Rotating disc electrode study of the electropolishing mechanism of NiTi in methanolic sulfuric acid

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Abstract

The mechanism during electropolishing of NiTi in methanolic 3 M sulfuric acid is elucidated based on the investigations carried out using a rotating disc electrode (RDE). The influence of the rotation rate, temperature and the addition of Ni and Ti ions in solution on the dissolution kinetics are investigated and analysed. The dissolution of NiTi during electropolishing exhibits Levich behaviour confirming mass transport as the rate-limiting step. The temperature dependence shows a typical Arrhenius behaviour and the activation energy for dissolution is $E_a = 19.2$ (± 1.33) kJ mol^{-1}. The addition of metal ions to the electropolishing solution results in a lower limiting current density for both, Ni^{2+} and Ti^{4+} addition. This confirms the mass transport of dissolved species from the anode surface to the bulk of the solution as the rate-determining step.
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1. Introduction

Equiatomic nickel titanium (NiTi) shape memory alloys possess superior mechanical properties and hence are more preferred in certain biomedical applications than conventional biomaterials like Ti alloys, and stainless steels (SS). Some examples are, stents, simon vena cava filters, and atrail septal occlusion devices [1]. The biocompatibility and corrosion resistance of NiTi in physiological media is attributed to the formation of an innocuous layer of TiO$_2$. Even though the corrosion behaviour is better than that of SS, higher concentrations of Ni may promote allergic reactions [2,3]. Various studies on NiTi alloys report the dependence of its biocompatibility and corrosion behaviour on surface conditions [4]. Efforts are directed in understanding and enhancing the surface stability of NiTi by surface modifications. Several surface treatments have been developed which promote oxidation of NiTi and improve the corrosion resistance of the alloy [5]. Among various methods, electropolishing is one of the conventional, inexpensive and effective methods in treating implants which generally have intricate shapes and geometries.

Efforts to understand fundamental mechanisms of electropolishing date's back to the 1930s and have been widely studied ever since. As a later development electropolishing was realised for various metals and alloys under different conditions and in different electrolytes. Landolt reviewed the fundamental aspects of electropolishing [6].

Tousek reported on electropolishing of various metals in alcoholic solutions of sulfuric acid [7]. Heinrich et al. carried out experiments to understand the mechanism during electropolishing of Ni in non-aqueous solution namely, 2 M methanolic sulfuric acid [8]. Electropolishing conditions for valve metals like Ta and Ti are well established using non-aqueous solutions [9,10] but little information has been reported on NiTi. Among few studies on electropolishing of NiTi, Pohl et al. reported on the electrolytic processing of NiTi using different solutions [11]. Later, electropolishing of NiTi using a methanolic sulfuric acid solution was studied by Barison et al. and Fushimi et al. [12,13]. Fushimi et al. described that electropolishing of NiTi at 263 K in 3 M methanolic sulfuric acid results in a mass transport controlled anodic dissolution which renders a smooth, flat and bright surface.

However, a systematic and complete investigation is still missing to substantiate these findings. The current study focuses

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on understanding the underlying mechanism of electropolishing of NiTi, to elucidate the mass transport phenomenon.

The rotating disc electrode (RDE) technique is a well-established method to study the reaction behaviour under hydrodynamic conditions to differentiate between charge transfer and mass transport controlled reactions [14]. RDE studies were extensively used to understand the mechanism which governs electropolishing of valve metals such as Ta and Ti [9,10]. Here we report on studies carried out using a RDE to understand the mechanism of electropolishing of NiTi in more detail.

2. Experimental

A commercially available pure NiTi wire (Goodfellow, Ni55/Ti45) of 0.8 mm diameter was used as a disc electrode (working electrode). The wire was inserted in a Teflon holder exposing only the cross section as disc with a surface area of 0.005024 cm^2. The discs were mechanically polished up to 4000 grit emery paper, 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 1600 rpm using external mode of control by a radiometer potentiostat (Voltalab-PST050). A 3 M KCl silver–silver chloride (SSE 3 M KCl) and gold were used as reference and counter electrode, respectively. All potentials in this paper refer to the SHE reference electrode at 298 K.

The test solution was a 3 M H$_2$SO$_4$ containing methanol which was prepared from analytical grade 95–97% sulfuric acid and methanol (pro analysi, Merck). To investigate the effect of addition of Ni and Ti ions, the electrolyte was prepared by electrolytically dissolving pure Ni or Ti respectively, in methanolic 3 M H$_2$SO$_4$ solution. The choice of electrochemical route was based on the fact that Ti(SO$_4$)$_2$ cannot be prepared from aqueous solutions, as it would form TiOSO$_4$. Similarly, for Ni ions, thermal dehydration of NiSO$_4$·6H$_2$O without decomposition was possible only down to the monohydrate (160 °C, 24 h). Addition of the salt to the saturation concentration for Ni^{2+} increased the water amount in the electropolishing solution too much where no bright surface could be achieved anymore. Drying at higher temperature yielded a product that was completely insoluble in the methanolic 3 M sulfuric acid. Heinrich and Feller recorded a similar observation while studying the electropolishing of Ni in methanolic 2 M sulfuric acid [8]. The experimental temperature of 298, 273 and 263 K were maintained using a cryostat (Lauda RC20-CP).

Anodic polarisation curves were determined by setting the potential at 8.207 V and then sweeping down to 0.207 V at a scan rate of 10 mV s^{-1} using a potentiostat. The anodic polarisation curves show only data from 8 to 0 V, as the initial data points are skipped because they show unrealistic current densities due to the Debye charging (capacitive charging) of the surface after the potential pulse associated with the start of the experiment.
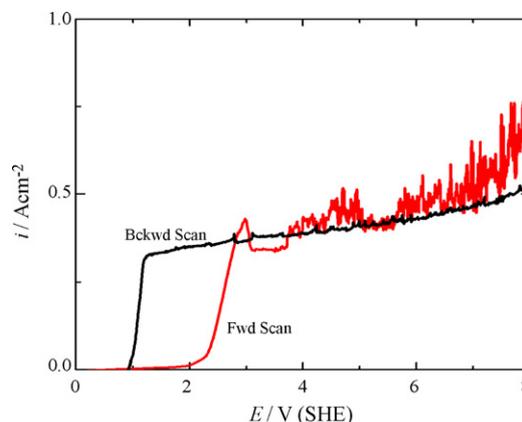

Fig. 1. Anodic polarisation curves of NiTi in methanolic 3 M H$_2$SO$_4$ at 298 K at 400 rpm. The potenial was swept from 0.207 to 8.207 V at a scan rate of 10 and −10 mV s^{-1}, respectively.

3. Results and discussions

3.1. Effect of scan direction

Fig. 1 compares the effect of scanning direction on polarisation behaviour of NiTi in methanolic 3 M sulfuric acid. The current versus potential behaviour of the NiTi disc electrode was recorded for a constant rotation rate of 400 rpm at 298 K by scanning the potential either from 0.207 to 8.207 V (forward scan) or back using a scan rate of 10 mV s^{-1}. The backward sweeping of potential renders a wider potential window of the limiting current density whereas a forward sweeping of potential leads to a narrow potential window of the limiting current density. The hindrance for the onset of limiting current during forward scanning is due to the formation of oxide. Even though the potential range for limiting current density plateau varies, the magnitude is more or less the same in both cases. This is quite different to the behaviour as described for Ti in methanolic 3 M sulfuric acid [10]. This indicates that the dissolution does not follow exactly the same mechanism as in the case of Ti. For NiTi, the dissolution of Ni plays an important role. A similar kind of behaviour was reported for NiTi in methanolic 3.3 M H$_2$SO$_4$ by Barison et al. [12].

In order to obtain consistent and comparable results, all polarisation curves were obtained by starting from 8.207 V and scanning in cathodic direction down to 0.207 V at a scan rate of 10 mV s^{-1}.

3.2. Effect of rotation and temperature

Fig. 2a–c show the anodic polarisation curves determined at different rotation rates and at 263, 273 and 298 K, respectively.

The curves exhibit a well defined and a wide potential range of limiting current density plateau. The wide potential range of limiting current density suggests the existence of a salt film, where the concentration of dissolved metal ions at the metal–electrolyte interface is constant and corresponds to saturated salt formed between the metal cations and the electrolyte anions. According to Grimm and Landolt [15] under these con-
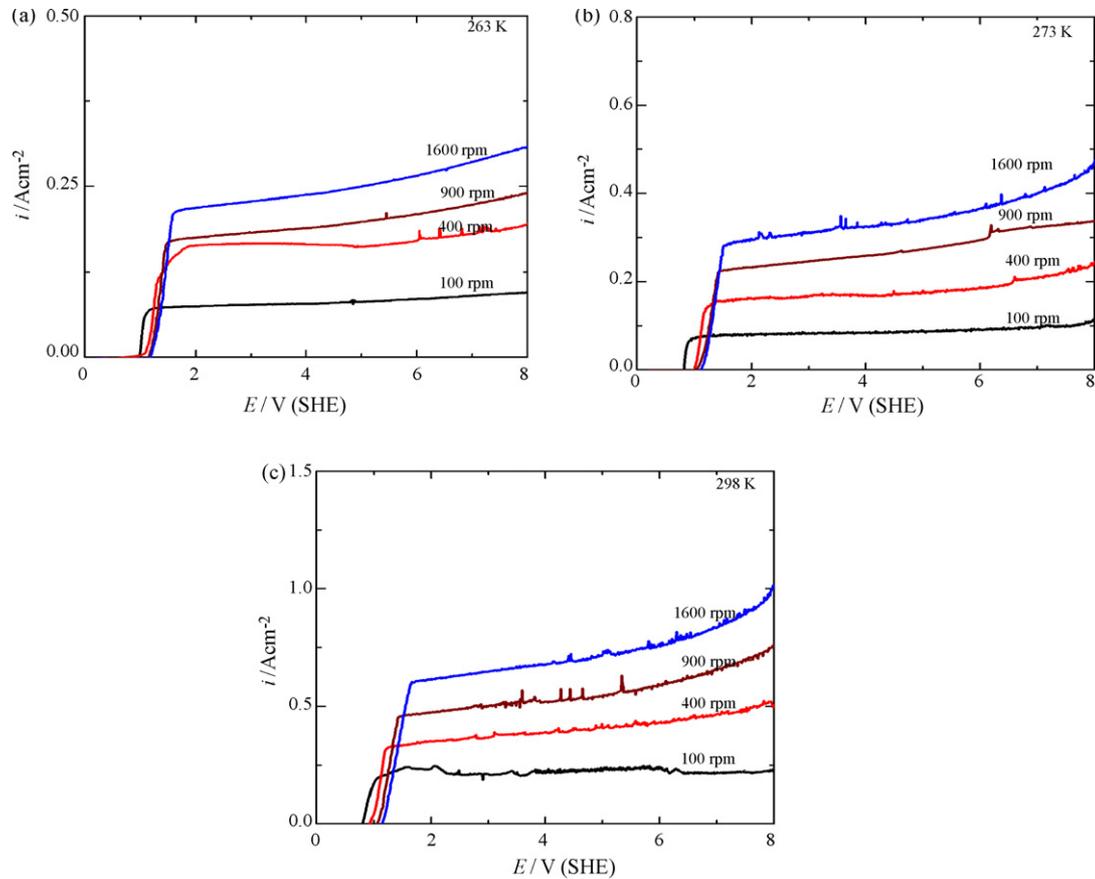
Fig. 2. (a) Anodic polarisation curves of NiTi in methanolic 3 M H_2SO_4 at 263 K at different rotation rates. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1}. (b) Anodic polarisation curves of NiTi in methanolic 3 M H_2SO_4 at 273 K at different rotation rates. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1}. (c) Anodic polarisation curves of NiTi in methanolic 3 M H_2SO_4 at 298 K at different rotation rates. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s.$^{-1}$.

ditions "…dissolution rate is mass transport controlled and involves diffusion and migration of metal ions through a stagnant (Nernst) diffusion layer, the thickness of which depends on rotation rate…". It is evident from the figures that upon increase in rotation rate the height of the plateau (magnitude of the limiting current) increases. Based on the above statement, the increase in rotation rate decreases the thickness of the Nernst diffusion layer, causing shorter path length for the diffusion of ions and hence a higher magnitude of the limiting current density

Based on the Levich theory, it would be possible to distinguish between mass transport control and charge transfer controlled reactions. Upon Levich behaviour at the rotating disc electrode, the limiting current density for the anodic dissolution of NiTi at limiting current density in the presence of the salt film is

$$i_L = 0.62 n F D_{eff}^{2/3} \upsilon^{-1/6} (C_{sat,NiTi} - C_{b,NiTi}) \Omega^{1/2} \qquad (1)$$

where n is the number of electrons involved in the reaction and D_{eff} is the effective diffusion coefficient of dissolving species, υ the kinematic viscosity, Ω the electrode rotation rate, $C_{sat,NiTi}$ the saturation concentration of dissolved species and $C_{b,NiTi}$ is the bulk concentration which is zero.

In the case of NiTi, the presence of two elements (Ni and Ti) makes it difficult to quantitatively determine the saturation concentration $C_{sat,NiTi}$. However, it is possible to qualitatively

elucidate the mass transport behaviour exhibited during electropolishing of NiTi. Fig. 3 shows the typical dependence of the inverse of the limiting current density on the inverse square root of the rotation rate. The limiting current density values were determined on the current plateau at a potential of 4 V from Fig. 2a–c. The variation of the limiting current density shows a linear behaviour with distinct slope and zero intercept indicating a mass transport controlled reaction [9,10].
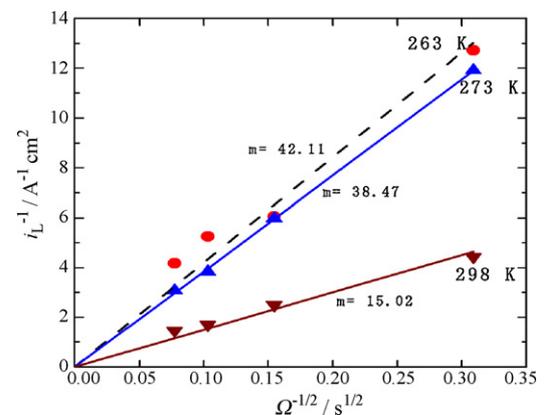

Fig. 3. Inverse of the limiting current density plotted as a function of the inverse of square root of rotation rate in methanolic 3 M H_2SO_4 at different temperatures.
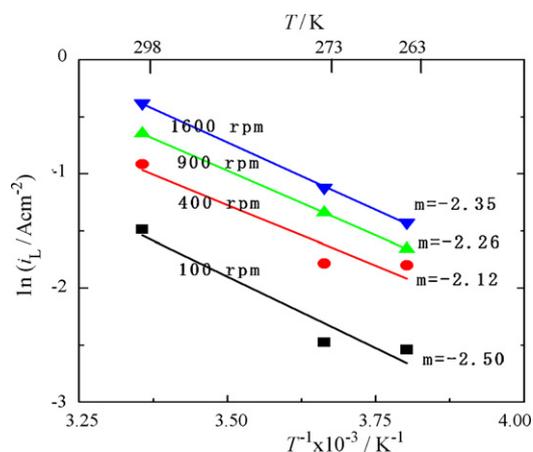
Fig. 4. Arrhenius plot of the limiting current density for different rotation rates in methanolic 3 M H_2SO_4.

Fig. 5. Anodic polarisation of NiTi in methanolic 3 M H_2SO_4 containing Ni^{2+} (0.74 M) and Ti^{4+} (0.18 M) at 263 K. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1} (under stationary condition).

Fig. 2a–c, also show the influence of the temperature on the magnitude of the limiting current density. The magnitude of the limiting current density increases with increasing temperature. The influence of the temperature on the slope is seen in Fig. 3 which exhibits a decrease of the slope with increasing temperature. The dependence of the limiting current density on the temperature can be depicted in an Arrhenius plot:

$$i_L = k_o \exp\left(\frac{-E_a}{RT}\right) \Omega^{1/2} \qquad (2)$$

where k_o is constant and independent on the temperature, R the gas constant and E_a is the activation energy for the process studied.

Fig. 4 shows the Arrhenius plot of the limiting current density for various rotation rates. The slope of the curve yields a value of $E_a = 19.2\ (\pm 1.33)$ kJ mol^{-1} for the activation energy. This value is higher than that of Ta, $E_a = 14.6$ kJ mol^{-1} but lower than that for pure Ti, $E_a = 21.6$ kJ mol^{-1} as reported by Piotrowski et al. [9,10].

3.3. Effect of addition of ions

In order to understand the rate-limiting step in electropolishing of NiTi, it is necessary to study the effect of presence of Ni and Ti ions in solution during electropolishing.

Fig. 5 shows the potentiodynamic polarisation of NiTi in a fresh electropolishing solution and in modified electropolishing solutions containing either Ni or Ti ions. The experiments depict two particular cases, one under addition of Ti ions to the saturation concentration (0.18 M) and the other one under addition of Ni ions at a known concentration of 0.74 M. Both were electrolytically prepared using pure Ti and Ni metals respectively. Assuming complete dissociation of the sulfuric acid and 100% current efficiency during Ti dissolution the maximum change of the pH value, as a measure for the compositional change of the solution, would be only from pH −0.77 to −0.72. This indicates that the procedure used does not significantly change the solution composition. The addition of ions causes a decrease in the limiting current density indicating a hindrance of the active
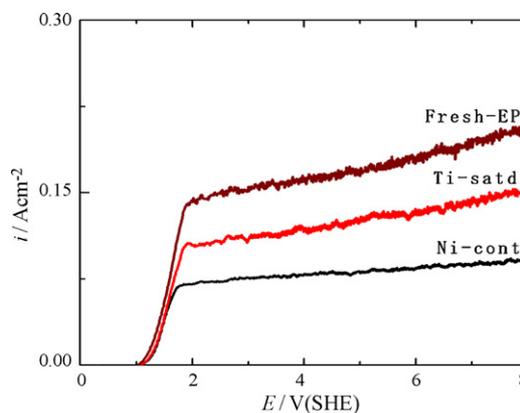
dissolution. The decrease in the limiting current density is 26% in a Ti saturated solution and 52% in a Ni containing solution as compared to the limiting current density recorded in a fresh electropolishing solution. The decrease in limiting current density in the presence of ions in the bulk of the solution is most probably due to lowering of the concentration gradient between the surface and the bulk of the solution, the driving force for mass transport. Attaining the saturation limit by addition of ions in electropolishing solution would cause a complete hindrance of the dissolution. A strict quantitative behaviour could not be ascertained here, as deviations could occur when side reactions dominate; for example the formation of NiS_2O_7 as suggested by Heinrich et al. [8]. For an intermetallic having an ordered structure of the constituting elements namely A and B, the dissolution of an element A, leads to the formation of a surface consisting solely of B and under these circumstances the reaction deviates to allow dissolution even in a saturated electropolishing solution.

RDE experiments were carried out in these modified solutions where Fig. 6a and b (in 6b only part of the curve is shown, i.e. up to 6 V) show the increase in the limiting current density with rotation rate similar to the case shown in Fig. 2. However, it can be easily seen that the limiting current density in Fig. 6a and b is comparatively lower than that in Fig. 2. Fig. 6b, shows an offset to a potential of 1.25 V for a rotation rate of 1600 rpm. The exact reason for this offset is not clear, still the resulting surface is similar to that obtained at lower rotation rates. Fig. 7 shows the Levich plot, where the variation of the limiting current density exhibits a linear behaviour with distinct slope and zero intercept confirming a mass transfer controlled reaction. Additionally, the Levich plot obtained in an unmodified electropolishing solution is shown for comparison. It is clear that the slope is higher after addition of ions, indicating an effective hindrance for active anodic dissolution due to the ions in solution. Piotrowski et al. [11] reported a decrease in the limiting current density with addition of Ti ions to solution during electropolishing of Ti in methanolic 3 M sulfuric acid solution. From an extrapolation of limiting current density for various Ti^{4+} concentrations they determined the saturation concentration at which the limiting current density is equal to zero. Heinrich et al. in their studies with Ni in methanolic 2 M sulfuric acid reported a
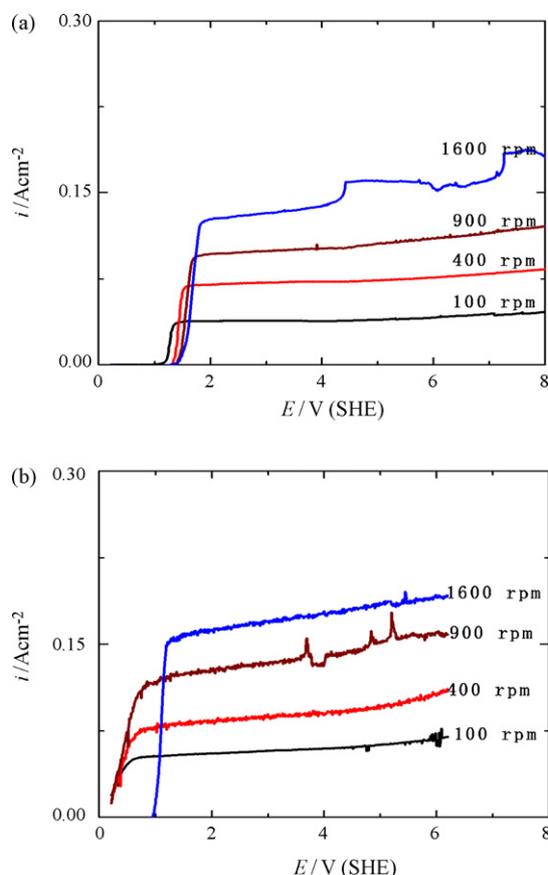
Fig. 6. (a) Anodic polarisation curves of NiTi in Ni^{2+} containing (0.74 M) methanolic 3 M H_2SO_4 at 263 K at different rotation rates. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1}. (b) Anodic polarisation curves of NiTi in Ti^{4+} saturated (0.18 M) methanolic 3 M H_2SO_4 at 263 K 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} (part of curve is shown, up to 6 V).
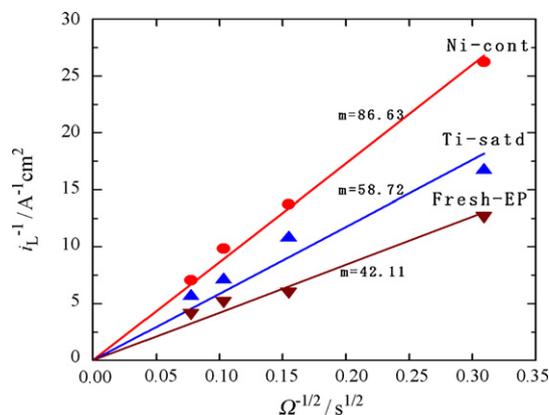

Fig. 7. Inverse of the limiting current density plotted as a function of the inverse of the square root of rotation rate in Ni^{2+} and Ti^{4+} containing methanolic 3 M H_2SO_4 at 263 K. Also shown for comparison are the values obtained in unmodified electropolishing solution as in Fig. 3.

linear decrease of the limiting current density as an effect caused by the presence of Ni ions in the bulk of the solution during electropolishing [7]. The similar argument holds good, in the case of NiTi suggesting the anodic dissolution as the rate controlling step which depends on both, dissolved Ni and Ti ions.

4. Conclusions

Systematic investigations on the influence of electropolishing parameters (scan direction, rotation rate, process temperature and addition of ions) provide a mechanistic understanding of the electropolishing of NiTi.

During potentiodynamic experiments, the scanning direction produces a significant difference in the current versus potential behaviour, suggesting that the history of the NiTi surface plays a significant role.

The mechanism of electropolishing was studied using rotating disc electrode experiments. The limiting current density increases with increase in the rotation rate. The Levich plot shows a mass transfer controlled reaction as the rate-limiting step during electropolishing of NiTi. The temperature dependence on the electropolishing of NiTi shows a typical Arrhenius behaviour with an activation energy of 19.2 ($\pm$1.33) kJ mol^{-1}

The addition of ions to the electropolishing solution shows a corresponding decrease in the limiting current density. Both, Ni and Ti ions influence the dissolution rate of NiTi, however in very different manner. This is concluded from the decrease of the limiting current density in the presence of the involved ions Ni^{2+} or Ti^{4+} in the electropolishing solution. This confirms that the mass transport of dissolved species from the surface to the bulk of the solution is the rate-determining step.

A quantitative prediction of the ion addition on limiting current density was not possible as even in Ti saturated solution still electropolishing was possible, probably due to the complex kinetics involving polysulfates such as NiS_2O_7. This question and the changes in viscosity are subject of ongoing research.

Acknowledgements

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