

ELECTROPOLISHING OF NIOBIUM FROM DEEP EUTECTIC SOLVENTS BASED ON CHOLINE CHLORIDE *

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Abstract

Niobium (Nb) was electropolished from choline chloride-based deep eutectic solvent (DES). The purpose of this paper was to systematically investigate the influence of various electropolishing parameters, including electropolishing time, electrolyte temperature and voltage, on the electropolishing rate, surface roughness and microstructure of Nb. The result showed that the electropolishing parameters had a significant impact on the performance of Nb. Prolonging electropolishing time and negatively shifting voltage, the electropolishing rate of Nb increased first and then decreased, and the roughness decreased first and then increased. With the electrolyte temperature increased, the electropolishing rate increased and surface roughness decreased. Based on surface analysis by scanning electron microscope (SEM), smoother Nb can be achieved under properly controlled conditions.

INTRODUCTIONS

The inner surface of niobium cavity plays a most important role in determining the efficiency and maximum accelerating gradient, various surface treatments are employed to get a smooth and clean surface. The electropolishing (EP) and buffered chemical polishing (BCP) processes have been used to polish the Nb surface of SRF cavities to eliminate the unevenness of the material's surface and to achieve possibly the highest surface smoothing effect. During the standard EP process, the electrolyte used for Nb surface is composed of HF and H₂SO₄ in a volume ratio of 1:9. BCP solution is a mixed acid solution of HF, HNO₃ and H₃PO₄ by volume ratio of 1:1:1 or 1:1:2. The mixed acid solution has huge potential hazards for operating personnel and environment. And some researches believed that only with the use of HF can breakdown of the strong passive film on the Nb surface. Due to the hazard of HF, HF-free electrolyte for the electropolishing of Nb is an important research direction. As an alternative, some non-aqueous solvents, for example, ionic liquid, provide an alternative to replace hazardous acidic mixtures for the electropolishing of Nb.

In recent decades, ionic liquids are of great interest for electrochemical purposes due to wide potential windows, thermal stability, high solubility of metal salts, avoidance of water and metal/water chemistry and high conductivity compared to non-aqueous solvents [1, 2]. Abbott and co-workers [3] introduced a relatively new class of ionic liquid, deep eutectic solvent (DES), based on eutectic mixtures of choline chloride (ChCl) with a hydrogen bond

donor species. DES is a powerful and potential media for the electropolishing of metals due to its low cost, environmental friendliness and high purity, and so on. To date, there are very few studies on the electropolishing of Nb from DES. Tarek M. Abdel-Fattah et al. [4, 5] used VB4 ionic liquid by mixing choline chloride, ethylene glycol and ammonium fluoride, in a 1:2:1 molar ratio. It was found that the VB4 polishing is capable of producing smooth Nb surfaces, and this ionic liquid is a viable replacement for acid-based methods for preparation of SRF cavities. However, the performance of Nb is affected by several experimental factors, such as the electropolishing time, voltage, current density, temperature, stirring process and so on. However, there was almost no paper reported the influence of electropolishing parameters on Nb.

Based on previous work, in the present study, we explored the electropolishing of Nb from a 1:2 ChCl-based ionic liquid. The effect of various electropolishing parameters, such as electropolishing time, temperature and voltage, on the electropolishing rate, surface roughness and microstructure of Nb was examined. The microstructure of Nb surfaces was investigated using scanning electron microscopy (SEM).

EXPERIMENTAL DETAILS

Choline chloride (ChCl), urea and ammonium fluoride (AF) were used as obtained. The ChCl-based ionic liquid was formed by stirring the mixture of the two components in a mol ratio of 1ChCl: 2urea in a beaker at 80°C until a homogeneous, colorless liquid formed. Then NH₄F was added to the mixture with gentle stirring to give the final ratio of 1ChCl: 2urea: 1AF.

The electropolishing of Nb samples was performed through a RST5200 electrochemical workstation with a three-electrode system, where a Cu plate (7 mm×20 mm) was used as working electrode, a Nb plate (20 mm×17 mm×3 mm) as counter electrode and a glassy carbon disk (1.0 mm diameter) as reference electrode. Before each set of experiments, the electrodes were cleaned in an ultrasonic acetone bath, rinsed with distilled water and dried. The set of parameters has been selected according to the most important factors established in preliminary trials, as follows: (1) duration time: from 10 to 30 min; (2) temperature: changed from 50 to 80 °C; (3) negative voltages: ranged from -3 V to -6 V, respectively. The stirring rate was approximate 100 rpm. After electropolishing, the sample was thoroughly cleaned with distilled water and ethanol, and then dried. Each sample repeated twice under the same condition before characterization. The electropolishing rate is: $v = m / (t * s)$,

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where m is the mass of metal removal, t is the electropolishing time, s is the metal electropolishing surface area.

Surface roughness was measured by RM-20 meter respectively. Each of the Nb samples was replicated ten times to find the average results for the roughness values. A scanning electron microscopy (SEM, Nova NanoSEM 450) was employed for the observations of the Nb morphology.

RESULTS AND DISCUSSION

Figure 1a shows the electropolishing rate for Nb as a function of the different electropolishing time. It can be seen that the electropolishing time strongly affects the electropolishing rate for Nb. With the electropolishing time increases from 10 min to 20 min, electropolishing rate for Nb sharply increase. Further increasing the electropolishing time, however, leads to decreases of electropolishing rate. During electropolishing process, noticeable bubbles are observed which may adsorb on anodic electrode. As a result, more bubbles absorbed on Nb surface may reduce the anodic dissolution rate with prolonging electropolishing time beyond a certain point. The variation of surface roughness of Nb with respect to the electropolishing time is presented in Fig. 1b. The surface roughness of Nb without electropolished is 1.5 μm , respectively. After electropolishing, surface roughness becomes lower than that of raw sample. With the electropolishing time increased from 10 min to 20 min, the roughness of Nb decreases. However, further prolonging the time to 25 min leads to the roughness decreasing. When the time ranges from 25 min to 30 min, the roughness slowly increases. As a result, we choose 20 min as the optimized electropolishing time.

In this test, the influence law of electrolyte temperature on the electropolishing rate and surface roughness of Nb was analyzed. It can be seen from Fig. 2a that the higher the electrolyte temperature is, the greater the electropolishing rate is. In low temperature, ionic liquid has high viscosity and insufficient dispersity, so the dissolution rate of anodic electrode (Nb) is low. With the temperature increases, the viscosity of electrolyte reduces and the moving speed of reactant and resultant increases, as a result the dissolution rate increases. The surface roughness of Nb with increasing the electropolishing temperature is given in Fig. 2b. The surface roughness is strongly effected by the temperature. Increasing temperature leads to the surface roughness decreasing. It is clear that the higher temperature gives rise to smoothening of the Nb surface. At low temperature, the electropolishing rate is very low and defects on Nb surface are not completely removed, so the roughness is relatively high.

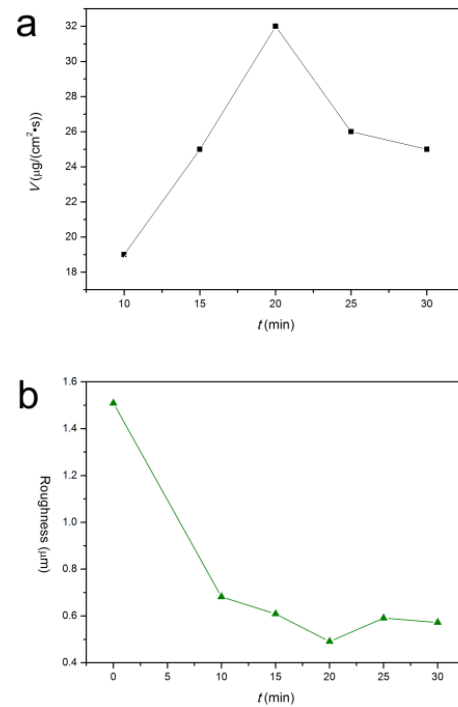


Figure 1: Effect of electropolishing time on (a) electropolishing rate (■); (b) surface roughness (▲) of Nb. The Nb samples were electropolished at -5 V and a temperature of 80 °C in different time varying from 10 min to 30 min.

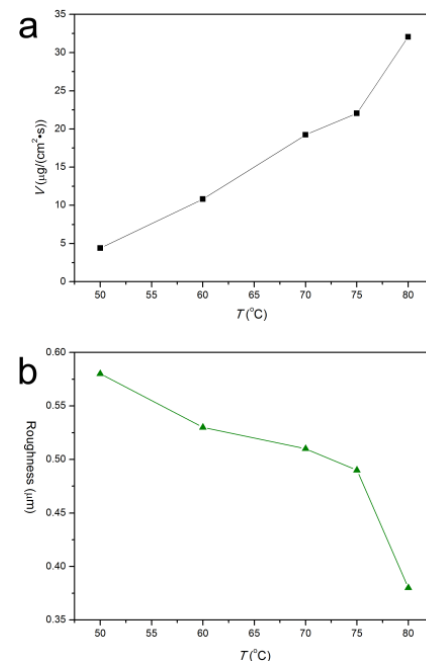


Figure 2: Effect of electropolishing temperature on (a) electropolishing rate (■); (b) surface roughness (▲) of Nb. The Nb samples were electropolished at -5 V and a temperature from 50 °C to 80 °C in 20 min.

The results of the determination of the electropolishing rate versus applied voltage are presented in Fig. 3a. It is found that the electropolishing rate increases with the voltage applies negatively shifting from -3 V to -5 V. The

electropolishing rate shows a downtrend as the voltage negative becomes more negative. When the anode potential is -6 V, an oxide film may be formed on the anode reducing dissolution rate [6]. The effect of voltage on surface roughness of Nb was investigated and the results are presented in Fig. 3b. With the voltage shifts negatively, the roughness decreases at first and then increases.

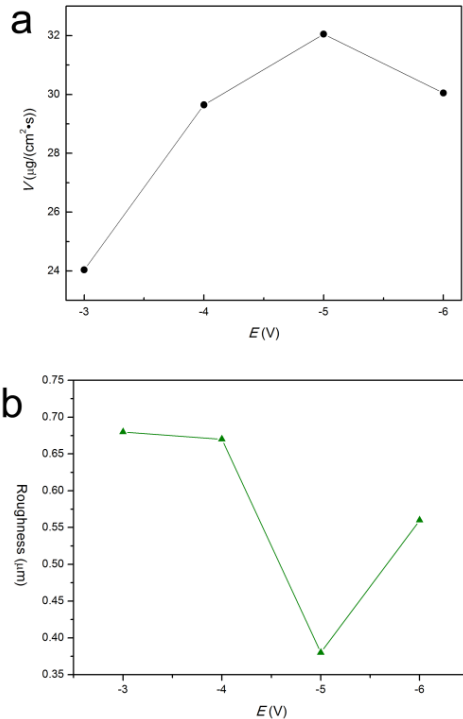


Figure 3: Effect of applied voltage on (a) electropolishing rate (■); (b) surface roughness (▲) of Nb. The Nb samples were electropolished at various voltages from -3 to -6 V for 20 min at 80 °C.

Figure 4 shows the surface micrographs of Nb before and after electropolished. SEM image of Nb without electropolished as shown in Fig. 4a, it is observed some grinding marks, scratches and irregular defects appeared on the surface due to the mechanical polishing. From Fig. 4b, it can be seen that the scratches are removed and an even Nb surface is produced. According to SEM image, the Nb surface before electropolishing is relatively rough and uneven while the Nb-polished surface is relatively even and smooth.

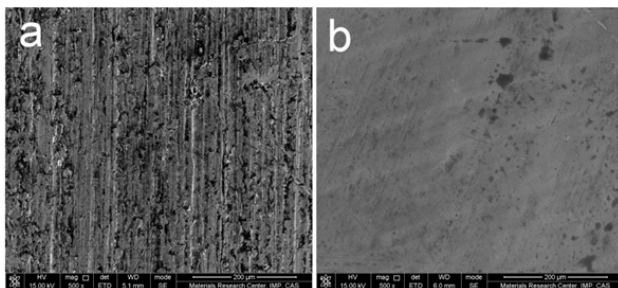


Figure 4: Surface micrographs of Nb samples: (a) without any treatment; electropolished at ionic liquid.

CONCLUSIONS

The influence of various electropolishing parameters (electropolishing time, temperature and voltage) on the electropolishing rate, surface roughness and microstructure of Nb was systematically investigated. The electropolishing parameters had a significant impact on the performance of Nb. Prolonging electropolishing time and negatively shifting voltage, the electropolishing rate of Nb increased first and then decreased, and the roughness decreased first and then increased. With the electrolyte temperature increased, the electropolishing rate increased and surface roughness decreased. A smoother Nb can be achieved from ChCl-based DES under properly controlled conditions.

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