

COMPARISON OF CORROSION RESISTANCE IN PHYSIOLOGICAL SALINE SOLUTION OF TWO AUSTENITIC STAINLESS STEELS – 316LV AND REX734

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Abstract: In this work two austenitic stainless steels, REX734 and 316LV were tested in terms of their microstructure and corrosion properties. The REX734 is a newer generation stainless steel, with modified chemical composition, in comparison to the 316LV grade. Potentiodynamic study of corrosion resistance was conducted in physiological saline solution (0.9% NaCl solution). In spite of the similarities of microstructure, grain size and phase structure in both materials, the corrosion tests revealed that the REX734, with lower nickel and higher nitrogen content, had better corrosion resistance than 316LV. Repassivation potential in the REX734 was almost six times higher than for the 316LV steel. Superior corrosion resistance of the REX734 steel was also confirmed by surface observations of both materials, since bigger and more densely distributed pits were detected in 316LV alloy.

Key word: REX734 Austenitic Stainless Steel, 316LV Austenitic Stainless Steel, Potentiodynamic Corrosion Tests, XRD Analysis, SEM Observation

1. INTRODUCTION

Biomaterials based on metals and metal alloys are commonly used in medicine. They can be used in objects such as implants, plates, screws or surgical instruments as a replacement for human body parts. These materials should meet the requirements of biocompatibility, good mechanical strength and corrosion resistance. It is known that the corrosion resistance is an effective prognostic of the biocompatibility and further application of these materials (Burnat et al., 2014; Sumita et al., 2004; Reclaru et al., 2003; Uggowitzer et al., 2003). From the very large group of biomaterials, an austenitic stainless steel 316LV (ISO 3581-A) is frequently used for various orthopaedic and surgical applications, due to good ductility and fatigue behaviour, decent corrosion resistance, good formability and low cost of production (Thomann and Uggowitzer, 2000, Giordani et al., 2004, Gotman, 1997). This steel however, has some disadvantages including: low biocompatibility, susceptibility to fracture due to fatigue and fretting corrosion, high amount of expensive nickel alloying element, toxicity of corrosion products or insufficient affinity for cells and tissues integrations (Sumita et al., 2004, Yang and Ren, 2010).

Corrosion, as one of the main issues of the austenitic stainless steels, leads to releasing of metal ions. They concentrate on the boundaries of an implant causing toxic and allergic reactions of tissues after relatively short time of implantation (Reclaru et al., 2003, Teoh, 2000). The 316LV steel, most frequently used in surgical applications with high nickel content, has aforementioned disadvantages (Sumita et al., 2004).

Nickel is one of the primary alloying element used in stainless steels production. It is stabilizing Fe- γ (Face Centered Cubic, FCC) austenite phase structure, increasing the stacking fault energy and therefore improving mechanical and fracture properties of steels. On the other hand, nickel ions (products of corro-

sion) cause toxic and carcinogenic response of the human tissue (Uggowitzer et al., 1996, IARC, 1996). Therefore, this toxic element has been gradually replaced by other strong austenite-stabilizing elements: nitrogen and manganese. Nitrogen occurring in austenitic stainless steel, added up to the solubility limit, improves tensile strengths and corrosion resistance, extends the passives range, promotes passivity that restrains the pitting corrosion and tightens an oxide layer (Yingli and Zhangjian, 2013, Filemonowicz et al., 1995, Bayoumi and Ghanem, 2005). If nitrogen content is higher than 0.4 wt %, the austenitic stainless steel is considered as high-nitrogen steel. However, the solubility of nitrogen in room temperature is quite low, Sawyer placed it at 0.03% and Fry at 0.0015% wt % (Epstein et al., 1929, Gillett, 1928). When nitrogen content exceeds the solubility limit, brittle Cr₂N precipitations may be formed, decreasing ductility and corrosion resistance of the steels. REX734 (ISO 5832-9) nitrogen- and niobium-bearing austenitic stainless steel, with reduced nickel content, higher amount of chromium, manganese and nitrogen has been designated to improve and replace the 316LV steel on the market (Giordano et al., 2010).

Basing on the present knowledge it has to be pointed out that available experimental data about corrosion resistance of the REX734 steel is very limited. Therefore, in this work, the potentiodynamic corrosion, phase structure, microstructure and hardness tests, of two conventional stainless steel, 316LV and REX734, commonly used in medical applications were carried out.

2. MATERIALS AND METHODS

Commercially available, 8 mm in diameter rods of austenitic stainless steels 316LV and REX734 were cut into cylinders 5 mm high. Those cylinders were mechanically grinded (using 600-

800- and 1200-grit papers), polished in an alumina (Al_2O_3) suspension, and cleaned in an ultrasonic bath. Prior to corrosion tests, the samples were kept in the physiological saline solution (0.9% NaCl solution), for 6 hours at room temperature. Potentiodynamic corrosion tests were performed according to ASTM G48 standard and carried out in a three-electrode electrolytic cell consisting of a platinum electrode as counter electrode, a saturated calomel electrode as reference electrode and the sample as a working electrode. The corrosion resistance (R_p), corrosion potential (E_{cor}), current corrosion density (I_{cor}), corrosion rate (C_R), breakdown potential (E_b) and repassivation potential (E_{cp}) were determined using software Volta Master 4. The E_{cor} , E_{cp} and R_p parameters were defined by applying Stern method while the I_{cor} and C_R were defined by Tafel method described elsewhere (McCafferty, 2010). The samples were polarized with the potential rate of 3 mV/s. Before and after the potentiodynamic tests, pH of the solution in which the process was carried out, was measured. The surface of the samples was observed by means of OLYMPUS BX51M Optical Microscope (OM) and Hitachi S-3000N Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS). Vickers hardness of the materials was measured using NEOPHOT 21 microscope equipped with Hanneman's apparatus with a load of 0.1 kg. Chemical analysis for both materials was performed by means of a Thermo ARL Quantis Gas Emission Spectrometer (GES). Phase structure of the prepared samples was studied using a Bruker D8 Advanced X-ray diffraction (XRD) diffractometer with the Cu-K α radiation ($\lambda = 1.5498 \text{ \AA}$). The all diffraction patterns were recorded at room temperature with a step 0.01° in the range of 20° to 100° two theta.

3. RESULTS AND DISCUSSION

Chemical compositions of tested materials are summarized in Tab. 1. As expected the REX734 steel has lower nickel and molybdenum, but higher chromium and manganese content. Higher level of chromium can affect corrosion properties by improving thickness of the passive layer and therefore, reducing corrosion rate of steels (Oksiuta and Och, 2013). Two times greater manganese quantity in the steel can increase the solubility of nitrogen and reduce nickel content (Tverberg, 2014). The REX734 also contains 0.4% of niobium and 0.3% (in wt.%) of nickel. Niobium is added to austenitic stainless steels to reduce formation of detrimental chromium carbides and to prevent reduction of corrosion properties (Sordi and Bueno, 2010). Since the solubility of niobium in austenitic steels is very low, a Laves brittle phase (Fe_2Nb) or $Nb(C,N)$ can be formed what may cause a decrease of ductility and corrosion resistance of steels (Itman Filho et al., 2014). Nitrogen, an interstitial solute element, has a limited solubility in steels, however, it was reported that with the amount of 0.7% it increases the breakdown potential, stabilizes the passive layer and enhances resistance to pitting initiation (Szkłarska-Śmiałowska, 2005).

Tab. 1. Chemical composition of the tested austenitic stainless steels (in wt.%)

Material	C	Si	Mn	Cr	Mo	Ni	Nb	N	Fe
REX734	0.04	0.25	4.10	21.10	2.35	9.10	0.40	0.28	Ball
316LV	0.03	0.40	1.85	17.25	2.65	14.30	-	-	Ball

The microstructure after etching is shown in Figure 1. After etching, both materials have typical austenitic microstructure with annealing twins and an average grain size of 25 ± 5 , measured using the mean interception length technique (according to ASTM E 112-96).

The hardness tests revealed that different chemical composition has no influence on the mechanical properties of both tested steels. This means that hardness of the 316LV steel ($HV_{0.1} 371 \pm 11$) is slightly lower in comparison to the REX734 grade ($HV_{0.1} 399 \pm 15$).

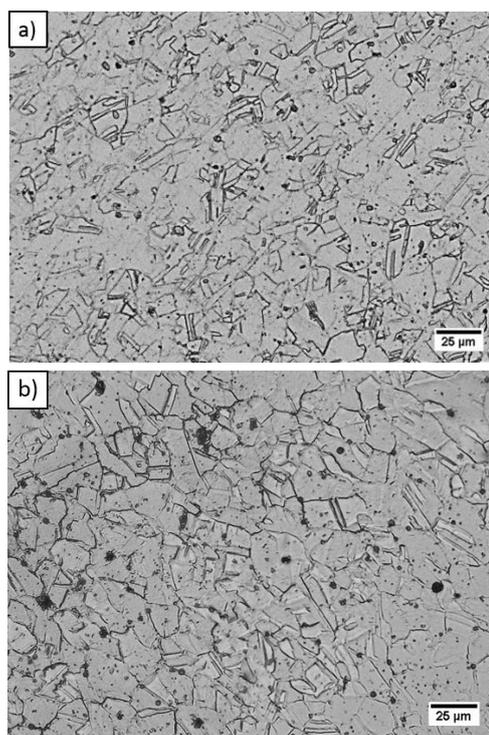


Fig. 1. Typical OM microstructure of the tested steels after etching: a) REX734 and b) 316LV, respectively

The phase structure of the austenitic steels measured by XRD is shown in Fig. 2. The X-ray diffractograms show that the samples contain only the austenite ($Fe-\gamma$). No peak of ferrite ($Fe-\alpha$) was detected.

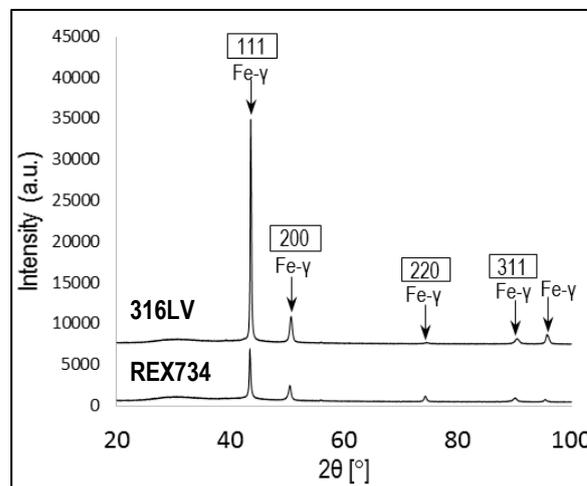


Fig. 2. XRD patterns of the REX734 and 316LV steels

Typical anodic polarization curves of both tested steels are presented in Fig. 3, and major parameters describing the corrosion properties are summarized in Table 2. Analyzing polarization curves, one can observe that in REX734 steel the passive range is about 65% longer in comparison to the 316LV (see Fig. 3). It is known that the transpassivation starts when the breakdown potential is achieved, and this is a moment of initiation of corrosion pits. For the 316LV steel, the breakdown potential took place at 0.7 ± 0.13 V, while for the REX734 steel this potential has considerably higher value (1.15 ± 0.1 V). Similar results were reported by other author (Burnat et al., 2008).

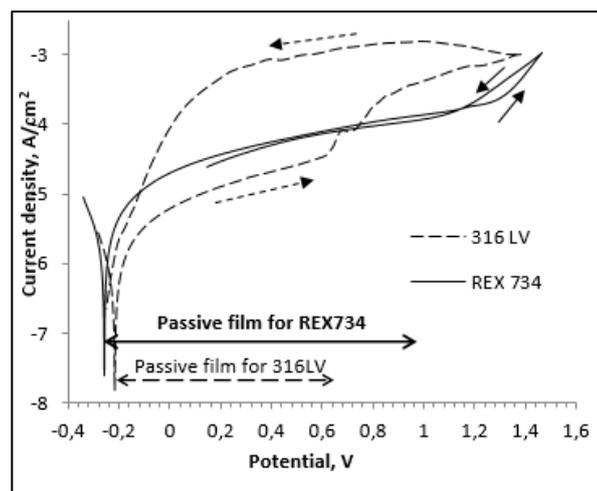


Fig. 3. Typical potentiodynamic polarization curves of: a) REX 734 steel, b) 316 LV steels.

The repassivation potential, measured at the moment when the polarization curve reverses and intersects the forward scan in the passive area (cross over potential measured during forward scan), revealed differences for both tested alloys. For the 316LV the potential is nearly six times lower than for the REX734 and reaches about -0.22V and 1.08V, respectively. Visible large hysteresis loop for 316LV can clearly indicate deep pitting attack and susceptibility of this alloy to crevice corrosion. According to other author (Rondelli et al., 1997), the passivation and repassivation potential is strongly related to the alloying elements concentration on the surface of the sample and the chemical composition inside the pit, mainly pH of a solution and ions concentration. Another author (Bayoumi and Ghanem, 2005) claimed that the hysteresis loop can be strongly suppressed by the presence of nitrogen. Nitrogen, not only delays the pit initiation, but also reduces the pit growth by fast repassivation. This process can be explained as follows. In the aggressive physiological solution, many anions of Cl^- , F^- and others may be introduced. The corrosion mechanism involves movement of these anions through the passive film to the metal-oxide interface, as it is presented in the Fig. 4. Negatively charged nitrogen N^{3-} particles deposited under passive layer can repulsively interact with the Cl^- anions causing desorption reaction and the further removal of these anions. This might be the main reason for fast repassivation process of the pits in the nitrogen containing stainless steels (Bayoumi and Ghanem, 2005; Grabke, 1996).

In potentiodynamic curves of the REX734 small hysteresis loop was clearly observed, thus less corrosion pits after initiation might be expected on the surface of this sample, in comparison to the 316LV grade. Indeed, surface observation in Fig. 5, confirmed

these anticipations. Careful stereological analysis of these images revealed that the surface of the 316LV steel has more corrosion pits, which are also bigger in size in comparison to the REX734. Average pits area presented in Table 2 as well as an average pit size of 12.33 ± 0.11 and 5.16 ± 0.18 μm for the 316LV and REX 734 steels, respectively, is significantly higher for the 316LV alloy.

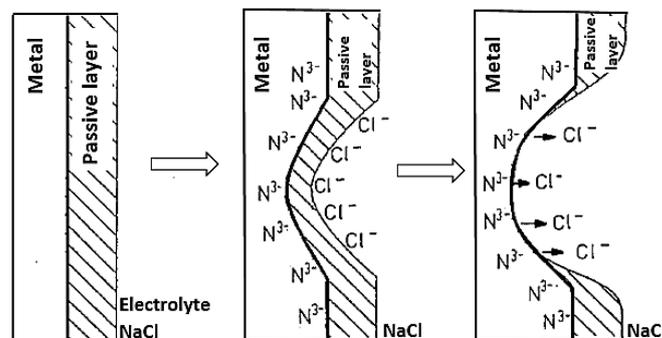


Fig. 4. Schematics view for pit initiation in steel (Grabke, 1996)

However, it is interesting to note that in the REX734 steel (see Fig. 3), after the moment when the curve reaches the repassivation point, the reverse scan follows slightly below the forward curve running and touches it again at 0.45 V. This emphasize that the passive layer is not very stable and pitting corrosion in some areas of the samples can take place. This is probably related to the chemical composition of the REX734 steel; not uniform distribution of main alloying elements on the surface or insufficient quantity of nitrogen content. According to the author's knowledge, this kind of behavior of the stainless steel was not reported by other research workers.

Tab. 2. Major parameters describing corrosion properties of both tested steels

Materials	E_{cor} , V	R_p , Ωcm^2	I_{cor} , $\mu\text{A}/\text{cm}^2$	C_R , $\mu\text{M}/\text{Y}$	E_b , V	E_{cp} , V	Pits area, %
REX 734	-0.25 ± 0.02	7.2 ± 0.7	2.8 ± 0.4	31.0 ± 1	1.15 ± 0.10	1.08 ± 0.13	1.52 ± 0.21
316 LV	-0.27 ± 0.04	15.6 ± 0.9	3.5 ± 0.2	39.8 ± 1.50	0.7 ± 0.13	-0.22 ± 0.11	8.02 ± 0.20

Also, in the data presented in Tab. 2 it is visible that the corrosion potentials (E_{cor}) of both steels are similar. The corrosion density (I_{cor}) however, is considerably lower for REX734 steel, which indicates higher corrosion resistance of this material. Furthermore, the polarization resistance (R_p), a parameter which is inversely proportional to the corrosion density, has the higher value for the 316LV and is two times higher than for REX734. Nonetheless, the corrosion rate (C_R) is only about 20% lower for the REX734 in comparison to the high nickel 316IV stainless steel.

In this work, pH of the sodium chloride solution was measured before and after the corrosion tests to find out more about the environment (in which the process took place), pits initiation and stability. The stability of corroding pits depends on the chemical composition of stainless steels, type of electrolyte used and pH value. Information about pH alterations, during various stages of corrosion tests, often provide an explanation about the stability of pits after the corrosion initiation (Bayoumi and Ghanem, 2005; Ghanem et al., 2015).

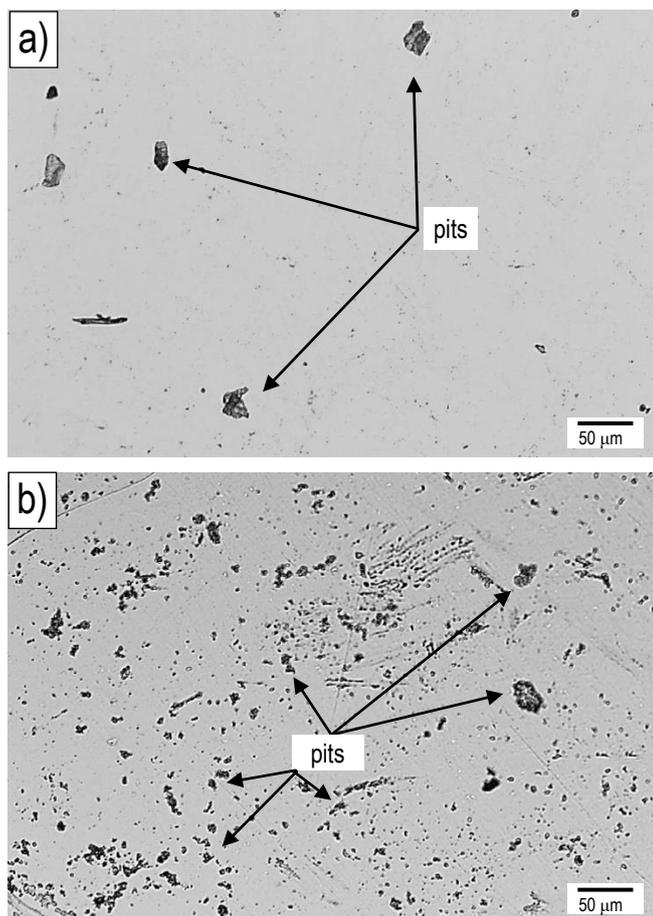


Fig. 5. Surface observations of the samples after the potentiodynamic corrosion tests: a) REX734 steel, b) 316LV steel

Results of pH measurements, presented in Fig. 6, revealed that the solution pH of both materials increased after corrosion tests. It means that OH^- ions, according to the equation (1), might have been released to the solution and form pits on the surface of both materials. On the other hand, it is well known (Grabke, 1996) that nitrogen reduces the acidification in pits, retarding the pitting corrosion process. It seems that in the case of REX734 steel some of the pits can be tightly protected by the passive layer and some of them remained open what confirms the need for increasing the nitrogen content that favours repassivation process.

These data also confirms the role of nitrogen in active corrosion protection of the stainless steel.

4. CONCLUSION

In this paper, the potentiodynamic corrosion tests of two austenitic stainless steels were performed. Commonly used in medical applications the 316LV steel was compared to the REX734 - modified version of the austenitic stainless steel. Both materials have similar microstructure, with an average grain size of $25 \mu\text{m}$, and hardness values of $\text{HV}_{0.1} 371 \pm 11$ and $\text{HV}_{0.1} 399 \pm 15$ for the 316LV and REX734, respectively. XRD analysis also confirmed presence of the only FCC (Fe- γ) austenite phase structure. The corrosion tests revealed however, that the REX734 steel, with lower Ni and higher Cr, Mn and N content, has better corrosion resistance in comparison to the 316LV grade. In spite of the microstructure similarities, higher amount of chromium and nitrogen ensures reduction of the current corrosion density, improves the breakdown potential and fast repassivation potential for the REX734 steel. Also, on the surface of tested 316LV steel, larger area of coarser pits were observed what confirms better potentiodynamic corrosion resistance of the REX734 alloy. pH measurements performed before and after corrosion tests revealed an increase in pH of both materials solutions, associated with pitting corrosion observed on the surface of the tested samples.

The results presented in this work confirmed that an appropriate selection and quantity of the alloying elements have great influence on the corrosion properties of steels. Therefore, it seems reasonable to continue researches leading to obtain optimal chemical composition of the austenitic stainless steel. Thus, future activity will be focused on the production of new generation, nickel-free austenitic stainless steel, with enhanced mechanical properties and corrosion resistance, where expensive and toxic nickel will be entirely replaced by nitrogen.

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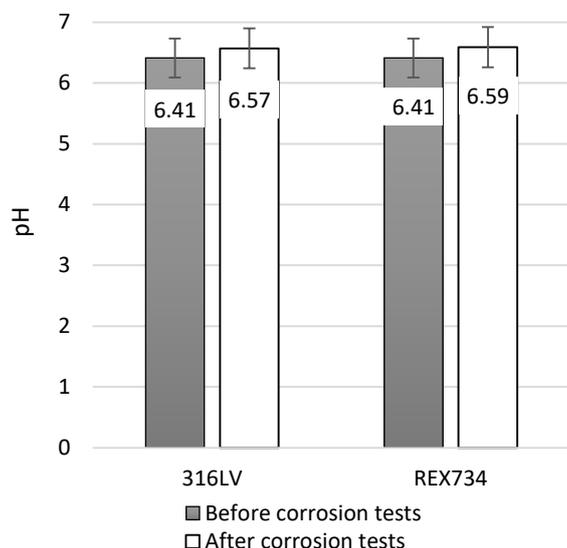


Fig. 6. Results of pH measurement of the 0.9% NaCl solution

At the time of pits formation, the surface of the sample becomes the anode, which means that the metal dissolves into the pit interior (McCafferty, 2010, Baba et al., 2002). Assuming that pit is the cathode, where oxygen is reduced, it leads to the reaction (McCafferty, 2010):



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