Introduction

The process of electropolishing (EP) has been developed for many decades now in view of obtaining shiny, bright and glossy surface on metals and alloys [1-5]. Some characteristic features of machine parts are usually obtained after EP [4-7] due to removal of surface roughness and formation of passive surface film on them, including possible changes in color [6]. Firstly it was considered as the process designed to improve surface finishing, much better than that gained after abrasive polishing processes [1,8]. During the years of studies it was found that not only surface roughness decay and gloss effects normally appear as the real effects of the EP process, but many more interesting features were revealed on the treated metal surface. They are generally an increase in corrosion resistance and a considerable improvement of mechanical properties of the treated parts [9-15]. In the anodic processes of electropolishing (EP) in acidic electrolytes, passive thin films revealing improved corrosion resistance are obtained [3-5, 11-22].

Progress in Electropolishing

By introducing a magnetic field into the EP process, a new process patented by Rokicki [9] named as a magneto electropolishing (MEP), has been developed. In view of displaying its advantages and features, extensive investigations over the MEP process were carried out [9-51]. Meanwhile, the studies on the theory of electropolishing were also continued [28,36]. Results of the studies have proved that the MEP process is characteristic with many meaningful features, prevailing over a standard electropolishing EP, starting from diminished surface roughness [10-12,14,15,17,20,24,30,43,45], more advantageous surface film composition [14-18,26,29,32-34,38,40,41,43,45-51], increased nanohardness [34,38-40,43,46,47], through the increased corrosion resistance [12-15,17-22,27,28,30,34,43,45,47-49], including one of the most significant improvement of biocompatibility of metallic biomaterials [11,12,15,18-21,22-24,30,31,34,35,43-45,48-51]. These improved characteristics were revealed to appear after MEP of both metals and alloys. To prove these, numerous metals and alloys, including metallic biomaterials were investigated, starting from austenitic stainless steels (AISI 304, 304L, 316, 316L, 316Lvm) [10-13,15-19,23,25,27,38,39,41-43,45], ferritic AISI 430 stainless steel [22], duplex stainless steels LDX 2101 [38] and 2205 [55], cobalt Co-Cr alloys [17], through titanium (CP Titanium Grade 2 [4,20,30,32,33,37,39], shape memory alloy – Nitinol [11,14,21,26-28,31,35,36,45,48,49,51-59]) and next titanium alloys (e.g. Ti6Al4V, Ti2448, or titanium niobium-zirconium TNZ alloy [42,46], as well as niobium and other metallic materials [34,50,57,63].
During MEP of alloys, magnetic elements such as iron in austenitic stainless steels, or nickel in Nitinol could be completely removed from the surface layer. This way, the surface film in stainless steel was highly enriched in chromium oxides, and mostly titanium oxide (TiO₂) was formed on NiTi alloy surface. Besides, the oxide layer formed during MEP of NiTi intermetallic compound appeared to be thinner (about 6 nm) than that one obtained after a standard EP with the increased regularity of oxide layer formed. Another characteristic feature is an increase of surface energy and with this a better surface hydrophilicity of parts obtained after MEP.

Mixture of concentrated acids is mostly used as the electrolyte for electropolishing processes, with some of them being proprietary and not revealed nor openly presented in literature. Low voltage (3-15 V) is used for a standard EP and magneto electropolishing MEP processes performed generally on the plateau level [1,2,8,25,36]. For instance, for Nitinol a mixture of non-halogen acid with alcohol was used as the electrolyte at temperature 0 °C, the processing time for 5 min, electropolishing voltage 10 V, current density was above plateau – under oxygen evolution regime, Al as electrode/cathode material, with no agitation under EP, and whirling caused by a Lorentz force during MEP. Besides, high-current density HDEP (EP1000 and EP2000) [47,52-55], and high-voltage electropolishing HVEP (up to 450 V) [56] processes were also studied, proving their usability for specific purposes, e.g. the HVEP disclosed the entrance to Plasma Electrolytic Oxidation PEO [64,65] in concentrated acids. Under a standard electropolishing EP on the plateau level, high-current density electropolishing HDEP, and magnetoelectropolishing MEP, the Nano-coatings on metals and alloys are formed. These Nano-coatings/films are characteristic with a variety of unique properties, concerning increased corrosion resistance in harsh environments and greatly improved important mechanical properties of parts for specific applications [57-63]. MEP additionally improves metal surface properties, fundamentally diminishes surface layer hydrogenation, and basically results in increased fatigue resistance of parts [27-34,42,43,45,46,59-61].

One of the most serious problems to solve was de-hydrogenation of the surface layer after numerous mechanical and electrochemical operations. The problem is of importance to avoid hydrogenation in titanium alloys (Nitinol) in implants, peripheral stents, needles, endodontic files and another medical device. The avoidance of hydrogenation is expected also in niobium used for superconducting radio frequency cavities, or electromagnetic radiation detectors, and in nuclear industries. Specifically, niobium as the alloying element improves the strength of the alloys, especially at low temperatures. Our recent studies performed on selected metals and alloys indicated consecutive lowering of hydrogenation, the highest noted in as-received (AR) samples of metals and alloys, some lower after EP, and the lowest in MEP samples [29,32,58,61,63]. The subsequent studies using secondary ion mass spectroscopy SIMS as well as glow discharge optical emission spectroscopy GDOES show that the depth of appearance and the amount of hydrogen content after MEP is very low, revealing only traces and/or decaying almost completely [61,63]. In some cases that de-hydrogenation may result also from a new electrolyte composition used for MEP of niobium [57] in comparison with that one used in Siemens process [66]. Our recent finding connected with the MEP process is a considerable increase of mechanical properties, specifically referred to the fatigue under samples bending. Over a decade ago, the Author noticed that during 180-degree bending (acc. to a Polish Standard, ±90 degree static bending) of a ϕ 1.6-mm titanium wire after EP the number of bends was about 3-4 cycles, whereas after MEP it was 7-8 cycles in both cases until fracture. Next a similar behavior of samples was also found in case of stainless steels, and Nitinol (surgical blades and suture needle pushers) [57,59-61]. Nitinol surgical needles after MEP under composed bending (90º in one direction and 70º in reverse) revealed 3 to 5 times higher resistance to bending than those after a standard EP.

One example of biomaterials performance is presented in Figure 1. Displayed in Figure 1 implants come from a human body after a period of time they were inserted. In Figure 1a, the austenitic stainless steel implant after a very fine finishing underwent corrosion in the harsh human environment. On the other hand, in Figure 1b a fatigue breakage is visible to occur in a very similar stainless steel implant. Our solution to prolong the life of this type of implants is the change of biomaterial used (say into a titanium alloy), and the advice for final surface finishing by MEP. A variety of measurement techniques were used to study Nano-coatings after EP, MEP. They are: scanning electron microscopy with electron dispersive X-ray SEM/EDX, Auger electron spectroscopy AES, X-ray photoelectron spectroscopy XPS, X-ray/grazing incidence diffraction XRD/GIXRD, glow discharge optical emission spectroscopy GDOES, secondary ion mass spectroscopy SIMS, atomic force microscopy AFM, contact angle measurement CAM, electrochemical impedance spectroscopy EIS, 2D and 3D surface roughness studies with Ra and Sa parameters noted, nanoindentation measurements, fatigue resistance testing, and others.

**Conclusion**

In conclusion, MEP effects in comparison with the samples after EP are: lower roughness and passive film thickness, advantageous
film composition with a modified compact structure, higher corrosion resistance, increased resistance to cyclic bending of part, until fracture. Interestingly, a huge increase in mechanical resistance to fracture is one of the most unexpected features of parts after that kind of metal finishing [32,57-61]. It may be connected with the decrease in surface roughness, thinner film with modified composition obtained after MEP, and general diminishing of hydrogenation in comparison with the same samples/parts after a standard electropolishing EP.

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Mr Ryszard Rokicki, recently deceased, inventor and the owner of Electrobright, Macungie PA, USA, as the author of PhD Thesis: “Magneto-electropolishing as a novel method for improving Nitinol parts and devices” (with my part as the Promoter), is greatly acknowledged for his long-term and fruitful co-operation by developing electropolishing processes on industrial scale. The acknowledgment is directed to the family, straight to his wife, Ms Małgorzata Rokicki.

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