



Electro-dissolution of 30Nb–Ti alloys in methanolic sulfuric acid—Optimal conditions for electropolishing

Lakshman Neelakantan^{a,*}, Aparna Pareek^a, Achim Walter Hassel^b

^a Max-Planck-Institut für Eisenforschung GmbH, Max-Planck Str. 1, D-40237 Düsseldorf, Germany

^b Institute for Chemical Technology of Inorganic Materials, Johannes Kepler University, Altenberger Str. 69, A-4040 Linz, Austria

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ABSTRACT

The electro-dissolution behaviour of a (30 at.%) Niobium–Titanium (NbTi) alloy in non-aqueous methanolic sulfuric acid solution using the rotating disc electrode (RDE) was ascertained. The optimal condition for electropolishing and the mechanism were proposed. The influence of the rotation rate, process temperature and sulfuric acid concentration on the dissolution kinetics was investigated. The dissolution rate (limiting current) increases linearly with increase in rotation rate and follows a Levich behaviour confirming a mass transport controlled process. The temperature dependence in terms of Arrhenius plot renders an activation energy value of $E_a = 16.1 \text{ kJ mol}^{-1}$ for the process. The dissolution rate shows a strong dependence on the sulfuric acid concentration (1 M, 3 M and 5 M). Higher sulfuric acid concentrations lead to decreased dissolution rates (limiting current). The dissolution process is mass transport controlled in all concentrations of sulfuric acid. From an electrochemical perspective, a 3 M sulfuric acid was chosen as optimum owing to better controllability of the material removal rate. The dissolving ions are the probable rate limiting species, indicating a compact salt-film mechanism. The average root mean square (RMS) roughness value for an electropolished surface was approximately 10 nm, which is significantly lower than a mechanically polished surface.

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1. Introduction

Titanium alloys have wide application as implant materials [1]. In the past Ti–6Al–4V alloy had been extensively used as an implantable material. However, it is now ruled out owing to the risk of metal (Al, V) ion release [2,3] and the mismatch of elastic moduli with bone (stress shielding effect) [4]. Consequently, the search and development of new types of titanium alloys with low elastic modulus and solely non-toxic elements as alternative, is on the rise. β -Ti alloys are better as biomaterials, as they are non-toxic, non-allergic and possess high-corrosion resistance [5,6]. The low modulus of elasticity similar to human bone makes them suited for load bearing surgical implants [7].

Normally, the surface stability dictates the corrosion resistance and the biocompatibility of any biomaterial and this is true for NbTi alloys as well. Naturally, these alloys are covered by a protective layer comprising of a mixture of both oxides Nb_2O_5 and TiO_2 . The interaction of tissues and cells with Ti alloy implants is

largely determined by the composition and microstructure of the oxide layer. Therefore, a good knowledge of the physical and chemical properties of the surface oxide becomes important, which will allow better control of these interactions by tailoring the oxide properties. The role of surface oxide on corrosion resistance and biocompatibility and the need for developing oxidation procedures was reported by Zorn et al. [8]. A comprehensive study utilising combinatorial approach and scanning droplet cell as a high throughput method on the passivation behaviour of wide compositional spread of NbTi thin films highlights the importance of oxide properties [9]. Various authors have reported on the corrosion behaviour of NbTi alloys and its dependency on the surface oxides [10–12]. Recently, Woldemedhin et al. [13] reported a full fledged study on the oxide properties of NbTi in acetate buffer. Normally, alpha Ti is known to show an electrochemical behaviour that widely depends on the crystallographic orientation of the material. This plays a decisive role on the type of oxide formed (anatase, rutile, brookite) and subsequently on the local reactivity [14]. Such dependency on the crystallographic orientation does not appear on monophasic Nb (30 at.%)–Ti alloys, and these differences were typically smaller than 10% [15]. Even the reactivity of the grains showed an encouraging small deviation from ideal passive behaviour [16]. Apart from growth and characterization of oxides, modification of the surface has also gained attention [17].

* Corresponding author at: Institute for Materials, Ruhr-University Bochum, Universitätsstr. 150, D-44801 Bochum, Germany. Tel.: +49 234 32 25910; fax: +49 234 32 14235.

E-mail addresses: Lakshman.Neelakantan@rub.de, lakshmanneelakantan@gmail.com (L. Neelakantan).

In the perspective of surface modification of any bio-implant, irrespective of any modification step, electropolishing is used as final surface treatment for almost all products being used in medicine. This is because, a smooth, flat and stress free surface enhances the mechanical properties (fatigue resistance), corrosion resistance and biocompatibility. Also, electropolishing of valve metals and alloys containing valve elements have always been a challenge [18–23]. Therefore it is necessary to perform a systematic and comprehensive study to understand the electro-dissolution behaviour and to identify the suitable condition for electropolishing of NbTi.

2. Experimental

The NbTi (30 at.% Nb–Ti) alloy was melted using an electric arc furnace in an inert atmosphere with a water cooled copper crucible for casting. The temperature of the electric arc was about 3000 °C, while the melt was held center at a peak temperature of 1830–1850 °C in order to assure complete dissolution. In order to obtain cast samples of optimal chemical and structural homogeneity all specimens were remelted several times. Finally, the sample was cast into a rectangular copper mould which had a temperature of about 30 °C. The full-fledged details on the procedure are described elsewhere [24].

NbTi (30 at.% Nb–Ti) specimens were machined into rods of diameter 1.7 mm, which were then used as a disc electrode (working electrode). These rods were inserted in a Teflon holder exposing only the cross section as disc with a surface area of 0.0226 cm². The discs were mechanically ground up to 4000 grit SiC emery paper, which has a particle size of ~3 μm, ultrasonicated in ethanol and rinsed with distilled water and dried. The EDI 101 (Radiometer Analytical S.A.) rotating disc electrode setup was used for experiments with CTV 101 (Radiometer Analytical S.A.) rate controller to adjust the rotation rate. The rotation of the disc was varied between 100 and 2500 rpm using external mode of control by a radiometer potentiostat (Voltalab-PST050). A 3 M KCl silver–silver chloride (Ag/AgCl–3 M KCl) and gold wire (99.999%) (Wielandt Dentaltechnik, Germany) were used as reference and counter electrode respectively. All potentials in this paper refer to the Standard Hydrogen Electrode (SHE) reference electrode at 298 K.

The electrolytes were methanolic sulfuric acids with concentrations of 1 M, 3 M and 5 M, which were prepared from analytical grade 95–97% sulfuric acid and methanol (Merck, Germany). The experimental temperatures of 298, 273 and 253 K were maintained using a cryostat (Lauda RC20-CP). Anodic polarisation curves were recorded by sweeping the potential from 8.207 V down to 0.207 V at a scan rate of 10 mV s⁻¹ using a potentiostat (Radiometer Analytical S.A.).

The surface topography and the surface roughness were followed by atomic force microscopy (AFM, Dimension 3100, Digital Instruments). In order to perform AFM measurements, the specimens were systematically ground with various grades of SiC papers and finally using a 4000 grit SiC emery paper, which has a typical particle size of approximately 3 μm. Subsequently, the specimens were electropolished in methanolic 3 M sulfuric acid solution by potentiostatically holding at 8 V for approximately 15 min. Surface topography was measured multiple times at different locations on the specimen. The average root mean square (RMS) roughness value was obtained using the WSxM software [25]. The field emission scanning electron microscope (FE-SEM, LEO 1550VP, GEMINI) equipped with an energy dispersive spectrometer for X-ray microanalysis (EDX) was also used to investigate the morphology of the electropolished specimen.

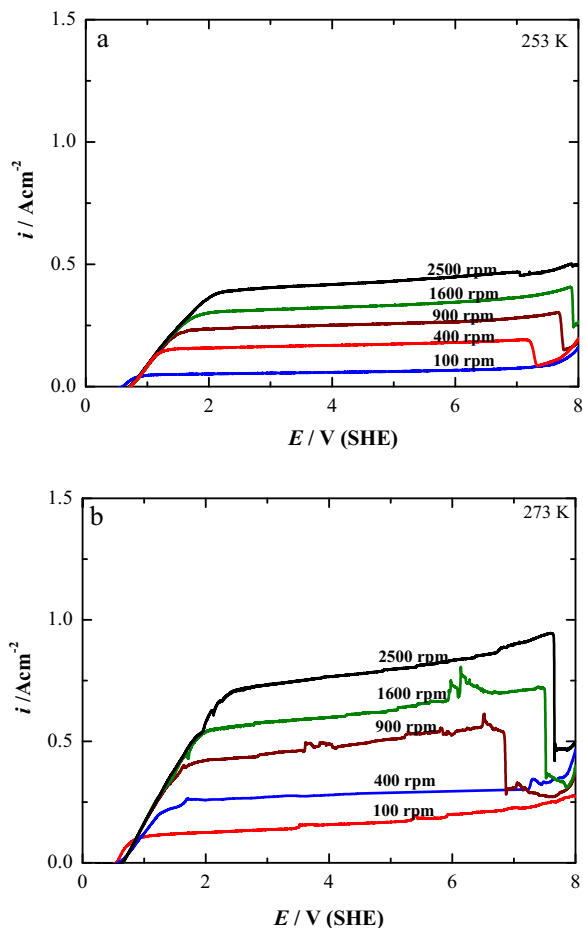


Fig. 1. Anodic polarisation curves of NbTi in methanolic 3 M H₂SO₄ at various rotation rates. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s⁻¹ at a temperature of (a) 253 K or (b) 273 K.

3. Results and discussion

To attain consistent and comparable results, all polarisation curves were obtained by scanning backward from 8.207 V to 0.207 V at a scan rate of 10 mV s⁻¹. This step was used to assure that the starting surface condition is similar for all experiments and to avoid any in-homogeneities.

3.1. Effect of rotation and temperature

Fig. 1 shows the polarisation curves obtained at different rotation rates and at constant temperatures of 253 K and 273 K. The curves exhibit a wide potential regime of limiting current density plateau. The observance of limiting current density plateau suggests a mass transport limited dissolution. Also it can be seen that, the magnitude of the limiting current density varies with change in rotation rate. The increase in rotation rate leads to increase in the limiting current density magnitude. The Levich equation allows identifying charge transfer and mass transport controlled reactions. Following the Levich behaviour conditions at the rotating disc electrode, the limiting current density in the presence of the salt film is given by Eq. (1)

$$i_l = 0.62nFD_{\text{eff}}^{2/3}\gamma^{-1/6}(C_{\text{sat,NbTi}} - C_{\text{b,NbTi}})\Omega^{1/2} \quad (1)$$

where n is the number of electrons involved in the reaction, F is Faraday constant, D_{eff} is the effective diffusion coefficient of dissolving species, γ the kinematic viscosity, Ω the electrode rotation

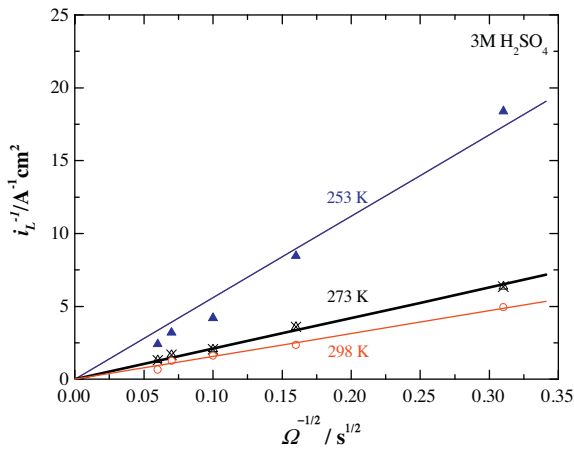


Fig. 2. Inverse of the limiting current density plotted as a function of the inverse of the square root of rotation rate in 3 M H₂SO₄.

rate, $C_{\text{sat,NbTi}}$ the saturation concentration of dissolved species and $C_{\text{b,NbTi}}$ is the bulk concentration which is zero in the beginning.

The mass transport behaviour can be described by a Koutecky–Levich plot as shown in Fig. 2. The inverse of the limiting current density is plotted as a function of the inverse square root of the rotation rate. The limiting current density values are taken from the current plateau at a potential of 4 V from Fig. 1. The limiting current density varies linearly with a distinct slope and zero intercept indicating a purely mass transport controlled process [18–20].

The temperature influence on the limiting current density can also be seen from Fig. 1. The magnitude of the limiting current density increases with increase in processing temperature. This can also be followed by the slope shown in Fig. 2. The slope decreases with increase in temperature. Fig. 3 shows an Arrhenius plot, which relates the limiting current density with process temperature:

$$i_l = k_0 \exp^{-E_a/RT} \Omega^{1/2} \quad (2)$$

where k_0 is constant and independent of temperature, R the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and E_a is the activation energy for the process studied.

The slope of the linear fit to the data points as shown in Fig. 3, would allow deducing the activation energy of the process. For the current case, the activation energy (E_a) was approximately 16.1 kJ mol^{-1} . Considering the typical activation energy for the electro-dissolution processes for valve metals like Ti and Ta, this

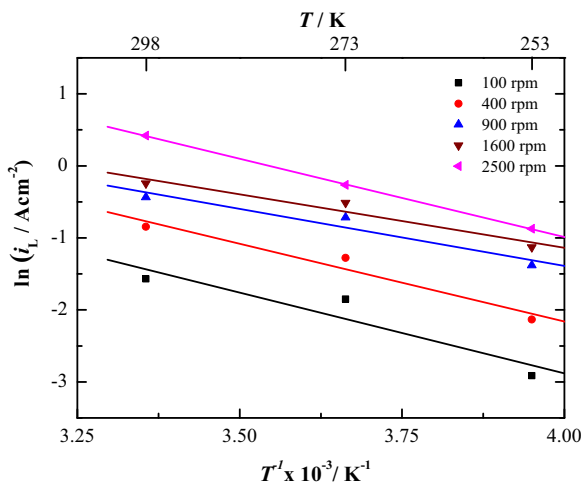


Fig. 3. Arrhenius plot of the limiting current density for various rotation rates in methanolic 3 M H₂SO₄ solution.

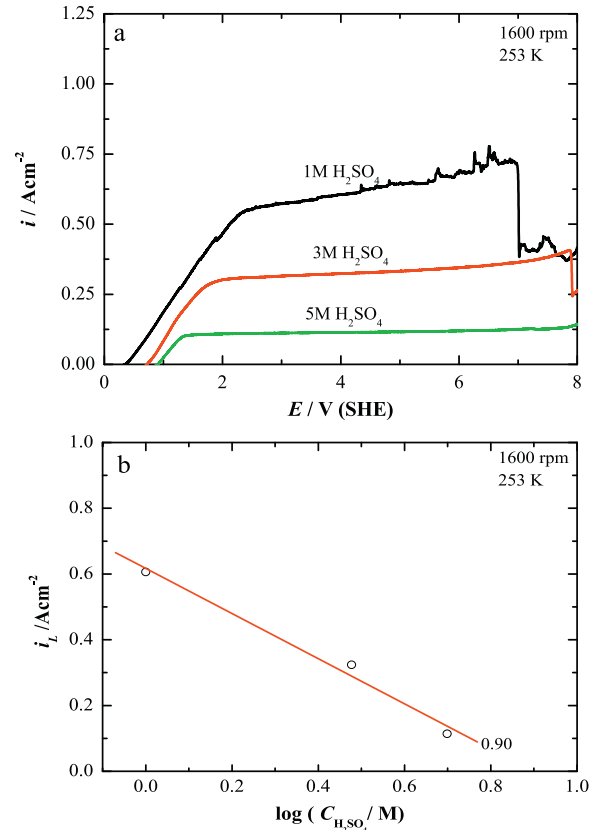


Fig. 4. (a) Anodic polarisation curves of NbTi at 253 K, at a constant rotation rate of 1600 rpm in various concentration of methanolic sulfuric acid. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1} . (b) Relation between limiting current density and logarithm of sulfuric acid concentration. The temperature was maintained constant at 253 K and is plotted for a constant rotation rate of 900 rpm.

value lies between that of pure Ta ($E_a = 14.6 \text{ kJ mol}^{-1}$) and pure Ti ($E_a = 21.6 \text{ kJ mol}^{-1}$) [18,19]. The discussion on electropolishing mechanism of pure Nb does exist, however there are no values quoted for the activation energy for electro-dissolution of Nb [22].

3.2. Influence of the sulfuric acid concentration

Fig. 4a shows the anodic polarisation behaviour of NbTi recorded in methanolic 1 M, 3 M and 5 M sulfuric acid solution at a constant temperature of 253 K and at a rotation rate of 1600 rpm.

In all the cases, the curves exhibit a typical limiting current density plateau extending over a certain potential range, which proves the mass transport controlled process. In methanolic 3 M and 5 M sulfuric acid solution, the limiting current density plateau is nearly flat (i.e. independent of potential) and extends over a wide potential window, whereas in 1 M sulfuric acid solution the limiting current density plateau is not that constant and shows a comparatively narrow potential window. Comparing the magnitude of the limiting current density, it decreases with increase in sulfuric acid concentration ($C_{\text{H}_2\text{SO}_4}$), showing the least limiting current density in methanolic 5 M sulfuric acid solution. This might be due to the decrease in solubility with increase in sulfuric acid concentration [19]. The viscosity changes associated with increase in sulfuric acid concentration can also be argued as a reason for the decrease in limiting current density. However, a quick calculation using the kinematic viscosity values (for 3 M and ~5 M) reported by Piotrowski et al. [19] shows that, even after kinematic viscosity correction, the limiting current density shows a clear decrease ruling out the effect of viscosity. In Fig. 4b, the limiting current density

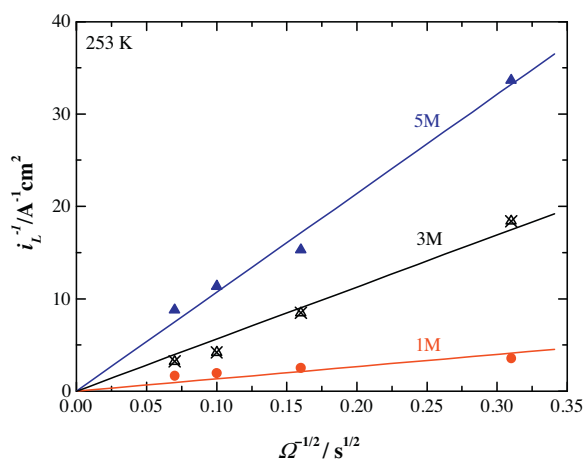


Fig. 5. Inverse of the limiting current density plotted as a function of the inverse of the square root of rotation rate in methanolic 1 M, 3 M, 5 M H_2SO_4 solution.

is plotted as a function of the logarithm of acid concentration. The limiting current density (i.e. the measure of dissolution) decreases linearly with increasing $\log c_{\text{H}_2\text{SO}_4}$. Extrapolation of the line to a zero current yields a concentration of 7.7 M. This defines a possibility to vary the material removal rate and to attain characteristic levelling.

As discussed earlier to establish the effect of rotation rate on the electro-dissolution in methanolic 3 M H_2SO_4 solution, similar experiments were performed for 1 M and 5 M H_2SO_4 solution. Fig. 5 shows the Koutecky–Levich plot obtained for the electro-dissolution of NbTi in 1 M and 5 M H_2SO_4 in 253 K (also compared with 3 M H_2SO_4). The variation of the inverse of limiting current density with inverse of rotation rate shows a linear behaviour with distinct slope and zero intercept. In all the sulfuric acid concentrations studied, the electro-dissolution is mass transport controlled. Normally, a mass transport controlled electro-dissolution is one of the pre-requisite to obtain smooth, flat and bright surface (electropolishing).

Thus in order to electropolish NbTi a mixture of methanol and 1 M, 3 M and/or 5 M sulfuric acid can be utilized. From an electro-chemical aspect, referring to Fig. 4, 1 M sulfuric acid solution might not be suitable because it shows very high, comparatively narrow and variable limiting current density plateau. This limits practically the available operating window. Therefore a 3 M and/or 5 M sulfuric acid solution could be a better choice for electropolishing. However, from processing time very low dissolution rate is not usually recommended, hence a 3 M sulfuric acid in methanol is considered optimal. An elaborate study relating the influence of sulfuric acid concentration and the resulting surface-topography and roughness from exclusive characterisation point of view, would be worthwhile to as a future study.

3.3. Rate limiting species and mechanism of electropolishing

The influence in dissolution due to change in sulfuric acid concentration allows to identify the possible rate limiting species. In general the possible rate limiting species taking part directly or indirectly in the dissolution reaction are the cations, i.e., the dissolving titanium and/or niobium in the anodic salt film, the electrolyte sulfate anions, and water molecules in the diffusion layer between alloy surface and the bulk solution.

As discussed earlier, with reference to Fig. 4, the limiting current density is inversely proportional to the change in sulfuric acid concentration. Obviously, the transport of sulfate anions from bulk

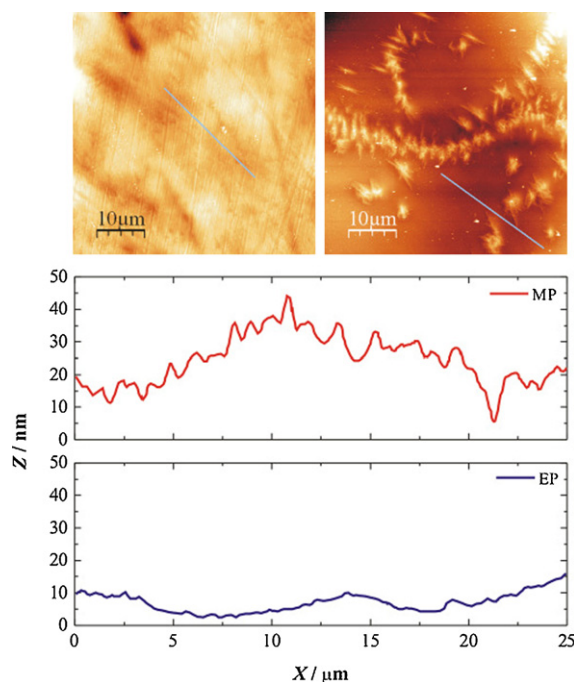


Fig. 6. The comparison of the AFM topography and roughness trace for a mechanically polished and an electropolished NbTi specimen. The surface was mechanically polished to a 4000 grit paper and subsequently electropolished.

of electrolyte towards surface cannot be the rate limiting species. If so, the removal rate should increase rather than decrease.

The other probable rate limiting species could be the transport of H_2O to hydrate the soluble titanium and niobium species, which can be transported away. Normally, the (95–97%) concentrated sulfuric acid used would have a water content between 2.7 and 1.6 M [23]. Therefore, as the sulfuric acid concentration in methanol increases there is an apparent increase in water content in the electrolyte. The qualitative influence of the residual water content on the dissolution can be seen in Fig. 4. The notable effect is a wider passive region in the polarisation curve and the decrease in the magnitude of the limiting current density. The limiting current density decreases with increase in residual water; hence H_2O cannot be the rate determining species. Therefore, the only plausible rate limiting species is the transport of soluble Ti and/or Nb cations into the bulk electrolyte. Thus, the electro-dissolution (electropolishing) of NbTi in methanolic sulfuric acid follows a salt-film mechanism. However, in order to confirm this, (i.e. the rate determining species and the nature of salt-film) further experiments using electrochemical impedance spectroscopy (EIS) during electropolishing are required, which would be the scope of future work.

3.4. Surface characterisation of NbTi electropolished in methanolic 3 M sulfuric acid

Mechanically polished (4000 grit paper) specimens were electropolished in methanolic 3 M sulfuric acid solution by potentiostatically holding at 8 V for approximately 15 min. The process temperature was maintained constant at 253 K. The surface of the electropolished specimen was visually bright and smooth. However, at certain spots, the surface was hazy and rough. Subsequently, surface topography and roughness was characterised by AFM measurements. To highlight the effect of electropolishing, the topography of a mechanically polished specimen is also compared. Fig. 6 shows the traced topography of a mechanically polished and an electropolished specimen. The average RMS roughness value for an electropolished specimen (~ 10 nm) is sig-

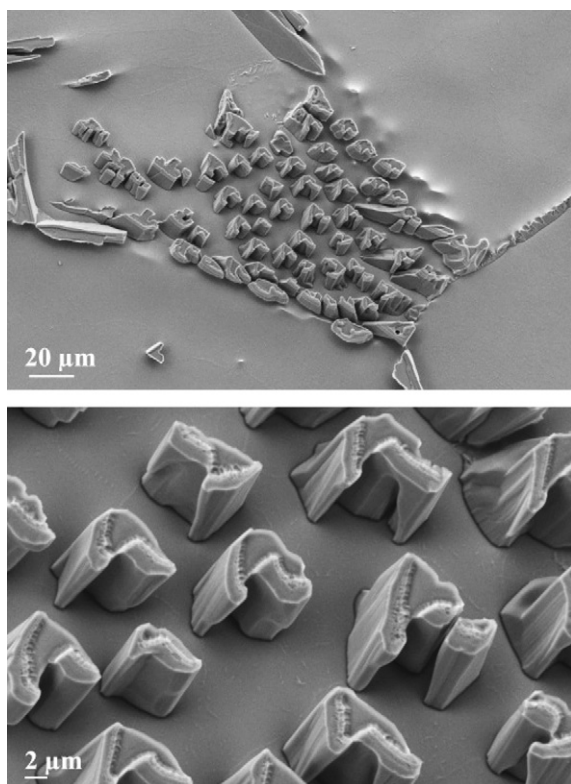


Fig. 7. (a) SEM micrograph of the electropolished NbTi specimen. The Ti enriched Nb particulates can be seen. (b) The magnified Ti enriched Nb particles.

nificantly lower as compared to that of a mechanically polished specimen (~ 48 nm). The wavy pattern as a result of electropolishing process is also clearly evident from the roughness trace. At certain spots, the topography reveals a variation in contrast (due to height difference), which appeared hazy and rough during visual observation. In order to confirm this, surface characterization by scanning electron microscopy (SEM) was performed. A typical morphology of an electropolished specimen is shown in Fig. 7. In general, the SEM micrograph shows smooth surface with randomly distributed particles. A semi-quantitative analysis by EDX revealed these particles as Ti enriched Nb particles of composition 95.4 at.% Ti and 4.6 at.% Nb. It is supposed that the origin of these particles in this instance is an artefact related with the casting process. Such a particle might be exposed after electropolishing of the alloy owing to the higher dissolution of the matrix surrounding it.

4. Conclusions

In the present study, the electro-dissolution behaviour of NbTi in methanolic sulfuric acid solution was examined. From the results obtained the following conclusions can be drawn.

1) Non-aqueous methanolic sulfuric acid solution is well suited for NbTi electropolishing.

- 2) The rotation rate, temperature and concentration of sulfuric acid influence the dissolution kinetics.
- 3) The activation energy for the dissolution process is 16.1 kJ mol^{-1} .
- 4) The removal rate (dissolution) decreases with increase in sulfuric acid concentration, owing to decrease in solubility.
- 5) The dissolution is mass transport controlled in all concentrations of the electrolyte investigated. Basically, all concentrations are suitable for electropolishing of NbTi alloys. From an electrochemical perspective, a 3 M sulfuric acid is preferred. An elaborate study relating the influence of sulfuric acid concentration and the resulting surface-topography and roughness from exclusive characterisation point of view, would be scope of future work.
- 6) The dissolving cationic species was identified to be rate limiting.
- 7) Smooth and flat surface can be obtained by holding at 8 V in methanolic 3 M sulfuric acid solution at 253 K. The roughness of such an electropolished surface is significantly lower than that of a mechanically polished surface (4000 grit).

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