



Direct observation of metal dissolution during anodization of niobium



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ABSTRACT

Direct in situ Nb release measurements were performed by ICP-MS during Nb anodisation. In the potentiodynamic regime (0–8 V_{SHE} , 10 mV s^{-1}), constant electrochemical current (45 $\mu\text{A cm}^{-2}$) and Nb dissolution rate (70 $\text{pg s}^{-1} \text{cm}^{-2}$) confirm the high field oxide growth. The valve metal character of Nb is demonstrated during the reverse scan when both electrochemical current and dissolution rate decrease, indicating that Nb release is solely triggered by the high field conditions. It was shown that an extremely small fraction of the current (0.75%) was responsible for Nb dissolution. During 1000 s of potentiostatic anodisations up to 9 V_{SHE} the dissolution rates decreased from 100 $\text{pg s}^{-1} \text{cm}^{-2}$ to 10 $\text{pg s}^{-1} \text{cm}^{-2}$ and were slightly potential dependent, with higher dissolution rates at higher anodisation potentials. The electrochemical current transients decayed faster than the dissolution rates, leading to an overall increase in the dissolution current fractions with time (up to 4.5% at 3 V). This fraction was also found to be slightly potential dependent. Interestingly, higher anodisation potentials resulted in lower dissolution fractions during potentiostatic oxide formation. Overall, the potentiostatic dissolution fractions were at least twice as high as in the potentiodynamic case.

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1. Introduction

Metallic niobium spontaneously oxidizes upon contact with air or water to produce a thin, chemically inert oxide film which renders the metal passive and unreactive in most common aqueous media [1,2]. For this reason metallic niobium, along with tantalum, is used in applications where high corrosion resistance is required [3,4]. Niobium is a valve metal whose initial thin oxide layer can be thickened upon anodic polarization [5–10]. This electrochemical oxide growth occurs via high-field assisted migration of Nb cations outwards and of oxygen ions inwards [11]. It is commonly assumed that anodisation of Nb occurs with nearly 100% current efficiency, leading to the assumption that no soluble Nb species are generated during the anodisation process [12–14]. However this assumption has never been experimentally verified. This communication describes the coupling of an electrochemical flow-through cell with a fast ultratrace solution analysis (inductively coupled plasma mass spectrometry, ICP-MS) for direct, quantitative determination of metal dissolution during electrochemical oxidation of niobium under different oxide formation conditions.

2. Experimental

In situ dissolution of Nb was monitored using an ICP-MS (I-CAP Q, Thermo Fisher) coupled to a flow-type scanning droplet cell microscope (FT-SDCM) for which the measuring head was manufactured by 3D-printing [15]. Peristaltic pumps were responsible for the electrolyte transport towards the investigated surface and the downstream electrolyte was analysed for ^{93}Nb using ^{89}Y as an internal standard. An ultra-high purity subboiled 0.1 M H_2SO_4 aqueous aerated electrolyte (Ultrapur®, Merck) was used for the electrochemical experiments. As received polycrystalline Nb (99.9%, Alfa Aesar) was electropolished before use as the working electrode/sample material. The electropolishing process was performed in concentrated H_2SO_4 containing 5% HF at room temperature using 100 mA cm^{-2} for 120 s. Potentiodynamic and potentiostatic anodic oxide formation regimes were used in sequence to study Nb release during oxide growth using a potentiostat (Ivium CompactStat.e) in a three electrode configuration. The potentiodynamic experiments were performed on freshly electropolished Nb at a constant rate of potential increase of 10 mV s^{-1} with a maximum applied potential of 8 V_{SHE} . The potentiostatic study was performed using a fresh sample in a three-step process by sequentially polarizing at 3, 6 and at 9 V_{SHE} for 1000 s at each step.

3. Results and discussion

The potentiodynamic oxide formation regime on Nb was investigated at potentials up to 8 V_{SHE} with a rate of potential increase of

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10 mV s⁻¹. In Fig. 1 a typical cyclic voltammogram corresponding to valve metal behaviour [11] can be observed (presented in green), linked to the left vertical scale. After an initial current overshoot, the current density settles into a plateau positioned at approximately 46.5 μA cm⁻², which is consistent with oxide growth according to the high field model [13]. The plateau indicates that oxygen evolution is not a significant side reaction during anodization of Nb. Oxygen evolution would be observed in an exponential current density increase for potentials above 1.6 V_{SHE}, which is not the case for Nb. The current density overshoot is attributed to a complete overlapping of both positive and negative space charge regions inside the pre-existing oxide e.g. oxide formed naturally at the beginning of the anodisation [11]. The average value of the current density plateau can be used to calculate an oxide formation factor of 2.9 nm V⁻¹, which is in the range of values previously reported for Nb [14]. Fig. 1 also shows (in black, associated with the right-side vertical scale) the Nb dissolution rate curve as measured by ICP-MS during the entire potentiodynamic anodic oxide growth process. The Nb release rate during anodisation (black curve) shows a potential-dependent behaviour very similar to the electrochemically measured current density (green curve). This resemblance is not a coincidence and suggests an almost constant release of Nb species caused by the oxide formation field.

The idea of Nb release under high field conditions is supported by previous studies of metal/insulator/metal structures (using anodic oxides of many valve metals) which showed that the oxide breakdown field is equal to the oxide formation field, therefore setting the high field condition as an onset limit for ion migration [16]. An average value of 66.5 pg s⁻¹ cm⁻² obtained from the dissolution rate curve indicates a rate of Nb oxide decrease of 15 fm s⁻¹ (assuming a homogeneous dissolution process as Nb⁵⁺ and an oxide density of 4.36 g cm⁻³). A small overshoot can also be observed for the Nb dissolution curve at low anodisation potentials. This may indicate that thinner Nb oxides formed below 1 V_{SHE} are more susceptible to corrosion (in the chosen low pH electrolyte) than those grown at higher potentials. This conclusion may also be supported by the mismatch of approximately 100 mV between the peak of the current density overshoot and the inflection point of the Nb dissolution curve. However, a potential uncertainty in the range of several mV (for a potential scan rate of 10 mV s⁻¹) is estimated for the typical 0.2 s time resolution of the ICP-MS measurements. During the reverse scan no additional Nb dissolution could be detected, confirming the nearly ideal valve metal character of Nb. The dissolution rate decreases during the reverse scan along with the electric field strength within the oxide [11], clearly indicating that the release of Nb species is triggered by the high field conditions in the oxide layer and not by interfacial/surface phenomena. The observed experimental noise of the Nb dissolution curve of ± 4 pg s⁻¹ cm⁻² was deliberately not corrected/smoothed since this

is characteristic of Nb detection within the present experimental setup. However, it can easily be concluded that a complete correlation between the electrochemical current density (green curve) and the Nb dissolution rate (black curve) is difficult. If the potential-dependent current density may be safely approximated as a plateau during anodisation (as expected from the high field theory), the dissolution curve shows slightly increasing values of Nb release rate as the anodisation potential increases. This observation is made absolutely clear in the inset of Fig. 1, where the fraction of the current directly responsible for Nb dissolution under high field conditions up to 8 V_{SHE} is plotted. The current fraction was obtained as the ratio between the Nb dissolution current directly calculated from the ICP-MS mass data (using Faraday's law and assuming dissolution as Nb⁵⁺) and the electrochemically measured current. A linear fit of this curve is provided in red and its numerical slope was measured as 0.006 V⁻¹, indicating an increase in the Nb dissolution current of more than 0.5% for each volt applied during the anodic oxide formation process. The overall low values of the current fractions obtained (below 1%) indicate very high current efficiencies for the potentiodynamic formation of anodic oxide on Nb.

Anodic oxide formation on Nb was also investigated under potentiostatic conditions using ICP-MS. Three different values were chosen for the applied potential (3, 6 and 9 V_{SHE}) and the oxide was grown at each potential for 1000 s. The time frame chosen is typically sufficient for reaching the corrosion regime under film formation conditions. The results obtained are summarized in Fig. 2. The transients of the current density as measured electrochemically are presented for each anodisation potential (linked to the left vertical scale). The time decay of the potentiostatic transients agrees very well with the high field model. The current density peak observable at the beginning of each potentiostatic anodization step originates from the initially extremely high electric field present inside the existing oxide. This initially causes a high oxide growth rate/electrochemical current, resulting in the observed current overshoot. This field decreases during oxide growth, leading to a continuous decrease in the electrochemical current. Even though time frames up to 10² s are usually sufficient for the full development of the anodic oxide, the measured current density values decreased continuously during the entire experimental time of 1000 s. In valve metals this is normally attributed to a process of oxide densification, during which defects are removed and trapped metallic ions fully migrate to the oxide/electrolyte interface [11]. As a result, a more compact oxide is obtained through this oxide aging/healing process, which accounts for the higher current density values after 1000 s observed for thicker oxides (grown at higher potentials) [17]. The quantified Nb dissolution during potentiostatic anodisation is also presented in Fig. 2 in two different forms. In the inset, the dissolution rate curves of Nb as measured by ICP-MS during the sequential anodization process are presented, while the same three curves are overlapped and linked to the right logarithmic vertical scale for an easier comparison of specific features. For all anodisations a sharp increase in the Nb dissolution rate follows each step of increase in potential. The initially higher oxide formation rate described above results in increased dissolution at the beginning of the anodization process. The heights of these peaks decrease linearly with the increase in anodisation potential, as can be seen in the inset of Fig. 2. This may be linked to the thicker oxides where more time is required for Nb species to migrate through the complete oxide layer before contributing to oxide formation. Also, the final dissolution rates after 1000 s of field treatment depend on the maximum applied potential, with values increasing with potential in a similar manner to the anodisation current densities. This indicates a good correlation between direct mass loss and current density measurements.

Assuming pentavalency of the anodically released Nb species during potentiostatic anodisation, the dissolution current was calculated from the ICP-MS based mass quantification using Faraday's law. The ratio of the dissolution current and the total electrochemical current constitutes

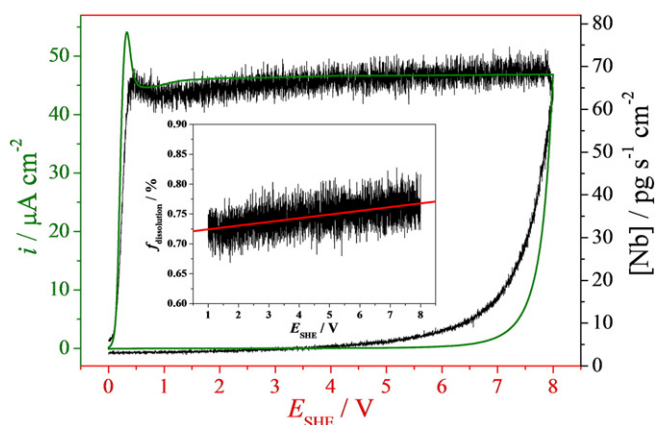


Fig. 1. Current density, dissolution rate and dissolution fraction (inset) during potentiodynamic oxide formation on Nb.

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