the experiment are presented in panel a of Fig. 1 for both rates of potential increase used in this study.

Starting from low potentials, a rapid increase of the current density is evident for both curves, indicating the start-up phase of the anodic oxide formation in agreement with the high-field model [2]. The approximately 2-nm-thick native oxide present on the Nb surface represents the initial dielectric where charge separation occurs due to the high-field conditions [2, 36]. Ion hopping is activated and space charge regions form at metal/oxide and oxide/electrolyte interfaces. New oxide grows as soon as both space charge regions fully overlap [37, 38]. However, during this time, the potentiostat continuously detects charge being transferred through the external circuit leading to a sharp increase of the current density as observed in Fig. 1a. Usually, this increase leads to a current overshoot whose observation depends on the experimental parameters, i.e. the potentiostat data acquisition speed. Such overshoot can be observed in case of anodisation with 200 mV s^{-1} but is not clearly defined for 100 mV s^{-1} .

Fig. 1 Current-voltage characteristics recorded during potentiodynamic oxide growth on Nb (**a**) and corresponding Nb dissolution curves measured in situ by ICP-MS (**b**) corresponding to both rates of potential increase (100 and 200 mV s⁻¹)

The origin of the current density overshoot is confirmed in panel b of Fig. 1 where the Nb dissolution rates are plotted as a function of the applied potential that was measured during the anodisation process. At low potentials, the Nb dissolution follows the anodisation current density curve measured by the potentiostat (Fig. 1a) but no dissolution overshoot can be observed. This indicates that the dissolution of Nb starts as soon as the potential is applied and the discussed current overshoot does not lead to higher dissolution rates since the ion hopping occurs under potential/electric field control. Above approximately 10 V vs. SHE, both the current density and Nb dissolution rate corresponding to each of anodisation conditions stabilise in plateaus, directly characterising the continuous oxide growth accompanied by its constant dissolution. The anodic current density plateaus are directly related to the oxide formation factor k :

$$i_{\text{an}} = k \frac{zF\rho}{M} \frac{dE}{dt} \quad (1)$$

where i_{an} is the plateau value of the anodic current density, z is the number of electrons exchanged, F is the Faraday constant, ρ is the oxide density, M is its molar mass and E is the applied potential.

Solely from the electrochemical current data presented in Fig. 1a, an oxide formation factor of $2.70 \pm 0.05 \text{ nm V}^{-1}$ can be calculated for Nb₂O₅ which is in reasonable agreement with previous studies on much thinner oxides [39, 40]. This value is independent on the rate of potential increase (at least in the range investigated here) and was calculated using the oxide density of 4.36 g cm^{-3} and its molar mass of $265.81 \text{ g mol}^{-1}$. In a similar manner, from the dissolution curves, a potential-dependent oxide dissolution factor can be calculated. A linear regression of all experimental data above 10 V from Fig. 1b indicated extremely stable plateau values of 293.8 and 184.1 pg s⁻¹ cm⁻² (slopes around $0.05 \text{ pg s}^{-1} \text{ cm}^{-2} \text{ V}^{-1}$) corresponding to anodisation at 200 and 100 mV s⁻¹, respectively. Using Faraday's law, it can immediately be calculated that these dissolution rates correspond to dissolution current densities of 107 ± 9 and $67 \pm 8 \text{ nA cm}^{-2}$, respectively. The error calculation is based on the dissolution rate uncertainty/noise of $50 \text{ pg s}^{-1} \text{ cm}^{-2}$ as observed in Fig. 1b. Oxide dissolution factors of 337 ± 20 and $422 \pm 50 \text{ fm V}^{-1}$ were finally calculated from the dissolution current densities corresponding to the two potentiodynamic anodisation conditions investigated (200 and 100 mV s⁻¹, respectively). Even though the dissolution factors are very small, their precise calculation is mainly attributed to the extreme sensitivity and resolution of the ICP-MS.

The fact that the proposed oxide dissolution factor depends on the anodising conditions and electrolyte of choice may provide insight into particularities of the Nb dissolution under high-field conditions. In comparison, the oxide formation factor is generally considered a material constant defined as the reciprocal of the electric field strength within the oxide growing in a given electrolyte [41]. A fraction from the dissolution current measured by the potentiostat needs to be attributed to the high-field dissolution process. This is easily done using again Faraday's law for converting the ICP-MS dissolution rates to charge/current. In Fig. 2, the dissolution fraction is plotted in percentage as the ratio between the total anodisation current and the dissolved mass-equivalent current for both potentiodynamic anodisation conditions under study.

Both fractions are slightly increasing with the increase of the anodisation potential. Moreover, the previously calculated increase of the oxide dissolution factor (from 337 to 422 fm V⁻¹) when decreasing the potential scan rate from 200 to 100 mV s⁻¹ is observed also here. Faster potential increase during anodisation leads to a slightly different dynamic equilibrium of the overlapping space charge regions within the oxide. One reason for this difference may be an increased probability that Nb cations would react with surface-adsorbed O anions to

Fig. 2 Dissolution fractions defined as the ratio between the total anodisation current and the dissolved mass-equivalent current for potentiodynamic anodisation of Nb for both scan rates used (100 and 200 mV s^{-1})

form new oxide (for 200 mV s^{-1}) as suggested by the lower dissolution fractions shown in Fig. 2 for all anodisation potentials used. However, this reasoning cannot simply be separated from the possibly changing current efficiencies during anodisation in different conditions.

So far, 100% current efficiency was implicitly assumed and in a first approximation, the possibility of side reactions (e.g. oxygen evolution) is neglected. However, the differences between the curves in Fig. 2 may suggest that this assumptions are not correct. For the given electrolyte, if the oxide dissolution factor is a material constant, just like the oxide formation factor, then the observed differences between the dissolution factors (and fractions, see Fig. 2) may be attributed solely to different current efficiencies which may vary as a function of scan rate. This would suggest a lowered current efficiency for lower rates of potential increase (i.e. “slower” potentiodynamic anodisation).

In order to characterise the entire potentiodynamic anodisation process, the total amount of dissolved species was quantified by numerical integration of the curves presented in Fig. 1b. The values obtained were 179 and 141 ng cm^{-2} corresponding to the low and high scan rates of 100 and 200 mV s^{-1} , respectively. Additionally, the total charge consumed during the anodic oxide formation (quantified in a similar manner from the electrochemical data presented in Fig. 1a) was found to be 0.467 and 0.460 C cm^{-2} for the low and high scan rates, respectively. In the same time, the overall dissolution fractions for the low and high scan rates were almost identical with values of 0.131 and 0.129%, respectively. Therefore, the scan rate has a clear influence on the total mass loss and charge consumption but has a weak effect on the total dissolution fraction.

Apart from experimentation under potential control, anodisation of Nb was also performed under current control for potentials up to 100 V vs. SHE. Two different current densities were used and the active dissolution of Nb was monitored by the ICP-MS during oxide formation. The obtained anodisation curves are presented in Fig. 3a as measured by the galvanostat in both cases. Perfect linearity can be observed for the time-dependent potential increase as a result of driving constant currents through the electrochemical cell. Applying 1 mA cm^{-2} resulted in anodic oxide growth for 461 s until the maximum potential of 100 V was reached. This is equivalent with a potential increase rate of 217 mV s^{-1} which is comparable with the potentiodynamic conditions used before.

Similarly, galvanostatic anodisations using a current density of 0.5 mA cm^{-2} resulted in anodic oxide growth for 920 s which is equivalent with a rate of potential increase of 109 mV s^{-1} (comparable with the second potentiodynamic condition used before). Integration of both curves from Fig. 3a indicates that the same total charge density of 460 mC cm^{-2} was used in both galvanostatic cases for potentials up to 100 V vs. SHE. This suggests that the same oxide thickness was grown in both cases and a charge equivalent of the oxide growth factor of 4.6 $\text{mC cm}^{-2} \text{V}^{-1}$ is obtained. Similar calculations to those performed for the potentiodynamic anodisations (assuming 100% current efficiency) have as a result a value of $2.90 \pm 0.05 \text{ nm V}^{-1}$ as the oxide formation factor in the galvanostatic case, which is higher than the previous one.

The Nb dissolution curves recorded during galvanostatic anodisation are presented in Fig. 3b for both current densities used. At this time, the dissolution values did not reach a stable plateau and in both cases, higher Nb amounts are released in electrolyte with increasing potentials up to 100 V vs. SHE. At the maximum potential, the highest dissolution rates of 680 and 394 $\text{pg s}^{-1} \text{cm}^{-2}$ were measured for 1.0 and 0.5 mA cm^{-2} , respectively. A similar calculation route as before leads to values of the oxide dissolution factors of 719 and 837 fm V^{-1} for current densities of 1.0 and 0.5 mA cm^{-2} , respectively. A comparison of potentiodynamic anodisations with the equivalent galvanostatic anodisations can be directly performed only if high (or at least equivalent) current efficiencies are assumed. However, higher oxide formation factors, dissolution rates and oxide dissolution factors indicate that galvanostatic anodic oxide formation may occur at a different current efficiency.

The larger galvanostatic oxide formation factor may be explained by a decrease in the current efficiency. The galvanostat keeps the current density at a constant level but not all charge used is responsible for oxide formation. Moreover, during the completion of a side reaction (e.g. oxygen evolution), this constant level is kept at the expense of potential. This means the electric field responsible for ion hopping may fluctuate and the space charge regions may weaken, acting towards stopping the ion migration, or may

Fig. 3 Galvanostatic anodisation curves (a) and their corresponding Nb dissolution curves (b) for different current densities (0.5 and 1 mA cm^{-2})

be enhanced accelerating the oxide growth. Such effects can lead to higher Nb dissolution rates as experimentally observed in Fig. 3b. The fluctuating character of the oxide formation field leads to a potential-dependent Nb release rate during anodisation at constant current densities.

The dissolution fractions (in %) calculated for the galvanostatic anodisation of Nb are presented in Fig. 4. For both current densities used, the dissolution fractions are higher at high potentials. Their increase confirms the idea of field-induced oxide instability leading to higher Nb release. When compared to the dissolution fractions measured during potentiodynamic oxide formation, an increase by 0.15% may be observed for 0.5 mA cm^{-2} (as equivalent to $100\text{-mV}\cdot\text{s}^{-1}$ scan rate). Disregarding the anodisation type, lower potential increase rates resulted in higher dissolution fractions, suggesting that time is a relevant variable for understanding this effect.

In order to characterise the complete galvanostatic anodisation process, the total amount of dissolved metallic species was again quantified by numerical integration, similar to the potentiodynamic case presented before. The mass loss values obtained from Fig. 3b were 324 and 256 ng cm^{-2}

Fig. 4 Galvanostatic dissolution fractions for anodisation of Nb using different current densities (0.5 and 1 mA cm^{-2})

corresponding to the low and high current densities of 0.5 and 1.0 mA cm^{-2} , respectively. However, the total charge consumed during the galvanostatic anodic oxide formation (from Fig. 3a) was found to be almost independent on the current density (0.460 and 0.461 C cm^{-2} for the low and high current densities, respectively). This leads to an increase of the overall dissolution fraction from 0.289 to 0.366% when lowering the current density from 1.0 to 0.5 mA cm^{-2} .

Thin films of Nb deposited by sputtering were used in an identical electrochemical experiment (i.e. anodised potentiodynamically to 100 V SHE). The purpose was to enable the morphological and crystallographic characterisation of the anodic oxide, which otherwise would be far more challenging due to small dimensions and cylindrical geometry of the embedded Nb wire. The surface morphology of the metallic Nb thin film (a), together with the image after anodisation (b) and the cross-section (c), is shown in Fig. 5. The morphology of the as-deposited metallic Nb film indicates pyramidal shaped-grains with sizes in the range of 10 to 80 nm and the film develops a columnar structure with densely packed columns. This type of microstructure is typical for sputtered Nb films and confirms previous findings [42, 43].

After the anodisation process, the surface appearance of Nb changes dramatically. There are no observable surface features (Fig. 5b), and the previous pyramidal grain morphology of metallic Nb is completely transformed into a very smooth surface belonging to the anodic oxide. The surface defect present in the top-left corner of the image is shown deliberately as a focusing point to demonstrate the absence of any surface structuring. The cross-sectional image (Fig. 5c) reveals a very dense and compact anodic oxide with no pores and no grains being present, as already indicated by the surface imaging. Also, the anodic oxide appears to adhere very well to the parent metal found underneath, and the interface between the oxide and metal is free of voids or pores. This is a direct

Fig. 5 Scanning electron microscope images of the surface of as-deposited metallic Nb thin film (a), and surface of anodically grown Nb₂O₅ at a scanning rate of 200 mV s⁻¹ (b) and the cross-section showing the metallic Nb thin film with the oxide grown on top (c)

result of the high field growth of the anodic oxide. The oxide thickness as measured from the cross-sectional image is approximately 210 nm for all applied growth conditions resulting in an oxide formation factor of 2.1 nm V⁻¹. Based on previous TEM measurements, values of 2.33 nm V⁻¹ for anodisation of Nb in 0.1 M (NH₄)B₅O₈ solution [44] and 2.45 nm V⁻¹ for anodisation in 0.1 M H₃PO₄ [45] are reported in the literature. In this study, the thickness measured by SEM cross-sectional imaging is lower than the value of 270 nm calculated purely based on the electrochemical data previously presented (formation factor of 2.70 ± 0.05 nm V⁻¹). The almost 20% lower oxide thickness observed in the SEM may be attributed to significant charge consumption due to oxygen evolution, which was previously observed for similar valve metals such as Ta [46] and Ti [47].

X-ray diffraction patterns were measured on both the as-deposited, metallic Nb layer and the anodically grown oxide (see Fig. 6). Grazing incidence geometry was used in order to

Fig. 6 X-ray diffractograms acquired on the sputter-deposited sample in regions where anodically grown Nb₂O₅ (200 mV s⁻¹) or only metallic Nb is present, together with the reference patterns for metallic Nb and Nb₂O₅ with different crystalline structures (α monoclinic, β tetragonal, γ orthorhombic)

obtain information about the thin-film crystallinity without having superimposed the signal from the amorphous (borosilicate glass) substrate. The two upper patterns from Fig. 6 correspond to the Nb₂O₅ grown anodically using a scan rate of 200 mV s⁻¹ and to the pure metallic Nb, respectively. Together with these measured diffractograms, the patterns from the International Center for Diffraction Data (PDF2-ICDD) data base corresponding to pure Nb (PDF 00-035-0789), as well as Nb₂O₅ polymorphs, are presented. Three variations of Nb₂O₅ are considered: α -Nb₂O₅ (PDF 00-037-1468), β -Nb₂O₅ (PDF 01-072-1484) and γ -Nb₂O₅ (PDF 00-027-1003). In general, amorphous Nb₂O₅ is crystallised upon heating at elevated temperatures. With increasing temperature, the Nb₂O₅ polymorphs occur in a well-defined order. First, γ -Nb₂O₅ (orthorhombic) and/or pseudohexagonal Nb₂O₅ structures are formed at approximately 500 °C. Further, at 800 °C, β -Nb₂O₅ (tetragonal) is found that is transformed into α -Nb₂O₅ (monoclinic) structure when the temperature exceeds 1000 °C. The pseudohexagonal (TT) structure diffraction peaks are found in nearly identical positions as the orthorhombic structure peaks; therefore, the pattern of TT structure is not shown in order not to overload Fig. 6 [48].

Commonly, amorphous Nb₂O₅ is obtained upon anodisation [49, 50], but upon certain experimental conditions (e.g. electrolyte type and temperature, time during which the anodisation was performed at constant voltage) high-field crystallisation has been shown to occur [43, 44]. Even though the anodic oxide on Nb studied here is formed at low (room) temperature, the described polymorphs are useful for a direct comparison, since there is no data available regarding the possible crystalline structures formed under electric field. From the diffractograms shown in Fig. 6, three peaks belonging to metallic Nb can be identified in both oxide and metal patterns. Additionally, when comparing the 2θ range from 18 to 31° of the metal vs. oxide, it

can be clearly seen that a pronounced curvature is present in the latter pattern. This extremely broad peak found solely in the anodised part of the sample coincides with the region where most intense reflections from crystalline Nb₂O₅ oxides are present. No indications of Nb suboxide presence were found that is in agreement with previous findings based on Rutherford back-scattering analysis [44]. Therefore, it can be inferred that under the present experimental electrochemical conditions, the formed anodic oxide is amorphous. This conclusion is supported by the SEM images of the anodic oxide which show the absence of crystallites and/or grains when inspected both on the surface and in the cross-section.

Conclusion

Downstream analytics quantification of field-assisted ion release during high-voltage anodisation (up to 100 V vs. SHE) of Nb was performed. High-field oxide formation under both potential and current control was studied separately. The quantification of in situ ion release by ICP-MS revealed an increase of the oxide dissolution factor (from 337 to 422 fm V⁻¹) when decreasing the potential scan rate from 200 to 100 mV s⁻¹. This was attributed to a slightly different dynamic equilibrium of the space charge regions during oxide growth under the assumption of high current efficiency. Dissolution rates measured during galvanostatic oxide formation allowed measuring oxide dissolution factors of 719 and 837 fm V⁻¹ for current densities of 1.0 and 0.5 mA cm⁻², respectively. As compared to the potentiodynamic case, higher dissolution rates and oxide dissolution factors were measured. The overall fraction of the charge used for generation of soluble Nb species under high-field conditions was less than 0.4% for all applied oxide growth regimes. Based on SEM imaging of the cross-section, an oxide formation factor of 2.1 nm V⁻¹ was found. This oxide formation factor as determined by optical imaging is almost 20% lower as compared to the one calculated based on electrochemical data. This difference may be attributed to significant charge consumption due to oxygen evolution, which was previously observed for similar valve metals such as Ta and Ti. The surface of anodised films was extremely smooth and featureless without any cracks or voids. Based on X-ray diffraction, the films were found to be amorphous, indicating that no field crystallisation under the applied oxide growth conditions is occurring.

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