Electropolishing of a Nickel–Titanium–Copper Shape Memory Alloy in Methanolic Sulfuric Acid

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Electropolishing of NiTiCu shape memory alloy was performed in methanolic sulfuric acid as a surface processing method. The current investigation, using a rotating disk electrode, aims at identifying appropriate electropolishing conditions for this alloy based on understanding the underlying mechanism. The influence of temperature, rotation rate, and sulfuric acid concentration (3 or 5 M H_2SO_4) was quantified. Electropolishing in methanolic 5 M H_2SO_4 is solely mass-transport-controlled, while a mixed control is found for the methanolic 3 M H_2SO_4. This behavior is different from that of the binary NiTi alloy. From the electrochemical perspective, a methanolic 5 M H_2SO_4 solution is more suitable for electropolishing NiTiCu. The activation energy for electrodissolution is 21.5 kJ mol^{-1}.
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Shape memory alloys such as NiTiCu, and the far more studied NiTi, show special mechanical properties, namely, superelasticity and the shape memory effect. This offers a wide range of application in mechanical and biomedical fields.[1-7] Their application as orthodontic arch wires, stents, and microactuators are well known.[1,8] The need for electropolishing NiTi is motivated by the fact that a smooth, flat, and shiny surface is attractive from both a biomedical engineering and cosmetic point of view.[9] The electrodissolution behavior of titanium and its alloys has been explored by various authors.[10-14] The addition of Cu to NiTi as the third alloying element influences various properties among which the characteristic temperature of martensitic transformation and the corrosion resistance are only two examples.[15] The leveling geometry of NiTi alloys in methanol containing 3 M sulfuric acid was explained by Fushimi et al.,[10] which proves the potential of this solution in electropolishing NiTi. The current study compares the electropolishing behavior of NiTiCu in 3 and 5 M methanolic sulfuric acid using a rotating disk electrode (RDE) setup and proves that there is a change in the mechanism as compared to the binary alloy.

Experimental

NiTiCu alloys of composition 44.59 wt % Ni; 44.76 wt % Ti; 10.65 wt % Cu (40.80 atom % Ni, 50.20 atom % Ti, 9.00 atom % Cu) in the form of disks or as small cylinders were used as specimens. The disks, 1 cm in diameter, were mechanically ground up to 4000 grit emery paper, finalized with 1 μm diamond slurry, rinsed with distilled water, ultrasonicated in ethanol, and dried. The electropolishing of the NiTiCu disks was performed by applying a potential of 8 V for 500 s.

Rods were metallographically prepared as described above and were inserted into a poly(tetrafluoroethylene) holder so as to expose a working area of 0.0226 cm^2 as a disk. A silver-silver chloride electrode and gold electrode were employed as reference and counter electrode, respectively. In this paper, the potentials are quoted with respect to a standard hydrogen electrode (SHE). For the rotating disk experiments an EDI 101 (Radiometer Analytical S.A.) RDE setup was used along with a CTV 101 (Radiometer Analytical S.A.) rate controller to set the rotation rate. The different rotation rates between 100 and 1600 rpm were externally controlled by the potentiostat (Voltalab PST050). The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1}. A cryostat (Lauda RC20-CP) was used to control the experimental temperatures of 263, 273, and 293 K. In the figures depicting anodic polarization,

only the data from 8 to 0 V is shown. The initial data points are skipped, as these contribute least to the scope of the current discussion. The solutions used for electropolishing consisted of 3 or 5 M sulfuric acid in methanol. These solutions were prepared from analytical grade 95–97% sulfuric acid and methanol (water content ≤0.05%, per analysis, Merck).

Results and Discussion

Figures 1a and b show the anodic polarization curves for NiTiCu, obtained in methanolic 3 M sulfuric acid at different rotation rates and temperatures. The limiting current density shows a potential-dependent behavior, with an evident slope in the plateau. This slope might be associated with Joule heating, as reported earlier.[16,17] Figures 2a-c show the anodic polarization curves obtained in methanolic 5 M sulfuric acid. These curves show a potential independent limiting current density plateau between 2 and 8 V, suggesting that the dissolution rate is mass-transport-controlled. In the presence of a salt film, the limiting current density at a rotating disk is related to the rotation rate by Eq. 1

$$i_l = 0.62nFD_{eff}^{2/3}\gamma^{-1/6}(C_{sat} - C_b)\omega^{1/2} \qquad [1]$$

with D_{eff} the effective diffusion coefficient, γ the kinematic viscosity, C_{sat} the saturation concentration of dissolving species, C_b the bulk concentration, and ω the rotation rate.

It is evident from Fig. 1 and 2 that an increase of the rotation rate results in an increase in the magnitude of the limiting current density (the measure of electrodissolution). The electropolishing of the binary shape memory alloy NiTi was investigated under exactly the same conditions.[11] A significantly higher dissolution current density is found for the ternary NiTiCu alloy for 263 and 273 K, which is approximately twice as large at a rotation rate of 1600 rpm. However, this is not a simple increase but comes along with a change in the mechanism, as will be shown later.

The effect of acid concentration can be ascertained by comparing the magnitude of the limiting current density at a particular temperature (e.g., 263 K) for methanolic 3 M H_2SO_4 and 5 M H_2SO_4 solutions. The magnitude of limiting current density is higher in the former than in the latter. This is certainly due to the higher dissolution rate in 3 M H_2SO_4 as compared to 5 M H_2SO_4. Comparison of Fig. 2a-c brings out the qualitative effect of temperature on the electrodissolution process. The quantitative effect of temperature can be described by an Arrhenius plot, as shown below.

The rate-determining step is commonly identified by a Levich plot. Figures 3a and b show the reciprocal limiting current density (values taken at 4 V) plotted as a function of the inverse of square root of the rotation rate. To allow a direct comparison between bi-
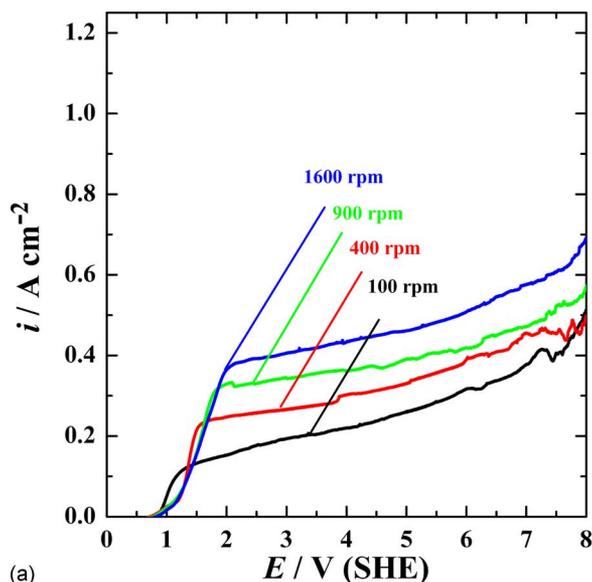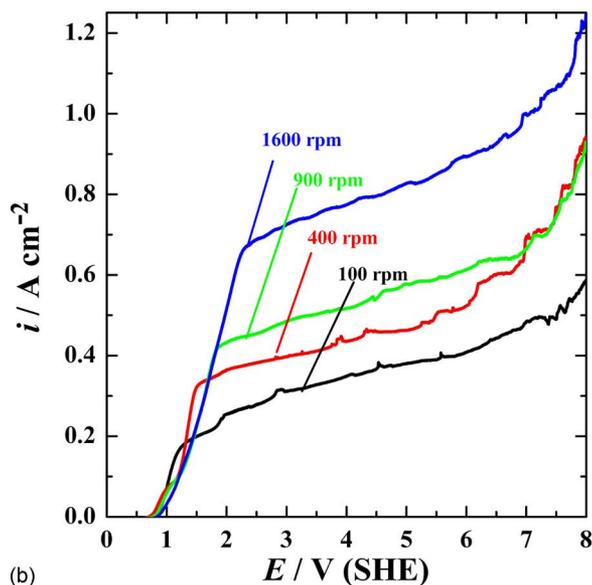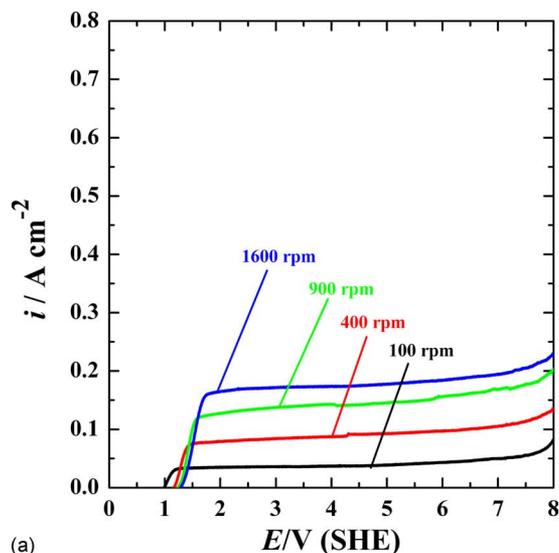
Figure 1. (Color online) Anodic polarization curves of NiTiCu in methanolic 3 M H_2SO_4 at different rotation rates. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1} at a temperature of (a) 263 and (b) 273 K.

nary and ternary alloys, the electropolishing data of NiTi in 3 M solution was reproduced from Ref. 11 and is given in Fig. 3a for both temperatures investigated here.

In Fig. 3a a linear regression of the data points produces a non-zero intercept for the NiTiCu, indicating mixed control with a significant contribution from a charge-transfer reaction. On the contrary, the electropolishing of NiTi is under pure mass control seen from the linear behavior with zero intercept. This demonstrates the strong influence of the Cu on the dissolution mechanism. Because Cu is a substitute of Ni but not of Ti, one might attribute this increase solely to acceleration by Cu. A quantitative estimation, however, shows an increase by roughly a factor of 2. This is surprising because the relative decrease of Ni, in a gedankenexperiment as the rate-determining element, is only 20%. Thus, a corresponding increase would be expected, but not a doubling.
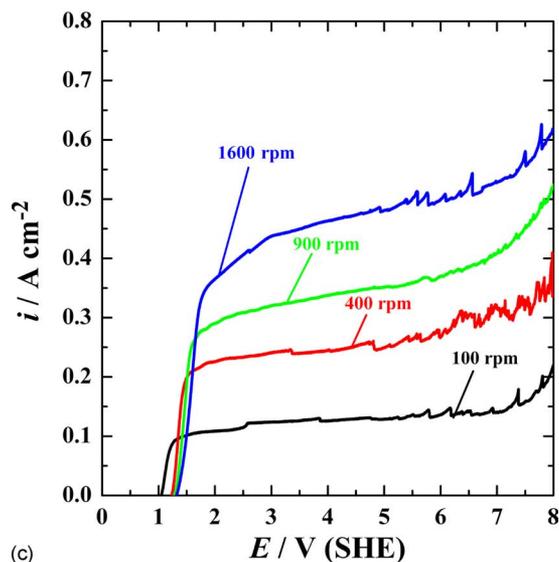
For a 5 M solution a linear behavior with a zero intercept is
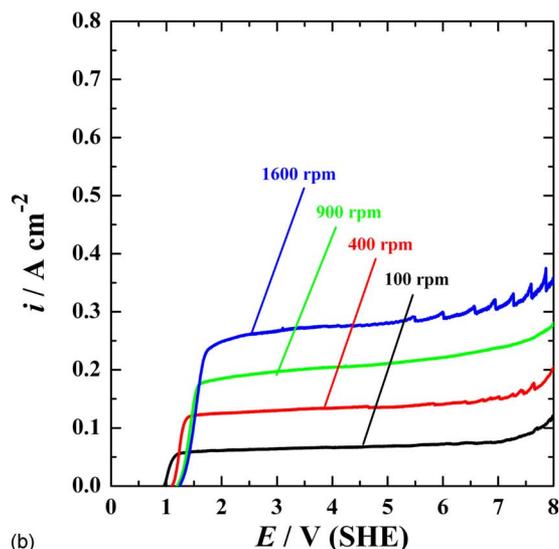
Figure 2. (Color online) Anodic polarization curves of NiTiCu in methanolic 5 M H_2SO_4 at different rotation rates. The potential was swept down from 8.207 to 0.207 V at a scan rate of 10 mV s^{-1} at a temperature of (a) 263, (b) 273, and (c) 293 K.
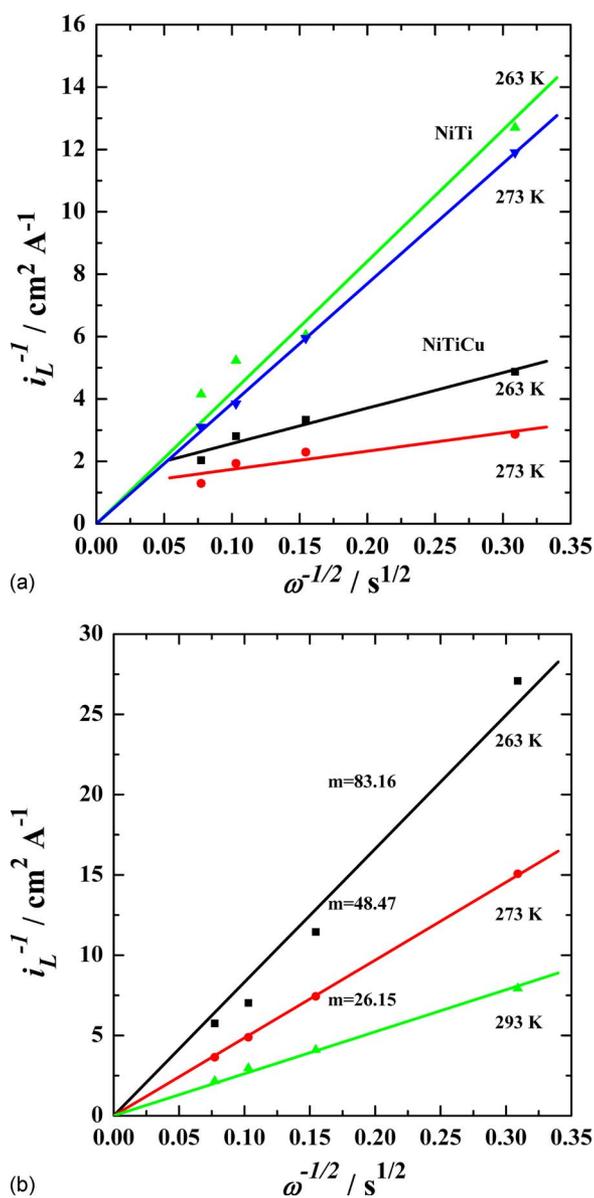
(a)

(b)

Figure 3. (Color online) Inverse of the limiting current density plotted as a function of the inverse of the square root of rotation rate in 3 M H_2SO_4. Data on the electropolishing of NiTi under identical conditions was reproduced from Ref. 11 to allow a direct comparison. (b) Inverse of the limiting current density plotted as a function of the inverse of the square root of rotation rate in 5 M H_2SO_4.

found even for the NiTiCu, as seen in Fig. 3b. Obviously the process becomes purely mass-transport controlled for the ternary system at this higher acid concentration.

According to Fushimi et al.,[10] the electrodissolution of NiTi was simultaneous for both elements involved and hence, the electrodissolution of NiTiCu can be represented as shown below

$$NiTiCu \rightarrow 41Ni^{m+} + 50Ti^{n+} + 9Cu^{p+} + (m + n + p)e^- \quad [2]$$
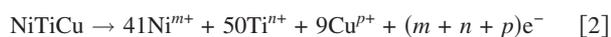
This formula represents the atomic composition of the materials used. The slope of Fig. 3b shows a clear increase with decrease in temperature. This effect of temperature can be analyzed by an Arrhenius plot, as elucidated in Fig. 4. The slope of the line allows calculating the activation energy for the electrodissolution (Eq. 2) in methanolic 5 M H_2SO_4 as 21.50 kJ mol^{-1}. This value is slightly higher than the value reported for electropolishing of NiTi in 3 M methanolic sulfuric acid.
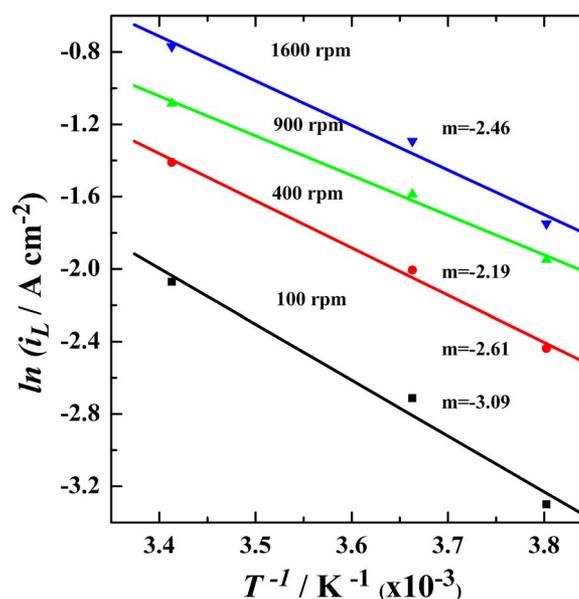

Figure 4. (Color online) Arrhenius plot of the limiting current density for different rotation rates in 5 M H_2SO_4.

The importance of mass transfer in leveling was elucidated by Landolt.[18] Therefore, from the electrochemical perspective, methanolic 5 M sulfuric acid solution is more suitable for electropolishing NiTiCu alloys, as it provides controllable electrodissolution with a well-defined limiting current density plateau. However, the electrodissolution rate is quite low compared to that in methanolic 3 M H_2SO_4. The strong concentration dependence may be the key point of further improvement of the electropolishing process. This may be realized by employing selectively saturated electropolishing solutions to allow both, a specific kinetic control and an improved dissolution rate. The determination of the required values such as solubility and element specific dissolution rate will be the scope of a further study.

Visual inspection of the polished samples in 3 and 5 M H_2SO_4 reveals a brighter surface for the latter. The surface roughness measurement gave a higher numerical value for 5 M H_2SO_4 compared to the sample polished in methanolic 3 M H_2SO_4. A similar relationship between surface roughness and acid concentration was reported for the binary NiTi alloy.[10]

Conclusion

The effect of temperature, rotation rate, and concentration of sulfuric acid in methanol on the electropolishing performance of NiTiCu was investigated using a RDE. From the Levich plot, electropolishing in methanolic 3 M H_2SO_4 reveals a mixed control, i.e., significant contribution of charge-transfer as well as mass-transfer behavior.

The ordered atomic structure of ternary alloy leads to a coupling of the three elements during dissolution. This process results in a change in concentration, however, confined to the surface of only a few nanometers. The electrodissolution in methanolic 5 M H_2SO_4 solution is mass-transfer-controlled, which is more suitable for electropolishing. A rather small change in acid concentration from 3 to 5 M represents both the borderline for two electropolishing mechanisms and a sensitive actuating variable for the rate. The activation energy was determined to be 21.50 kJ mol^{-1} by means of an Arrhenius plot. It is noteworthy that the mechanism does not change with temperature. Thus, a precise concentration control is compulsory for successfully governing the overall process. Electropolishing in 3 and 5 M H_2SO_4 solution renders an optically brighter surface for the latter, however with higher nominal roughness than the former.

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