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Electrochemical behavior of austenitic stainless steels in different chloride solutions

Krzysztof Rokosz^{1a}, Gregor Mori^{1b}, Grzegorz Solecki^{1,2c}

The presented paper presents the results of the effect of different polishing methods on passive layer chemistry and the corrosion behavior of austenitic stainless steels. It was found that CrNiMo have a substantially better corrosion behavior than CrMnN samples. The nickel is enriched underneath the passive layer, while manganese tends to be enriched in the passive layer. It was also noted that immersion of manganese into an electrolyte preferentially causes its dissolution. It was found that high amounts of chromium (27.4%), molybdenum (3.3%), nickel (29.4%), with the addition of manganese (2.8%) after mechanical grinding, generates a better corrosion resistance than after electrochemical polishing. This is most likely because of the introduction of phosphates and sulfates into its structure, which is known for steels with a high amount of manganese. For highly alloyed CrNiMo steels, which do not contain a high amount of manganese, the addition of phosphates and/or sulphates via the electropolishing process results in a decrease in pitting corrosion resistance, which is also observed for high manganese steels. Electropolished samples show detrimental corrosion properties when compared to mechanically polished samples. This is attributed to substantial amounts of sulfate and phosphate from the electropolishing electrolyte present in the surface of the passive layer.

Keywords: stainless steels; passivity; electropolishing; mechanical polishing; electrochemical behavior;

INTRODUCTION

To smoothen steel surfaces, mechanical polishing and electropolishing can be performed. Mechanical polishing can introduce cold deformation, residual stresses, and debris into the steel surface. On the other hand, electropolishing will dissolve more active sites, such as chromium poor segregations and nonmetallic inclusions, especially manganese sulfides. Therefore, it has often been found that electropolished steels have better corrosion properties than mechanically polished ones. Examples are given by Lee and Lai [1] in their investigation of the surface condition of stainless steel 316L by electropolishing in a sulfuric acid-phosphoric acid mixed electrolyte. Through electrochemical tests (polarization scans and electrochemical potentiokinetic reactivation (EPR) tests), they found a substantial increase in corrosion properties in sulfuric acid after electropolishing. Furthermore, Hryniewicz, Rokosz et al. [2–5] found a substantial improvement in the corrosion properties of AISI 304L and AISI 316L after electropolishing when tested in Ringer solution, 3% NaCl, and distilled water at 25°C (aerated conditions). Most authors [6–10] investigated the effect of electropolishing on stainless steel 316L and characterized corrosion properties in various media. They conclude that electropolishing improves corrosion properties. Ziemiak [11] comes to more diverse conclusions by considering papers of Perge, Robertson, Maekawa et al., Warzee et al., and Guinard et al. [12–16]. Electropolished stainless steel in water at temperatures below 350 °C shows better corrosion properties due to simultaneous oxide layer formation (outer layer ferrite or chromite rich and inner layer (chromite rich)), with the latter growing faster at cold worked, energy rich sites. At higher temperatures (>450 °C), when steam is present, short-circuiting at cold worked sites and enhanced chromium diffusion along grain boundaries favors corrosion resistance of mechanically polished surfaces over electropolished ones. There are different alloying concepts of austenitic stainless steels. The CrNiMo austenitic stainless steels get their fcc microstructure mainly by alloying with nickel. Nickel in this case is the most noble alloying element in these steels. Therefore, it is depleted in the passive layer and enriched underneath the passive layer in the so-called interface between the passive layer and bulk alloy [17–19]. The second, less widely spread group of austenitic stainless steels are the CrMnN austenites, where manganese is the alloying element that stabilizes the fcc lattice. CrMnN has been widely investigated by Speidel and Uggowitzer [20,21] and later by Mori and his group [22,23]. Manganese in contradiction to nickel is less noble than iron and behaves similarly to chromium with its electrochemical potential. However, Manganese is not a passivating metal, consequently it is enriched in the passive layer, though does not contribute to an increased passivity like molybdenum. The goal of the present paper is to compare mechanical and electrochemical polishing and their effect on passivity and pitting corrosion resistance of austenitic stainless steels. Not only the most widely investigated stainless steel (316L), but also steels with different chemical compositions and alloying concepts (CrNiMo austenites vs. CrMnN austenites) are part of this study.

METHOD

AISI Four austenitic stainless steels were investigated, two CrNiMo austenites and two CrMnN austenites (Table 1). They have different alloying contents yielding to different pitting resistance equivalent numbers (PREN—PREN is indicated in the footnote of Table 1). Throughout this work the less widespread PREN_{Mn} is used. A negative factor of 1 for the alloying element manganese is included in the PREN formula. This is necessary when investigating high-manganese and low-manganese stainless steels together in one work. The mechanical properties of the investigated materials are shown in Table 2. All materials were solution annealed and had a purely austenitic grain, free from precipitates. Grain size was between 80 and 200 μm for all materials.

Table 1. Chemical composition of investigated stainless steels, in wt. %.

Material	C	Si	Mn	Cr	Ni	Mo	N	PREN	PREN _{Mn}
18Cr21Mn2NiN	<0,06	0,1	21,2	18,2	1,7	0,5	0,6	29	8
20Cr20Mn7Ni2MoN	<0,03		20,0	20,0	7,0	2,3	0,7	39	19
18Cr15Ni3Mo (S31603)	<0,03	0,3	1,8	17,5	14,7	2,8	0,1	28	26
27Cr29Ni3Mo (N08028)	<0,03	0,3	2,8	27,4	29,4	3,3	0,3	43	40

PREN = %Cr + 3.3 × %Mo + 16 × %N [24,25]. PREN_{Mn} = %Cr + 3.3 × %Mo + 16 × %N - 1 × %Mn [26,27].

Mechanical polishing was done with SiC abrasive papers from 1 #20 up to #1000. Then, polished specimens were stored for 24h in a desiccator for passive film formation. Electropolishing was done in a commercial H₂SO₄-H₃PO₄ electrolyte E269 from Poligrat. Current density was 500 mA/cm² at a temperature of 60 °C. Polishing time was 4 minutes.

Table 2 Mechanical properties of investigated stainless steels at room temperature

Material	Yield Strength [MPa]	Tensile Strength [Mpa]	Fracture Elongation [%]
18Cr21Mn2NiN	560	920	65
20Cr20Mn7Ni2MoN	510	900	54
18Cr15Ni3Mo (S31603)	290	560	65
27Cr29Ni3Mo (N08028)	380	790	64

Pitting corrosion properties were determined in a conventional three-electrode cell. As counter and reference electrodes, a platinum sheet and saturated calomel electrode (SCE) with a potential of 241 mV vs. H were used, respectively. As electrolyte, a high chloride containing NaCl solution with 80000 ppm Cl₋ at starting pH = 7 was used at a temperature of 80 °C. The scan rate was 200 mV/h (forward and reverse scans), and prior to polarization scans, open circuit potential was measured for 1 h. The start of the scanning was done from E_{OCP} -100 mV_{SCE} to the limit of current density at 1 mA/cm² or a potential of 2000 mV_{SCE}. Each specimen was tested a minimum three times.

Results

Polarization scans are shown in Figures 1–4 and in Supplementary Materials in Figures 1–4. In all Figures, the left image refers to mechanically polished samples and the right one to electropolished ones. It has to be pointed out that repeatability was good in all cases. Every experiment was done three times to prove repeatability.

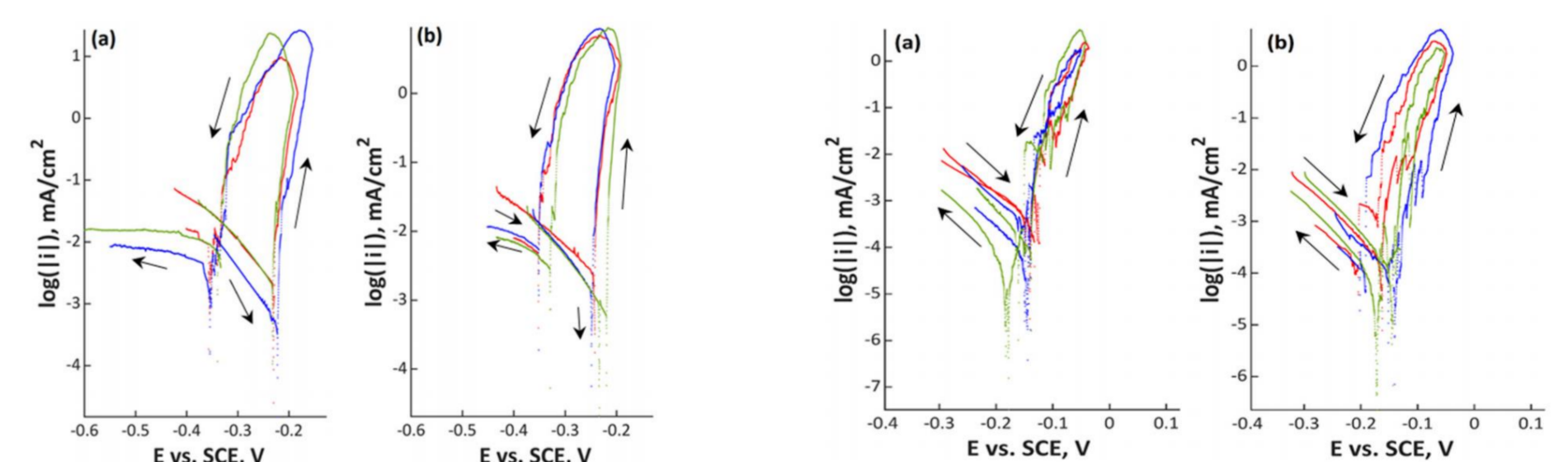


Figure 1. Polarization curves of (a) mechanically polished and (b) electropolished 18Cr21Mn2NiN stainless steel in aerated water solution with NaCl (80000 ppm Cl₋, pH 7; 80 °C, 200 mV/h).

Figure 2. Polarization curves of (a) mechanically polished and (b) electropolished 20Cr20Mn7Ni2MoN stainless steel in aerated water solution with NaCl (80000 ppm Cl₋, pH 7; 80 °C, 200 mV/h).

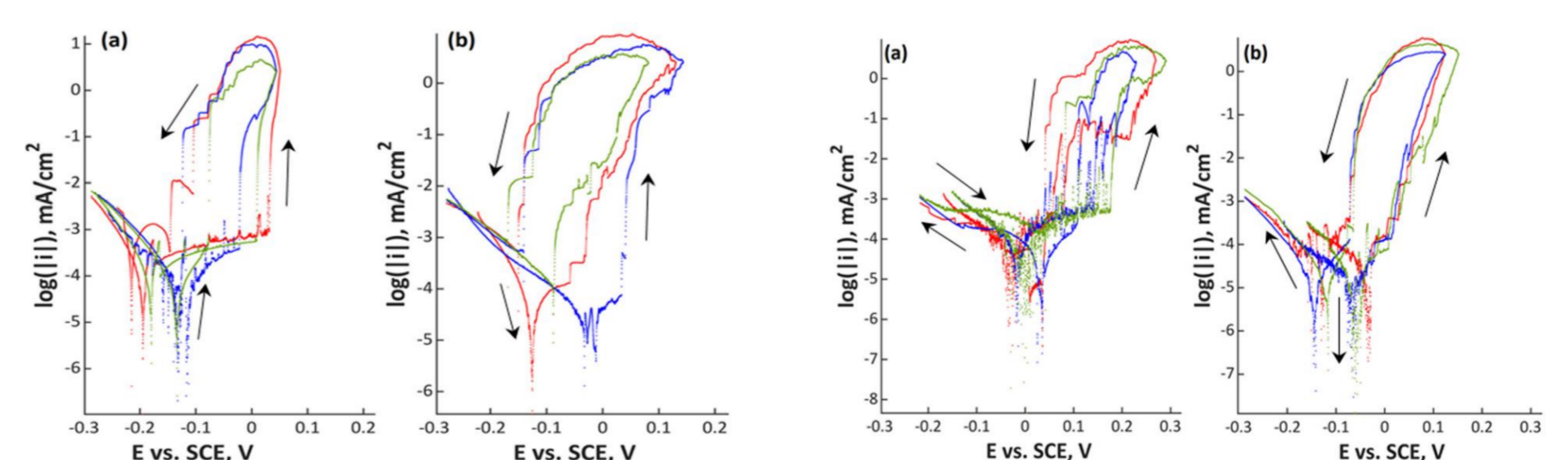


Figure 3. Polarization curves of (a) mechanically polished and (b) electropolished 18Cr15Ni3Mo stainless steel in aerated water solution with NaCl (80000 ppm Cl₋, pH 7; 80 °C, 200 mV/h).

Figure 4. Polarization curves of (a) mechanically polished and (b) electropolished 27Cr29Ni3Mo stainless steel in aerated water solution with NaCl (80000 ppm Cl₋, pH 7; 80 °C, 200 mV/h).

The lowest alloyed material 18Cr21Mn2NiN (Figure 1) in both surface conditions demonstrated an open circuit potential of between -0.25 and -0.22 V_{SCE}. There is no passive range for this steel in the investigated electrolyte and pitting starts immediately at the open circuit potential. The hysteresis in the curves shows that pitting occurred. Repassivation potential is in the range of -0.35 and -0.32 V_{SCE} independent of surface condition. Polarization curves of the higher alloyed manganese containing steel 20Cr20Mn7Ni2MoN are shown in Figure 2. The open circuit potential was between -0.16 and -0.14 V_{SCE}, which is slightly more noble compared to the lower alloyed 18Cr21Mn2NiN. Again, there was no recorded passive region, though the repassivation potential shifted closer to the open circuit potential (from -0.20 up to -0.10 V_{SCE}). In Figures 3 and 4, the two stainless steels with low amounts of manganese are shown. Material 18Cr15Ni3Mo with an open circuit potential between -0.20 and -0.09 V_{SCE} showed a passive range with a width between 0.05 (electropolished) and 0.15 V (mechanically polished). This steel already showed a small difference between the mechanically and the electrochemically polished surface.

The passive range was slightly wider for the mechanically polished condition. Repassivation potential was close to the open circuit potential for both specimens. The highest alloyed stainless steel 27Cr29Ni3Mo, a superaustenitic steel, showed the largest difference between the two investigated surface treatments. For the mechanically polished specimens, there was a clearly visible passive region, while it was not observed in the electrochemical-treated ones. The open circuit potential was close to 0 VSCE for the mechanically polished samples, and it was slightly negative for the electropolished ones. A clear distinction was observed for the repassivation potentials: mechanically polished specimens repassivate at more noble potentials compared to the open circuit potential; electropolished ones repassivate close to the open circuit potential. Electrochemical parameters E_{corr} , i_{corr} , E_{pit} , and E_{rep} are presented in Table 3.

Table 3. Summary of electrochemical parameters from polarization curves of investigated stainless steels in aerated water solution with NaCl (80000 ppm Cl⁻, pH 7; 80 °C, 200 mV/h).

Material	After Mechanical Grinding				After Electrochemical Polishing			
	E_{corr} mV _{SCE}	i_{corr} mA/cm ²	E_{pit} mV _{SCE}	E_{rep} mV _{SCE}	E_{corr} mV _{SCE}	i_{corr} mA/cm ²	E_{pit} mV _{SCE}	E_{rep} mV _{SCE}
18Cr21Mn2NiN	-230	8.21×10^{-4}	-230	-331	-240	9.74×10^{-4}	-240	-350
	-222	2.21×10^{-4}	-222	-322	-250	5.13×10^{-4}	-250	-350
	-232	8.21×10^{-4}	-232	-329	-220	2.36×10^{-4}	-220	-320
20Cr20Mn7Ni2MoN	-145	1.44×10^{-4}	-100	-100	-160	1.06×10^{-4}	-120	-200
	-138	6.82×10^{-5}	-108	-108	-140	4.70×10^{-5}	-90	-190
	-140	2.58×10^{-4}	-108	-113	-140	7.58×10^{-5}	-110	-130
18Cr15Ni3Mo (UNS S31603)	-195	5.13×10^{-5}	32	-104	-130	2.26×10^{-5}	-30	-150
	-111	1.79×10^{-5}	-22	-124	-120	9.74×10^{-6}	30	-140
	-179	5.13×10^{-5}	9	-76	-90	4.72×10^{-5}	-22	-130
27Cr29Ni3Mo (UNS N08028)	-32	1.23×10^{-5}	219	41	-30	1.08×10^{-5}	20	-70
	-97	1.90×10^{-5}	209	-10	-60	5.13×10^{-6}	20	-70
	-10	2.15×10^{-5}	176	-82	-50	5.13×10^{-6}	10	-60

In the present paper, the effect of different polishing procedures on the passive layer chemistry and corrosion behavior of stainless steels, based on potentiodynamic corrosion and XPS measurements, is presented. It was found that CrNiMo austenitic stainless steels show a better corrosion than CrMnN ones. It was also noted that the pitting potential is a function of PREN_{Mn}, which is shown in Figure 5. For the three lower alloyed steels, surface treatment has no effect on pitting potential, while for the highest alloyed 27Cr29Ni3Mo, there is a substantial difference of almost 0.2 V (with the mechanically polished specimens being superior over electropolished ones). After the electropolishing process, the passive layers were less noble than the ones after mechanical treatments.

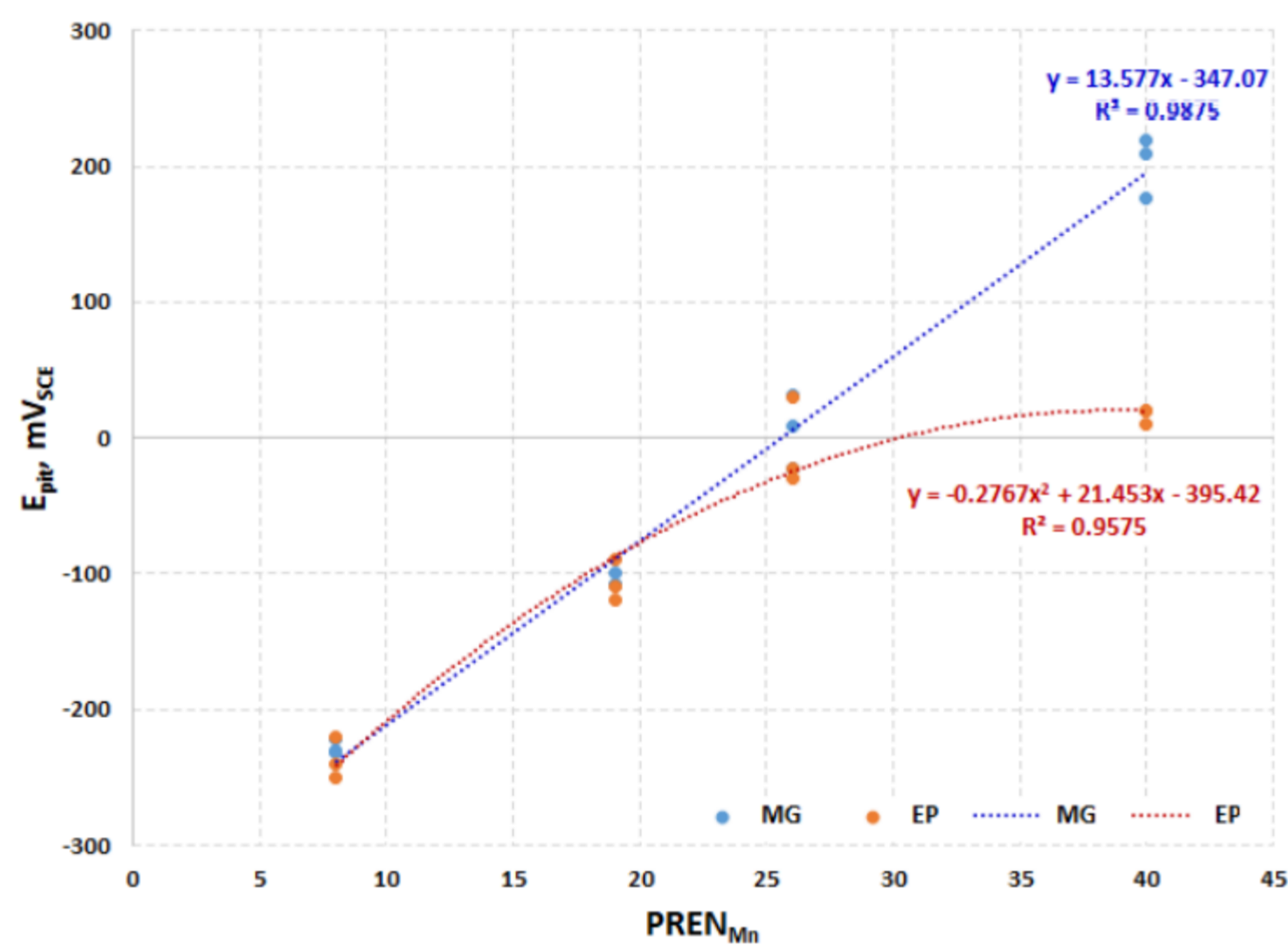


Figure 5 Comparison of pitting potential of studied stainless steels in function of modified pitting resistance equivalent with Mn (PREN_{Mn}), mechanically grinded (MG), electropolished (EP).

It was shown that the addition of molybdenum causes the formation of a compact layer, while manganese adds-on, negatively affecting its corrosion resistance. It was demonstrated that steels containing a lot of manganese (20–21%), low amounts of nickel (1.7–7%), and molybdenum (0.5–2.3%) with a PREN_{Mn} of less than 19 do not show differences in pitting corrosion resistance after mechanical and electrochemical treatments. In the case when the amount of manganese decreased (1.8–2.8%), with a simultaneous increase in nickel (14.7–29.4%) and molybdenum (2.8–3.3%), the pitting corrosion resistance of mechanically polished samples was significantly higher than that of the electrochemical ones. This phenomenon can be explained by the fact that a large addition of manganese in the steel structure probably has a negative effect on the pitting corrosion resistance of the passive layer, and any additional incorporation of phosphates and/or sulphates into the chromium–molybdenum structure has no significant influence on its corrosion resistance. In the case of steel with a high amount of chromium (27.4%), molybdenum (3.3%), nickel (29.4%), and a small amount of manganese (2.8%), after mechanical polishing, a stable and tight passive layer is formed, which is weakened by the introduction of phosphates and sulfates to its structures. From this, we can draw the conclusion that for high-alloyed steels that do not contain large amounts of manganese, the addition of phosphates and/or sulphates by electropolishing results in a decrease in the pitting corrosion resistance, similar to the one observed in the case of steels with high amounts of manganese. In this discussion, the possible effect of nickel on pitting has thus far been neglected. Nickel usually is not included in PREN, so most authors believe that nickel has no effect. Speidel et al. [21,28–31] found nickel to have a small negative effect with respect to the pitting corrosion resistance, and they published this by proposing a measure of alloying as a resistance to corrosion (MARC) value. They also included the effects of carbon and manganese in MARC (Equation (1)).

$$\text{MARC} = \%Cr + 3.3 \times \%Mo + 20 \times \%N + 20 \times \%C - 0.5 \times \%Mn - 0.25 \times \%Ni$$

Conclusions

- CrNiMo austenites show a substantially better corrosion behavior than CrMnN austenites;
- For all steels, chromium enrichment was noted in the passive layers;
- For CrNiMo austenites, there is nickel enrichment underneath the passive layer, while for CrMnN austenites, manganese tends to be enriched in the passive layer;
- After electropolishing, sulfate and phosphate are present in the passive layers. The poor corrosion properties of electropolished specimens, as compared to mechanically ground ones, can be explained by this.

LITERATURE

1. Lee, S.-J.; Lai, J.-J. The effects of electropolishing (EP) process parameters on corrosion resistance of 316L stainless steel. *J. Mater. Process. Technol.* 2003, 140, 206–210.
2. Hryniewicz, T.; Rokosz, K. Corrosion resistance of magneto-electropolished AISI 316L SS biomaterial. *Anti-Corros. Methods Mater.* 2014, 61, 57–64.
3. Rokosz, K.; Simon, F.; Hryniewicz, T.; Rzakiewicz, S. Comparative XPS analysis of passive layers composition formed on AISI 304 L SS after standard and high-current density electropolishing. *Surf. Interface Anal.* 2015, 47, 87–92.
4. Rokosz, K.; Hryniewicz, T.; Raaen, S. Cr/Fe ratio by XPS spectra of magneto-electropolished AISI 316L SS fitted by gaussian-lorentzian shape lines. *Teh. Vjesn. Tech. Gaz.* 2014, 21, 533–538.
5. Rokosz, K.; Hryniewicz, T.; Raaen, S. Characterization of Passive Film Formed on AISI 316L Stainless Steel after Magneto-electropolishing in a Broad Range of Polarization Parameters. *Steel Res. Int.* 2012, 83, 910–918.
6. Sutow, E.J. The influence of electropolishing on the corrosion resistance of 316L stainless steel. *J. Biomed. Mater. Res.* 1980, 14, 587–595.
7. Lee, E.-S. Machining Characteristics of the Electropolishing of Stainless Steel (STS316L). *Int. J. Adv. Manuf. Tech.* 2000, 16, 591–599.
8. Han, Y.; Mei, J.; Peng, Q.; Han, E.-H.; Ke, W. Effect of electropolishing on corrosion of nuclear grade 316L stainless steel in deaerated high temperature water. *Corros. Sci.* 2016, 112, 625–634.
9. Sojitra, P.; Engineer, C.; Kothwala, D.; Raval, A.; Kotadia, H.; Mehta, G. Electropolishing of 316LVM Stainless Steel Cardiovascular Stents: An Investigation of Material Removal, Surface Roughness and Corrosion Behaviour. *Trends Biomater. Artif. Organs* 2010, 23, 115–121.
10. Rokosz, K.; Hryniewicz, T. Pitting Corrosion Resistance of AISI 316L Stainless Steel in Ringer's Solution after Magneto-electrochemical Polishing. *Corrosion* 2010, 66, 035004-035004-11. *Materials* 2020, 13, 3402 12 of 12
11. Ziemniak, S.E.; Hanson, M.; Sander, P.C. Electropolishing effects on corrosion behavior of 304 stainless steel in high temperature, hydrogenated water. *Corros. Sci.* 2008, 50, 2465–2477.
12. Berge, P. Importance of surface preparation for corrosion control in nuclear power stations. *Mater. Perform.* 1997, 36, 56–62.
13. Robertson, J. The mechanism of high temperature aqueous corrosion of stainless steels. *Corros. Sci.* 1991, 32, 443–465.
14. Maekawa, T.; Kagawa, M.; Nakajima, N. Corrosion Behaviors of Stainless Steel in High-Temperature Water and Superheated Steam. *Trans. Jpn. I. Met.* 1968, 9, 130–136.
15. Warzee, M.; Hennaut, J.; Maurice, M.; Sonnen, C.; Waty, J.; Berge, P. Effect of Surface Treatment on the Corrosion of Stainless Steels in High-Temperature Water and Steam. *J. Electrochem. Soc.* 1965, 112, 670.
16. Guinard, L.; Kerrec, O.; Noel, D.; Gardey, S.; Coulet, F. Influence of the initial surface condition on the release of nickel alloys in the primary circuit of PWRs (EDF-97-NB-00045). *Nucl. Energy* 1997, 36, 19–27.
17. Holzleitner, S.; Kranister, W.; Mori, G.; Schmuki, P. Applying A Multi Method Approach To Chloride Induced SCC Of Two Austenitic Cr-Ni-Mo-N Stainless Steels, Corrosion 2008, New Orleans, LA, USA, 16–18 March 2008; NACE International: Houston, TX, USA, 2008; pp. 1–18.
18. Mori, G.; Sonnleitner, R.; Holzleitner, S.; Panzenböck, M.; Pippin, R. Spannungs- und Schwingungsrissskorrosion Gemeinsamkeiten und Unterschiede. *Mater. Test.* 2010, 52, 42–51.
19. Elsener, B.; Rossi, A. The passive film on stainless steels—Results of XPS surface analysis. In *Korrosions nichtrostender Stähle—Auf die Oberfläche kommt es an!* Proceedings of the 3-Länder-Korrosionstagung 2008, 24–25 April 2008; Technical University of Vienna: Vienna, Austria, 2008; pp. 13–22.
20. Uggowitzer, P.J.; Magdowski, R.; Speidel, M.O. High Nitrogen Steels. Nickel Free High Nitrogen Austenitic Steels. *Isij Int.* 1996, 36, 901–908.
21. Speidel, M.O. Nitrogen Containing Austenitic Stainless Steels. *Materialwiss. Werkst.* 2006, 37, 875–880.
22. Holzleitner, S.; Mori, G.; Falk, H.; Eglsaeer, S. Electrochemical and SCC Behavior Of Highly Alloyed Austenitic Stainless Steels In Different Chloride Containing Media, Corrosion 2007, Nashville, TN, USA, 11–15 March 2007; NACE International: Houston, TX, USA, 2007; pp. 1–17.
23. Vichytil, C.; Sonnleitner, R.; Mori, G.; Panzenböck, M.; Fluch, R. Corrosion Fatigue Investigations on Austenitic Stainless Steels with Different Alloying Concepts; Corrosion 2010; NACE International: Houston, TX, USA, 2020.
24. Forsén, O.; Aromaa, J.; Tavi, M. Examples of Electrochemical Testing of Stainless Steels in Industrial Environments. *Mater. Sci. Forum* 1995, 192–194, 41–52.
25. Merello, R.; Botana, F.J.; Botella, J.; Matres, M.V.; Marcos, M. Influence of chemical composition on the pitting corrosion resistance of non-standard low-Ni high-Mn–N duplex stainless steels. *Corros. Sci.* 2003, 45, 909–921.
26. Mori, G.; Bauernfeind, D. Pitting and crevice corrosion of superaustenitic stainless steels. *Mater. Corros.* 2004, 55, 164–173.
27. Rondelli, G.; Vicentini, B. Heat exchanger Technologies for the global Environment. In *Proceedings of the 1994 International Joint Power Generation Conference*, 2–6 October 1994; Maurer, J.R., Ed.; ASME Orders: Fairfield, NJ, USA, 1994; Volume 25, p. 61.
28. Speidel, M.O. Ultra High Strength Austenitic Stainless Steels, 2nd Stainless Steel World 2001, 13–15 November 2001, The Hague, The Netherlands; KCI Publishing BV: Zutphen, The Netherlands, 2001; pp. 98–106.
29. Speidel, M.O.; Zhend-Cui, M.L.; Kowanda, C.; Speidel, H.; Diener, M. High-nitrogen austenitic stainless steels - Future materials for the chemical industries. *Trans. Ind. Inst. Met.* 2003, 56, 281–286.
30. Speidel, M.O.; Zheng-Cui, M. High-Nitrogen Austenitic Stainless Steels, High Nitrogen Steels, HNS 2003, 26–28 March 2003; Speidel, M.O., Ed.; vdf Hochschulverlag AG: Zurich, Switzerland, 2003; pp. 63–73.
31. Jargelius-Petersson, R.F.A. Application of the Pitting Resistance Equivalent Concept to Some Highly Alloyed Austenitic Stainless Steels. *Corrosion* 1998, 54, 162–168.

Affiliation

1 Faculty of Mechanical Engineering, Koszalin University of Technology, Raclawicka 15-17, PL 75-620 Koszalin, Poland; grzegorz.solecki.sg@gmail.com

2 Department of General, Analytical and Physical Chemistry, Montanuniversitaet Leoben, A-8700 Leoben, Austria