



The alternative, novel technology for improvement of surface finish of SRF niobium cavities

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ABSTRACT

Pure niobium is used for making superconducting radio frequency (SRF) cavities. These cavities need to have a good surface finish to achieve maximum performance. The high smoothness, lack of subsurface hydrogen content and sulfur contamination removal of SRF niobium cavities are the three most important factors to achieving a high accelerating gradient. For finishing niobium surface, electropolishing (EP) in hydrofluoric/sulfuric acid electrolyte is commonly used as a final process. Unfortunately this process had been considered to cause hydrogen absorption that could result in hydrogen Q-disease in niobium SRF cavities. This is why a new electrolyte was compounded to substitute the one presently used. Moreover, the additional imposition of a magnetic field during the electropolishing process (magneto-electropolishing MEP) not only increases hydrogen removal, but also results in reduction of surface roughness when compared to the roughness achieved by the electropolishing process alone (R_z much over 300 nm). This effect of sharp decrease in hydrogen content was found previously in our experiments with titanium and stainless steels after MEP processing. Our present studies, with the electrolyte consisting of a mixture of 70% methanesulfonic acid with 49% hydrofluoric acid by volume in 3:1 ratio, resulted in intensifying and speeding-up the

electrochemical processes of dissolution and polishing niobium surface. It was found that the imposition of a magnetic field of ≈ 100 mT upon the EP process is able to reduce niobium surface roughness of up to 50% (R_z below 200 nm) compared to the roughness achieved by conventional electropolishing.

Keywords: SRF niobium cavities, surface roughness, electrochemical polishing, hydrogen content

1. INTRODUCTION

The smoothness, subsurface hydrogen content and sulfur contamination of superconducting radio frequency (SRF) niobium cavities are the three most important prerequisites to achieving a high accelerating gradient. Presently, the best method to obtain the smoothest inner surface of niobium cavities is the electropolishing process. However, the presently used electropolishing process is intrinsically linked to the subsurface hydrogenation of niobium cavities. This hydrogenation of niobium cavities measurably degrades the performance of the cavity by increasing electrical surface resistance, which is called hydrogen Q-disease. At room temperature and hydrogen concentrations below 6 at % there exists the α phase only. At higher hydrogen concentrations, the ϵ^- phase precipitates resulting in distortion of the niobium lattice so much that Nb is superconducting only at $T < 1.3$ K, and this phenomenon is called Q-disease [1,2].

The annealing process to remove hydrogen from electropolished niobium cavities is a costly and time-consuming process. The process consists of two steps: the vacuum baking of an electropolished cavity at 800 °C for three hours followed by BCP (buffered chemical polishing), which removes 20 μm of material. This process removes most of the hydrogen from electropolished niobium cavities absorbed during electropolishing and is essential to eliminate Q-disease. However, traces of hydrogen remain and even additional hydrogen is reabsorbed in the furnace during the cool down period as well as during the BCP process, which could possibly result in the creation of nanohydrides. The nanohydrides can surely increase the surface resistance of cavities above ≈ 100 mT surface magnetic field-a-so called high field Q slope (HFQS). This detrimental effect of present nanohydrides is reduced by additional mild-baking of cavities in 120 °C [3,4].

Here we show that using different electrolyte formula alone can prevent hydrogen uptake and reduce residual hydrogen content in subsurface of niobium after electropolishing. The additional imposition of a magnetic field during the electropolishing process not only increases hydrogen removal, but also reduces surface roughness when compared to roughness achieved by the electropolishing process alone. The required removal of metal is sped up around 15 times when compared to metal removal by the presently used process. Taking under consideration that planned LINAC (linear accelerator) will require about 18 000 niobium cavities, the speeding up electropolishing process and eliminating of vacuum baking (800 °C) and mild-baking (120 °C) of niobium cavities operations could significantly cut the costs of the accelerator.

As for now, the best method to achieve the smoothest inner surface of SRF niobium cavities is the electropolishing EP process. The currently used EP process is based on the electrolyte formula first mentioned by W. Tegart [5] in 1956 as electrolyte for electropolishing titanium. This formula was later adopted by H. Diepers *et al.* [6] in 1971 for

electropolishing niobium cavities and is commonly referred to as the Siemens process. It consists of mixture of 96% H₂SO₄/49% HF acids by volume in a 9:1 ratio. The process gives satisfactory smooth finish to the inner surface of niobium cavities, however it is not totally free from drawbacks. The main problems of this electrolyte is hydrogenation and sulfur contamination [7] of subsurface of niobium cavities during the electropolishing process, both of them coming from the electrolyte used. In fact, these problems require costly and time-consuming post-electropolishing procedures, such as vacuum backing, BCP and pressure washing. The smoothness of inner surfaces of niobium cavities required to achieve high gradient $E_{acc} > 30$ MV/m according to Saito [8] has to be below Rz equal 2 μm . This requirement is reached by the currently used heavy electropolishing process which removes more than 120 μm of material. After this process a roughness of Rz 0.303 μm can be reached [9]. Here we show that by using different electrolytes, which consist of a mixture of 70% methanesulfonic acid with 49% hydrofluoric acid by volume in 3:1 ratio [10], the comparable smoothness of niobium cavities surface is obtained.

However the new electrolyte formula doesn't introduce hydrogen to the subsurface of electropolished niobium layer as the currently used electrolyte does. Moreover by using the new electrolyte, dehydrogenation of niobium subsurface layer occur. Additionally improved surface smoothness, and further decrease in hydrogenation together with speed-up of electropolishing can be achieved by the imposition of magnetic field upon the electropolishing process (magneto-electropolishing). The current electropolishing process, which uses a H₂SO₄/HF (9:1) electrolyte mixture, can be described as an intermittent, diffusion-limited process [6]. The process consists of two repeating electrochemical reactions: oxidation of niobium to Nb₂O₅ (niobium pentoxide) by H₂SO₄ under applying potential and dissolution of Nb₂O₅ by HF. When the electropolishing process starts, the niobium is oxidized to Nb₂O₅. Simultaneously HF starts to diffuse into this electrically insulating freshly created oxide layer and dissociates it. This diffusion process is determined by thickness and compactness of Nb₂O₅ layer. When HF reaches concentration needed to dissolve Nb₂O₅ the current reaches maximum. As the concentration of HF becomes depleted the Nb₂O₅ starts to grow again, the current starts to drop until diffusion raises the concentration of HF back to the level when dissociation of Nb₂O₅ can proceed again. This constantly oscillating current will sustain during electropolishing process, however long a concentration of HF acid is necessary to dissolve newly created Nb₂O₅ will be maintained.

The electropolishing process which uses the new electrolyte formula in principle works almost the same way as the old process, meaning in current oscillation mode and produces comparable smoothness result (Rz of about 0.35 μm). However by using the new electrolyte formula material removal is sped-up five times and the amount of hydrogen in the subsurface layer is minimized. The increased speed of material removal is caused by increased amount of HF in the new electrolyte. The minimized hydrogen content is most probably due to the lower corrosiveness of the new electrolyte mixture toward niobium when niobium has contact with electrolyte and the applied potential is already terminated. However, imposition of magnetic field ≈ 100 mT on the electropolishing process, totally changes the mode of the process and the properties of the electropolished niobium surface samples. The current oscillation vanishes and electropolishing process ongoing, what we call proportional dissolution mode. The change of the electropolishing mode from diffusion limited to proportional dissolution is due to decrease of Nb₂O₅ thickness. The imposition of a magnetic field on the electropolishing process introduces the new force to the system: namely, the Lorenz force. The Lorenz force

swirls electrolyte around the electropolished sample and reduces the thickness of the viscous layer which is created during the electropolishing process. The thinner viscous layer allows HF to more quickly reach the thinner Nb₂O₅ layer covering the electropolished niobium sample and dissolve it immediately. The thickness of Nb₂O₅ is reduced because the time needed for HF to reach and dissolve it, as well as to replenish its concentration, is shortened. This explains the sped-up niobium dissolution of around 15 times. The improved smoothness of niobium surface electropolished under imposed magnetic film can be explained on the base of viscous film theory by Jacquet [11]. The main principle of this theory is the variable thickness of viscous layer, which covers metal during electropolishing. The viscous layer is a byproduct of ions of dissolved metal and electrolytes. Assuming a planar nature of a viscous film-solution interface the viscous layer is thinner above surface promontories than over valleys. The unevenness of thickness of the viscous layer covering the surface of electropolished metal gives rise to varied electrical resistance over electropolished surface. The current density over promontories is higher and by this they dissolve faster than valleys which leads to surface leveling.

This theory of electropolishing was recently developed and extended by Rokicki & Hryniewicz [12]. However, under the imposition of a magnetic field [13-17], with the process named magneto-electropolishing [13], the above explanation is changed. The swirling movement of electrolyte caused by Lorenz force will reduce the thickness of the viscous layer over the promontories rising current density and by this speeding-up their dissolution. Therefore the swirling movement of the electrolyte will push portion of viscous layer from the promontory over the neighbouring valley and by this resistance in this place will be changed. The current density will be lower and the dissolution of the valley will be retarded. Consequently, Lorentz force is responsible for smoothing the electropolished metal surface.

The aim of this work was to study the electropolishing niobium, the surface finishing obtained in a newly compounded electrolyte and reveal the effect of the magnetic field applied. The level of hydrogenation in the surface film of niobium samples before and after electrochemical processing was also investigated.

2. METHOD

2. 1. Sample preparation

The rectangular niobium samples of the area of about 160 mm², cut off of the metal sheet about 32 mm thick (state AR – as received) were electropolished for two hours in stagnant electrolyte mixture of 70% methanesulfonic acid (CH₃SO₃H) and 49% hydrofluoric acid (HF) by volume in 3:1 volume ratio. The electropolishing EP was performed in potentiostatic conditions of 5 V in constant temperature of 25 °C.

The magneto-electropolishing MEP was performed in the same electrolyte under the same voltage, temperature and time, with the magnetic field applied of about 100 mT.

2. 2. Surface measurements

2D surface roughness of the electrochemically polished niobium samples was measured using a computerized HOMMELTESTER T800 system of Hommelwerke GmbH. Both as received AR, and electropolished (EP) and magneto-electropolished (MEP) samples were measured.

The hydrogen secondary ion current versus depth profiles were measured with the use of SAJW-05 SIMS system described elsewhere [18]. 5 keV Ar⁺ primary ion beam was digitally scanned over 3.5 mm × 3.5 mm area while the emission of secondary ions was measured from 1.35 mm × 1.35 mm area.

3. RESULTS AND DISCUSSION

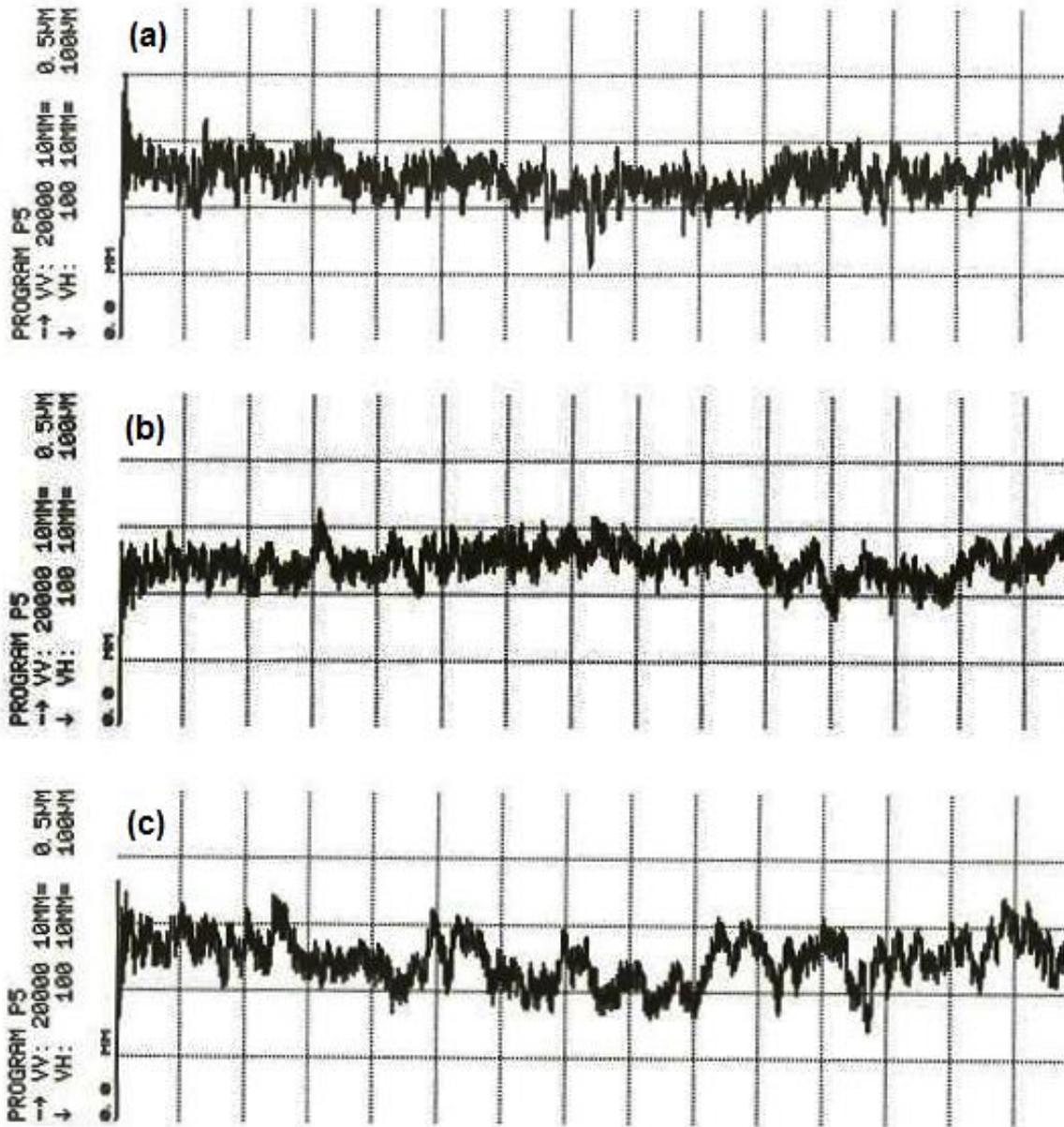


Fig. 1. Surface roughness measured on Niobium samples: (a) as received AR, (b) after EP, (c) after MEP

Our primary results on surface roughness performed on niobium samples are given in **Fig. 1**. Fig. 1a presents roughness parameters of niobium sample measured before any electrochemical treatment (Rz equals 690 nm). Next two measurement results done on EP and MEP samples are displayed in Fig. 1 (b) and (c), respectively. They were not encouraging, showing comparable surface roughness (Rz from 560 on EP sample, up to 800 nm on MEP sample) for two electrochemical treatments.

In **Fig. 2**, values of surface roughness measured, as of Fig. 1, referred to particular parameters, Rt, Ra, Rz, Rq, Pt, Wt are displayed. The characteristic feature is that after electropolishing EP, all of them were decreased regarding AR state. On the other hand, first four of them and the last one were higher after magnetoelectropolishing MEP, in reference not only to the ones of EP, but also against those ones of AR.

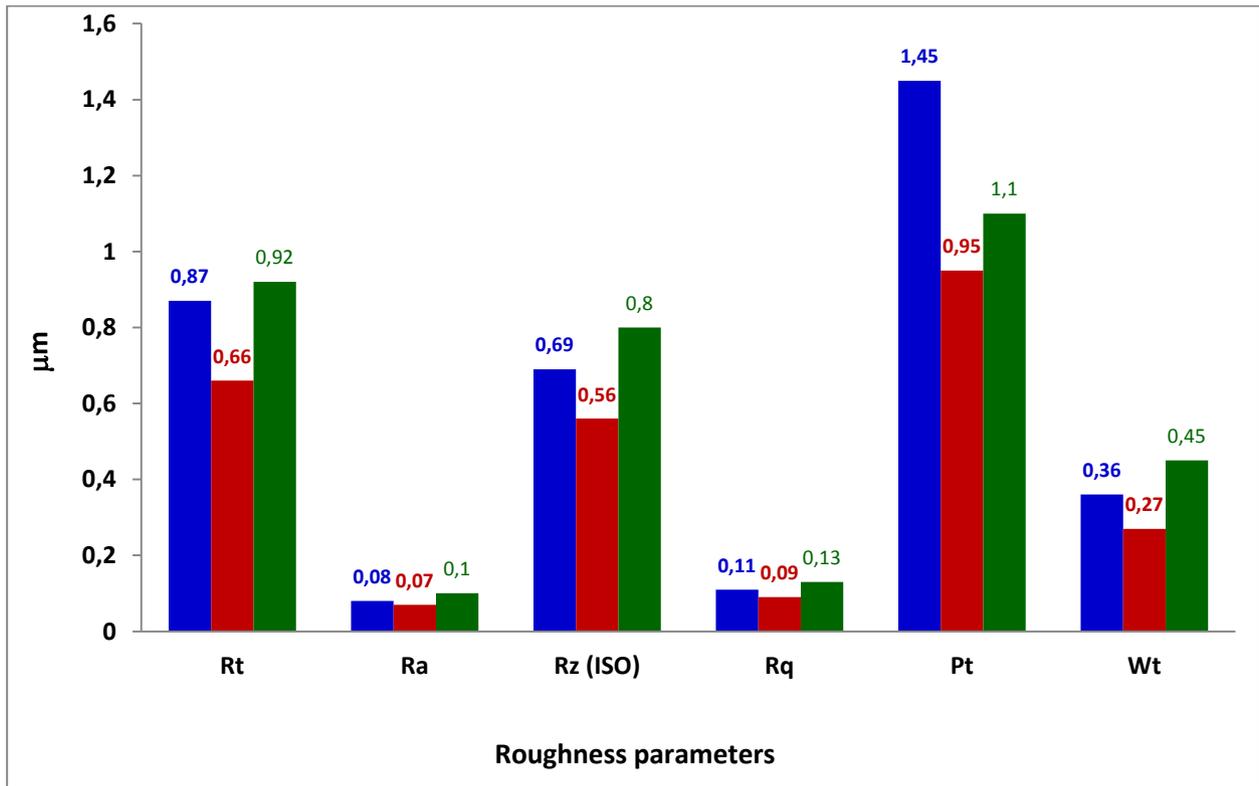
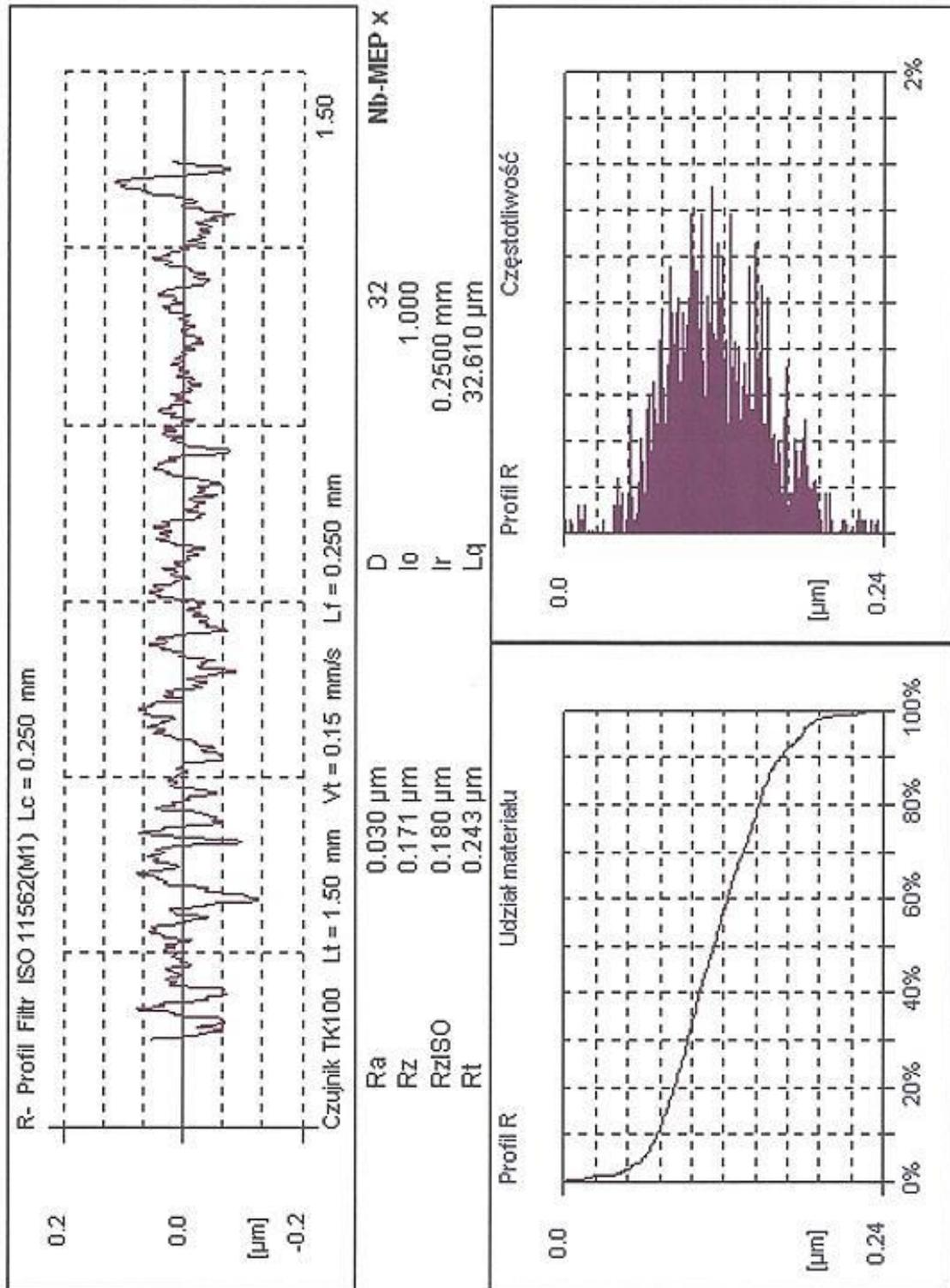
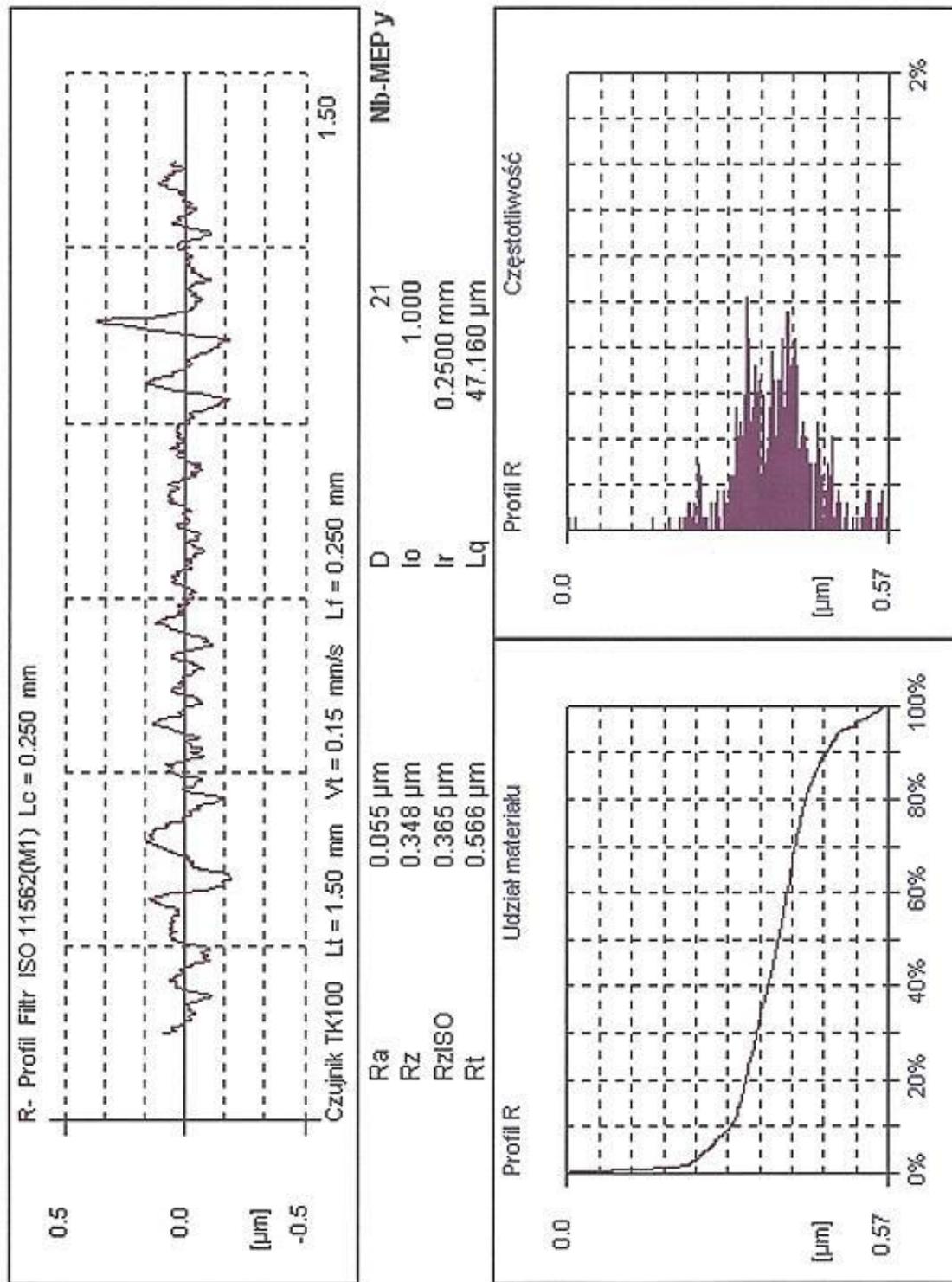


Fig. 2. Values of surface roughness parameters of Fig. 1, measured on Niobium samples: blue – referred to as received AR (a); red – after EP (b), and green – after MEP (c)

After establishing proper conditions, concerning the electrolyte mixture [10] and electropolishing parameters, the new measurements of surface roughness were performed. It appeared that surface roughness of MEP sample is the lowest, with Rz equaling below 200 nm (see **Fig. 3**). This way one of the most important conditions concerning smoothness of SRF niobium cavities was achieved. Our experiment showed that the imposition of a magnetic field of ≈ 100 mT upon the electropolishing process is able to reducing niobium surface roughness of about 50% compared to the roughness achieved by conventional electropolishing.



(a)



(b)

Fig. 3. Niobium 2D surface roughness after MEP in 2 perpendicular axes: (a) x axis, and (b) y axis

The studies on hydrogen content in the niobium samples required a methodic approach and they will be presented elsewhere under a separate paper. For this aim, a series of SIMS measurements were carried out both on as-received AR, electropolished EP and magnetoelectropolished MEP niobium samples. Herewith the final results on hydrogen distribution going in-depth from the surface are given.

Results obtained in our experiments (**Fig. 4**) show that the niobium sample as-received AR was highly contaminated with hydrogen. A decreasing trend in each of the studied samples is observed. Electropolishing in the newly compounded electrolyte resulted in much decreased content of hydrogen, referred both to EP and MEP niobium samples. Moreover, much steeper and deeper hydrogen decrease in MEP sample is noted. Also thickness of the oxide film is much lower on MEP sample in comparison with that one on EP sample.

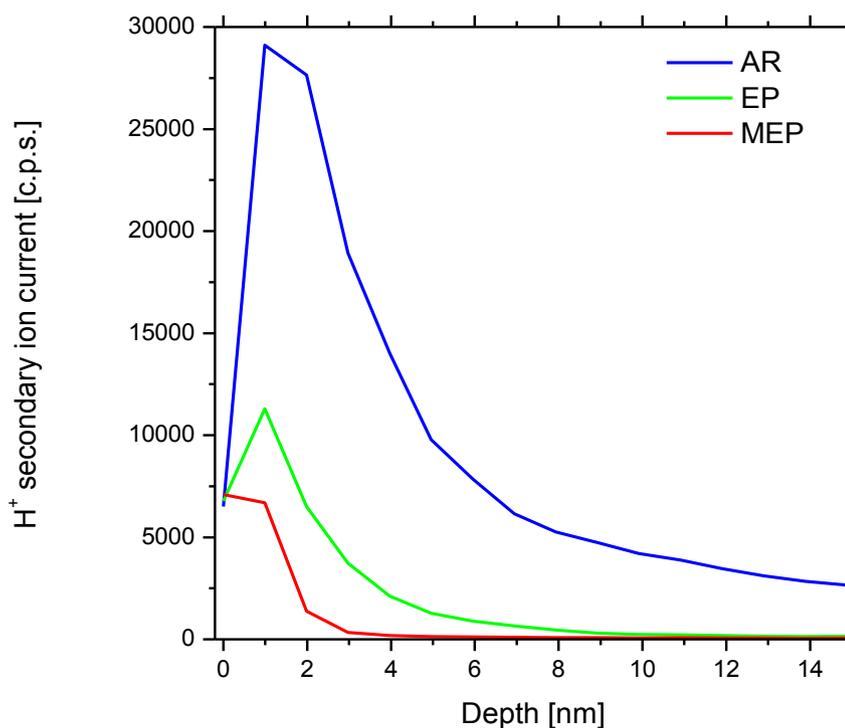


Fig. 4. Comparison of plots obtained for H^+ ion currents against the depth of ion etching: results covering range of the etching down to stabilized values. As received (AR), electropolished (EP) and magnetoelectropolished (MEP) niobium samples are compared.

The hydrogenation level on MEP sample was lower than that one measured on EP niobium sample with much thinner layer affected. The same trend in decreasing hydrogen content of MEP samples was also observed in our earlier studies performed on AISI 316L stainless steel [19], and CP Titanium Grade 2 [20]. One should add, the thickness of the oxide film, alike in other our studies [19,20], is much lower on MEP sample in comparison with that one formed on EP niobium sample.

4. CONCLUSIONS

The cleanliness of the inner surface of superconducting niobium cavities is an indispensable condition for the successful performance of these accelerating devices. The studies carried out on niobium samples, concerning surface finishing and SIMS measurements, allow to formulate the following conclusions:

- the new electrolyte of 70% methanesulfonic acid with 49% hydrofluoric acid by volume in 3:1 ratio may be effectively used to electropolishing niobium
- it was proved the magneto-electropolishing MEP of niobium provides the best surface finish
- AR niobium samples reveal the highest content of hydrogen, decreasing with the depth of penetration
- MEP niobium samples display the lowest content of hydrogen, going down to zero on the depth of 3-4 nm
- an alternative novel technology for effective surface finishing of SRF niobium cavities is proposed.

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References

- [1] Kenji Saito, Hitoshi Inoue, Eiji Kako, Takeo Fujuno, Shiichi Noguchi, Masaaki Ono and Toshio Shishido. Superiority of Electropolishing over Chemical Polishing on High Gradients. *Particle Accelerators*, 60, 193-217; <http://www-project.slac.stanford.edu/lc/wkshp/RFBreakdwn/references/Electro%20polishing.pdf> (1998).
- [2] Myneni G., and Kneisel P., High RRR Niobium Material Studies. JLAB-TN-02-01 Report (12 pages); <http://tnweb.jlab.org/tn/2002/02-001.pdf> (2002).
- [3] Romanenko A., Barkov F., Cooley L. D., and Grassellino A., Proximity breakdown of hydrides in superconducting niobium cavities, *Superconductor Science and Technology*, 26 (2013) 035003 (5 pages); DOI: 10.1088/0953-2048/26/3/035003 (2013).
- [4] Bonin B., Henriot C., Antoine C., Coadou B., Koechlin F., Rodriguez J. P., Lemalle E., Greiner P., A new surface treatment for niobium superconducting cavities, Proc. IEEE, (1993) 798-799, PAC 1993.
- [5] Tegart W. J. McG., The electrolytic and chemical polishing of metals for research and industry. Pergamon Press, London, UK (1956).

- [6] Diepers H., Schmidt O., Martens H., Sun F. S., A new method of electropolishing niobium, *Physics Letters A* 37(2) (1971) 139-140.
- [7] Morgan A.V., Romanenko A., Windsor A., Surface studies of contaminants generated during electropolishing. WEPMS010 Proceedings of PAC07, 2346-2348; Albuquerque, New Mexico, USA
<http://accelconf.web.cern.ch/Accelconf/p07/PAPERS/WEPMS010.PDF> (2007).
- [8] Kenji Saito, Surface smoothness for high gradient niobium SC RF cavities.
<http://srf.desy.de/fap/paper/ThP15.pdf> (2003).
- [9] Wu G., Ge M., Kneisel P., Zhao K., Cooley L., Ozelis J., Sergatskov D., and Cooper C., Investigations of Surface Quality and SRF Cavity Performance. 2LP1C-02, FERMILAB-CONF-10-430-TD, 1-4, <http://lss.fnal.gov/archive/2010/conf/fermilab-conf-10-430-td.pdf> (2010).
- [10] Rokicki R., US Patent Application 20100213078 – Electrolyte composition for electropolishing niobium and tantalum and method for using same, published on August 26, 2010 <http://www.patentstorm.us/applications/20100213078/description.html>
- [11] Jacquet P.A., Le Polissage Electrolitique, *Nature* 135 (1935) 1076.
- [12] Rokicki R., Hryniewicz T., Enhanced oxidation-dissolution theory of electropolishing, *Transactions of The Institute of Metal Finishing* 90(4) (2012) 188-196.
- [13] Rokicki R., Hryniewicz T., Nitinol™ Surface Finishing by Magneto-electropolishing, *Transactions of the Institute of Metal Finishing* 86(5) (2008) 280-285.
- [14] Hryniewicz T., Rokicki R., Rokosz K., Corrosion and surface characterization of titanium biomaterial after magneto-electropolishing, *Surface and Coatings Technology* 203(9) (2008) 1508-1515.
- [15] Hryniewicz T., Rokosz K., Valiček J., Rokicki R., Effect of magneto-electropolishing on nanohardness and Young's modulus of titanium biomaterial, *Materials Letters* 83 (2012) 69-72.
- [16] Hryniewicz T., Rokosz K., Rokicki R., Magnetic Fields for Electropolishing Improvement: Materials and Systems, *International Letters of Chemistry, Physics and Astronomy* 4 (2014) 98-108; <http://www.ilcpa.pl/wp-content/uploads/2013/10/ILCPA-4-2014-98-1081.pdf> (2014).
- [17] Hryniewicz T., Rokosz K., Rokicki R., Prima F., Nanoindentation and XPS Studies of Titanium TNZ Alloy after Electrochemical Polishing in a Magnetic Field, *Materials* 8 (2015) 205-215; DOI:10.3390/ma8010205.
- [18] Konarski P., Mierzejewska A., B₄C/Mo/Si and Ta₂O₅/Ta nanostructures analysed by ultra-low energy argon ion beams, *Applied Surface Science* 203-204 (2003) 354-358.
- [19] Hryniewicz T., Konarski P., Rokosz K., Rokicki R., SIMS analysis of hydrogen content in near surface layers of AISI 316L SS after electrolytic polishing under different conditions, *Surface and Coatings Technology* 205 (2011) 4228-4236; DOI: 10.1016/j.surfcoat.2011.03.024 (2011).

- [20] Hryniewicz T., Konarski P., Rokicki R., Valíček J., SIMS studies of titanium biomaterial hydrogenation after magnetoelectropolishing, *Surface and Coatings Technology* 206 (2012) 4027-4031; DOI: 10.1016/j.surfcoat.2012.03.083.

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