IMPROVING PITTING CORROSION OF 304 STAINLESS STEEL BY ELECTROPOLISHING TECHNIQUE

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Received: May 2012 **Accepted: November 2012**

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Abstract: *Several surface modification techniques such as ion implantation, surface laser melting, have been employed to improve pitting corrosion resistance of stainless steel. Electropolishing is a technique in which the surface roughness is eliminated through a selective electrochemical dissolution. The effect of electropolishing on pitting corrosion of 304 stainless steel (SS) was investigated employing polarization technique in conjunction with the scanning electron microcopy examination. Electropolishing process was carried out on wire of 2 mm diameter in 70% phosphoric acid solution at room temperature for 30 min. To elucidate the effect of roughness elimination on pitting corrosion, investigation was carried out on as-received specimen with surface finishing of 60 SiC grit and electropolished specimen in 0.5M NaCl solution at room temperature. A significant decrease on passive current density and also shift of pitting potential towards noble value was recorded on electropolished specimen revealing a pronounce effect of this technique on surface modification. Further investigation was carried out by employing slow ramp anodic potentiodynamic polarization on as received and electropolished specimen. Plot of metastable pitting current transient revealed the reduction on the number and magnitude of metastable pitting transients prior to occurrence of stable pitting on electropolished specimen. EDX analysis of the surface area of as received and electropolished specimens showed modification in surface roughness during electropolishing was the main reason of pitting corrosion improvement. Scanning microscopy investigation of polarized specimens beyond the pitting potential revealed that in as-receives specimen pits were nucleated in at and in the vicinity of surface scratches that was created during surface abrading.*

Keywords: *Pitting Corrosion, Breakdown Potential, surface treatment, Electropolishing*

1. INTRODUCTION

Surface characteristics of alloys can be changed by electropolishing, coating, etc [1-4]. Electropolishing (EP) is a polishing process of electrochemical anodic dissolution which is the most extensively used in surface technology for austenitic stainless steels [3,4]. The process consists of an anode (work piece), a cathode and electrolyte. Generally, the electrolyte is composed of viscous acid fluid. Because of selective dissolution, the metallurgical compositions of the passive film may be different from those of the substrate [3]. High corrosion resistivity of austenitic stainless steels is primarily attributed to the passive oxide film formed on its surface that, exposed to an aqueous solution, is a mixture of iron and chromium oxides, with hydroxide and water-containing compounds located in the outermost region of the film, and chromium oxide enrichment at the metal-film interface [5]. The remarkable improvement in corrosion resistance of electropolished surfaces of austenitic stainless steels is created by several interconnected events occurring during the electropolishing process, presented extensively elsewhere [6–8]. Thus treated stainless steel exhibits excellent corrosion resistance in a wide range of atmospheric environments and many corrosive media. This polishing method also applied on medical implant materials to promote corrosion resistance and biocompatibility because traditional mechanical polishing processes may result in deformed layer and residual stresses on the workpiece surface. This will affect durability of the components. Debris and impurity may also be rolled or presses into the work piece surface which may become loose during its lifetime. These undesirable inclusions may become sources of contamination to the operating process. [9]. Pitting corrosion of stainless steels (SS) is result from a combination of electrochemical and metallurgical factors including the effect of alloying elements, the nature and distribution of the non-metallic inclusions, cold working, heat treatment, grain size, sensitization and secondary precipitates [10-13]. The properties of the chemical environment (pH,

temperature, concentration, velocity etc.) and that of the passive film (conductivity, structure, composition, capacitance etc.) are also known to influence the pitting resistance, which have already been extensively studied [14-17]. It has been reported that modification in surface roughness increases pitting potential and has significant effect on pitting corrosion [18-21]. In this study effect of electropolishing process on pitting corrosion of 304 SS is investigated by means of electrochemical tests and microstructure observations.

2. EXPERIMENTAL

2. 1. Material Characterization

In this study the effect of electropolishing on pitting corrosion of 304 stainless steel was investigated. Chemical composition of 304 candidate alloy in weight percent was as a follow:

C: 0.085 , Cr: 18.25 , Ni: 8.15 , Mn: 1.85, Si: 0.52, S: 0.035, P: 0.045, Fe: Balance

2. 2. Electropolishing Procedure

As-received wires of 2mm diameter SS were prepared into categories; in order to compare the surface roughness effect some of the sires were abraded with abrasive paper up to 60 SiC grit and other wires were electropolished. Electropolishing process was carried out by immersing an as-received specimen in 70% phosphoric acid at 50°C temperature and an anodic potential of 2V for 30 min was applied while the cathode was a piece of graphite. After electropolishing, sample was rinsed by water and alcohol and was dried by hot air.

2. 3. Potentiodynamic Polarization

0.5M NaCl solution was selected to evaluate the effectiveness of electropolishing on pitting corrosion behavior of prepared working electrodes. Pitting potential of working electrode was measured by potentiodynamic polarization of working electrode from 50 mV below corrosion potential (Ecorr) towards noble values with a sweeping rate of 60mV/min. A sharp and continues increase in current density at the passivity domain was attributed to the occurrence of pitting corrosion. Precise difference of pitting corrosion behavior was also assessed by slow ramp anodic potentiodynamic polarization. To achieve reliable steady stat in this test, potentiodynamic polarization was carried out by employing 3mV/min potential scanning rate. Furthermore, to elucidate the results of potentiodynamic polarization tests, potentiostatic polarization was performed at selected anodic potentials in the passive domain for 900 seconds. All potentials were measured with respect to saturated calomel electrode (SCE) as a reference electrode and a foil of platinum with 2 cm^2 area was chosen as a counter electrode. Electrochemical tests were conceded by means of Gill AC automated potentiostat (ACM Instruments). Before each polarization test, sample was at corrosion potential for 30min.

2. 4. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

Microstructure of pits initiated on surface of polarized specimens beyond the pitting potential was observed by means of a scanning electron microscope (SEM) model (LEO 1450 VP). Compositional analysis of electropolished and as-received specimen surface was investigated using the energy dispersive X-ray spectroscopy (Oxford LTD) unit attached to the SEM.

3. RESULTS AND DISCUSSION

3. 1. Polarization results

Polarization results of two 304 SS samples in 0.5M NaCl are shown in figure 1. It is obvious that by electropolishing, passivity current density and corrosion current density were decreased and pitting potential as well as corrosion potential has shifted towards noble values. For instance, electropolishing increased 100mV in corrosion potential, 200mV in pitting potential and also passivity current density decreased for a decade. In view of the fact that pitting corrosion almost begins from deteriorated zones of passivity, such as surface inclusions and etc [10-17], superior pitting corrosion behavior of electropolished sample demonstrates a more integrated passivity with fewer defects in the passivity film in compare with

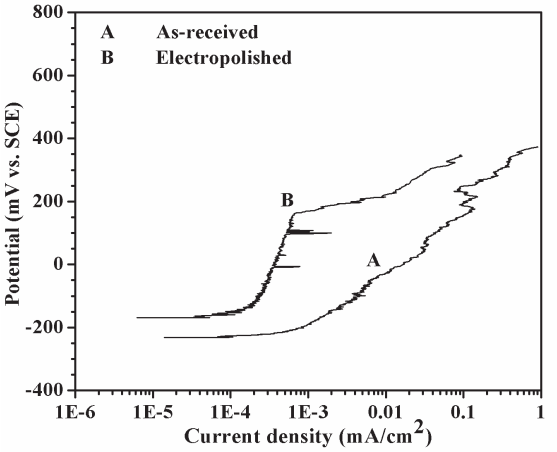

Fig. 1. Potentiodynamic polarization results for electropolished (red) and as-received (black) 316 StSt in 0.5M NaCl solution and 60mV/min scanning rate

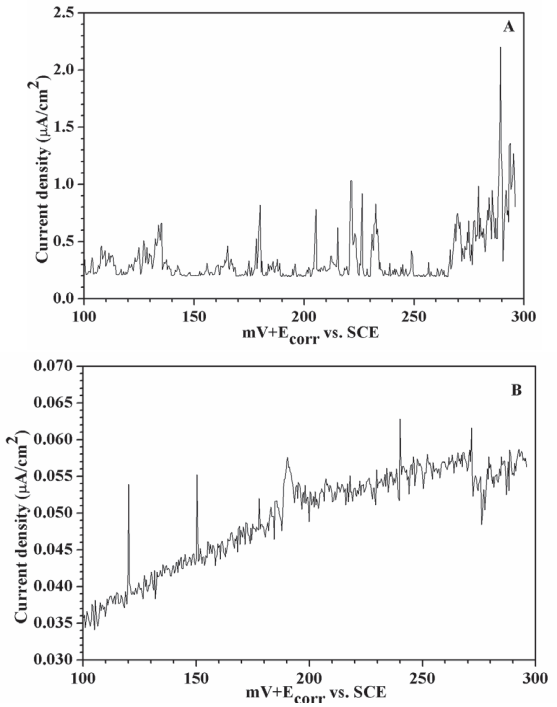

Fig. 2. Slow ramp anodic polarization of (A) as-received and (B) electropolished 316 StSt with 3mV/min scanning rate in potential range of 100-300 mV higher than E_{corr}

abraded as-received specimen. It elucidates that electropolishing process has a beneficial effect on pitting corrosion of 304 StSt. To evaluate the pitting corrosion behavior through metastable pit events, both of specimens were polarized from 100mV

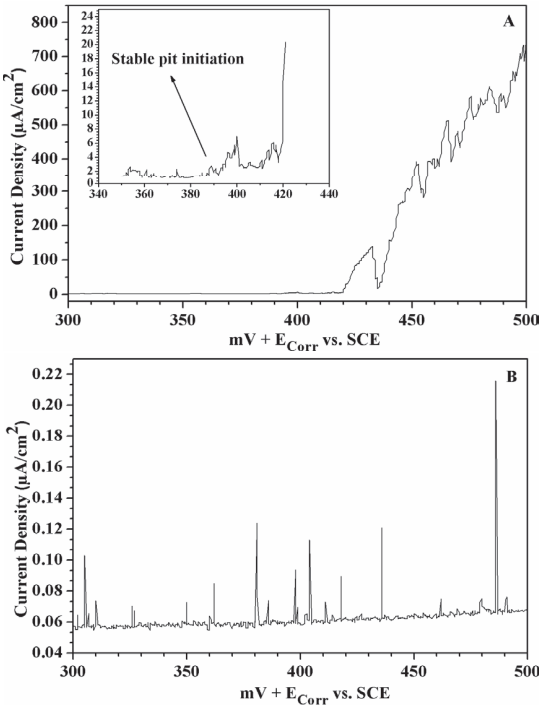

Fig. 3. Slow ramp anodic polarization of (A) as-received (inserted micrograph shows potential which is pitting corrosion started) and (B) electropolished 316 StSt with 3mV/min scanning rate in potential range of 300-500 mV higher than E_{corr}

below corrosion potential towards anodic potentials and beyond pitting corrosion potential with a very slow sweeping rate (3mV/min). Figure 2 shows associated current density of polarization at the potential range of 100 to 300 mV above corrosion potential where the metastable pits were quiet obvious. It can be noticed that both as-received and electropolished samples were in passive state and no stable pit can be observed. However the magnitude of passive current density of electropolished specimen is much lower than abraded as-received one. Moreover decrease in the number and magnitude of metastable pits can be observed in electropolished sample. These results verify that pitting initiation sites have been considerably decreased in electropolished. This behavior was repeated in higher potentials, as an example the result of current density created in potential range of 300-500 mV above corrosion potential is shown in figure 3. It is evident that in this potential range electropolished sample still has lower passive current density than abraded

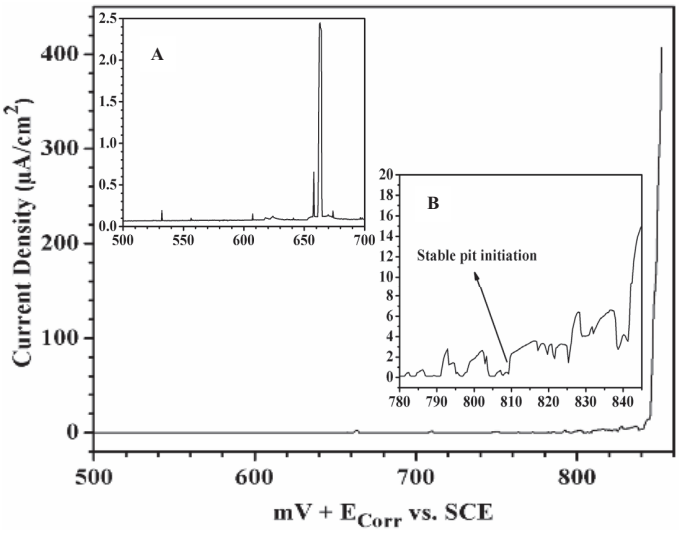

Fig. 4. Slow ramp anodic polarization of electropolished 316 StSt with 3mV/min scanning rate in potential range of 500-860 mV higher than E_{corr} (inserted micrograph A shows results in a range of 500-700 mV higher than E_{corr} and B shows potential whish is stable pit initiated on surface

as-received specimen. Besides as-received sample shows a sudden increase in its current density at 390 mV which is the indication of stable pits nucleation (inserted micrograph figure 3.a). However electropolished specimen is still in the passive state and only some metastable pits initiate in this potential range although the magnitude and number of these pits as well as passive current density are higher than previous potential range. By comparing these two potential ranges, it is apparent that current density in passive state for electropolished specimen has value of almost 100 times lower than as-received sample. To identify the pit initiation potential in electropolished specimen, the applied potential was continued to increase between 500 to 850mV above corrosion potential which is shown in figure 4. The working electrode is in passive state up to 810mV beyond corrosion potential and stable pits are nucleated at this potential. Current density was still in passive state in potential range of 500-700mV (inserted micrograph A) above corrosion potential. However the background value of passive current density and also magnitude of metastable pits was higher than two previous potential ranges. By judging against the result in noticed potential ranges for both specimens, it is comprehensible that electropolished specimen in potential range of 500-700mV has a comparable behavior of as-received specimen in potential range of 100-300mV even though number and magnitude of metastable pits in as-received specimen in range of potential of 100-300mV is higher than electropolished specimen in 500-700mV. Moreover the results of slow sweeping potentials for these two specimens showed that electropolishing process increases pitting potential from 390 to 810 mV. It is revealed that electropolishing process in 70% phosphoric acid has considerable beneficial effect on pitting corrosion behavior of 304 SS. This method promotes pitting potential and also significantly decreases passive current density as it reported for mechanical polishing [18-21]. Moreover, the passive current density of electropolished specimen is much lower than as-received one. For instance, figure 5 shows result of potentiostatic at 400mV above rest potential on both working electrodes. The value of passive current density for electropolished sample is approximately 1000 times lower than as-received one. Additionally electropolished sample shows a current density in a range of passivity current density (<10μA) and despite the fact that as-received sample does not show pitting corrosion in this potential but its current density is not in a range of passivity current densities. Further anodic potentiostatic polarization even clarified the beneficial effect of electropolishing on electropolished specimen. For

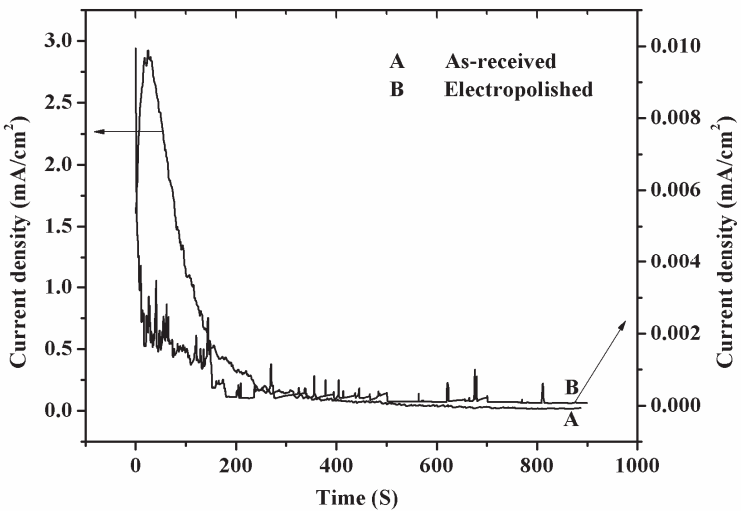

Fig. 5. Potentiostatic polarization results of (A) as-received and (B) Electropolished specimens in 400mV higher than corrosion potential

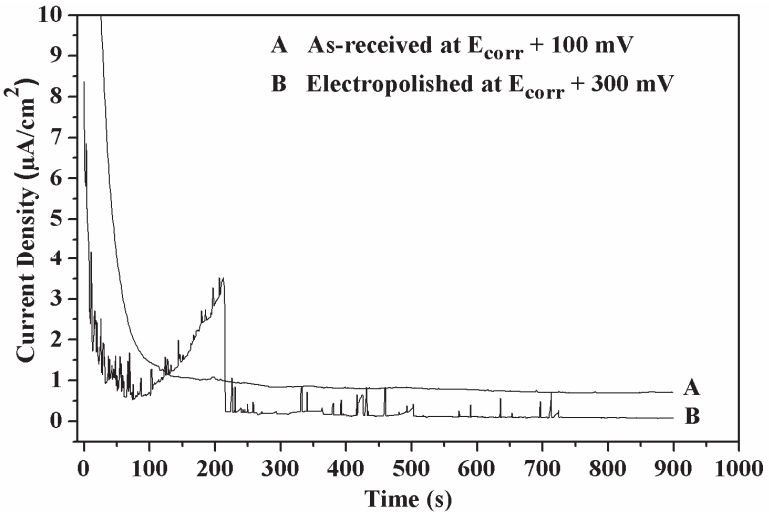

Fig. 6. Potentiostatic polarization results of (A) as-received in 100mV higher than E_{corr} and (B) Electropolished specimens in 300mV higher than E_{corr}

example figure 6 shows results of potentiostatic test in which as-received specimen was polarized in 100mV and electropolished sample in 300mV above corrosion potential. Even though electropolished specimen has been polarized 200mV more than as-received specimen but still shows remarkably lower passive current density. The reason of featuring metastable pitting current transients which can be observed as fluctuation of current density on electropolished specimens is attributed to the lower passivity current density background. When the passive current density background is very small, the small metastable pit events can also be observed which shifting the passive current density background to a higher values; as for as-received specimen, the small events are not able to rise beyond the background and so they can not be observed.

3. 2. Energy dispersive X-ray spectroscopy (EDX) results

Electrochemical results demonstrate that electropolishing has significant beneficial effect

on pitting corrosion behavior of 304 SS and an improvement on pitting potential and also passive current density of an electropolished specimen was observed. To evaluate the main beneficial effect of electropolishing on pitting corrosion, EDX analysis was carried out on the alloy surface before and after the course of electropolishing.

The superior pitting corrosion properties of electropolished sample can be explain by either modification in surface roughness or chemical composition changes mainly due to chromium enrichment on the surface [14-18]. EDX analysis of specimen surface is shown in figure 7. In electropolished specimen the presence of manganese is not observed and in contrast with as-received specimen its distinguishable peak was eliminated. Besides the intensity of peaks related to Fe, Cr and Ni elements have not significantly changed. Consequently the enhanced pitting properties of electropolished sample can be explained by modification in surface roughness and removal of MnS inclusions rather than significant chemical composition changes of the surface. In fact as it was explicated above, electropolishing may change the surface chemical composition and by enrichment of chromium, the surface creates a better passivity property with lower defects [10-14]. However in this case, although the absence of manganese in electropolished surface may confirm a surface with different chemical composition in compare with as-received one, but it suggests that the most essential reason of improving in pitting properties was modification in surface roughness and possible removal of MnS inclusions. As it reported elsewhere [22], electropolishing and acid pickling are two methods that causes manganese sulfide removal. Conclusively, electropolishing process reduces

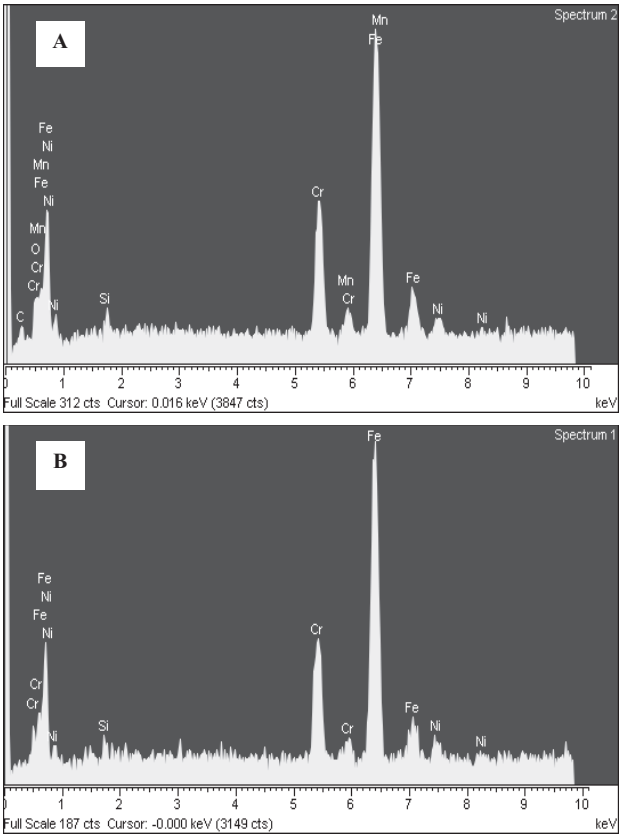

Fig. 7. EDX analysis results for (A) as-received specimen and (B) electropolished

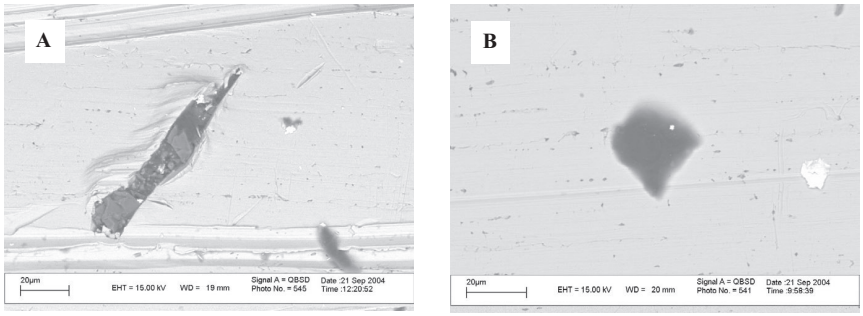

Fig. 8. SEM micrograph analysis of pit initiated on surface for (A) as-received and (B) electropolished specimen

amount of scratches on surface and as a result the number of pit nucleation sites [10-13] even though removal of manganese may be resulted in a surface with lower inclusions and therefore lower pitting initiation sites [12,14].

Scanning electron microscopy (SEM) results

To evaluate the morphology of pits initiated beyond pitting potential, both surfaces were analysis with scanning electron microscope (SEM). Figure 8 shows the SEM result of pits morphology on both sample surface. Figure 8.a shows that on as-received sample, pit was initiated from surface scratch which was created in polishing process by 60 SiC grit. In fact these surface scratches act as a nucleation site for pits [14-18]. During surface electropolishing, removal of surface roughness, decrease the pit nucleation sites. Figure 8.b shows the picture of stable pit which is nucleated on vicinity of remaining groove of surface scratch which may be preserved from scratches that already created from abrading with SiC paper prior to electropolishing.

These results reveals that as it elucidated in previous section, electropolishing improved passivity by modification in surface structure and removing surface scratches which were produced in surface finishing of 60 SiC grit step. Moreover another reason behind this enhancement of pitting corrosion potential of electropolished specimen can be attributed to producing a surface with lower residual stress in compare with surface polished of 60 SiC grit. In fact as it clarify elsewhere [9], electropolishing process produce a more favorable surface in compare with conventional mechanical polishing processes which may create deformed layer with residual stresses. Furthermore debris and impurity may be rolled or presses into the work piece surface and accordingly produce a surface with more contaminations in traditional mechanical polishing. In other word for the reason that a regions with higher energy level have deteriorated corrosion behavior, a layer on surface which is deformed and has higher residual stress level, more contaminations and accordingly higher level of energy resulted from surface finishing of 60 SiC grit step, in electropolishing process was substituted with lower energy level layer with lower amount of contaminations and consequently superior pitting corrosion behavior. In addition modification in surface roughness and small change in surface chemical composition which is essentially removing manganese sulfides (MnS) as well was produced by this polishing procedure.

4. CONCLUSIONS

Pitting corrosion of 304 SS after electropolishing in 70% phosphoric acid was studied and the following results were obtained:

1. Electropolishing increased both corrosion and pitting potentials and passivity current density as well as corrosion current density was decreased.
2. Slow ramp anodic potentiodynamic polarization on as-received and

electropolished specimens were carried out. Plot of metastable pitting current transient revealed the reduction on the number and magnitude of metastable pitting transients prior to occurrence of stable pitting on electropolished specimen.

3. EDX analysis showed that electropolishing has no effect on chromium enrichment on surface but has eliminated manganese from the surface. This removal of manganese is featured as the reduction on the amount of surface inclusions particularly MnS inclusions.
4. SEM micrograph investigation demonstrated that pits were nucleated in vicinity of scratches on surface finishing of 60 SiC grit which demonstrate electropolishing improved pitting behavior of 304 SS by modification in surface roughness.
5. Another rationale behind improvement of pitting corrosion behavior of electropolished specimen can be attributed to producing a surface with lower residual stress in contrast with polished surface with 60 SiC grit

ACKNOWLEDGMENT

Authors would like to appreciate the financial support from Ferdowsi University of Mashhad provision of laboratory facilities during the period that this research was conducted.

REFERENCES

1. Golazar, M. A., Mostaghimi, J., Coyle, T. W., "Wear resistance of nanaostructureed and conventional Yttria-stabilized zirconia coating", IJMSE 3, 2006, 9-15.
2. Karaminezhaad, M., Maghsoudi, A. A., Nozhati, R., Sakhaei, A.,"Corrosion behavior of zinc coated steel rebar in high-strength reinforced concrete", IJMSE 1 , 2004, 9-15 .
3. Lee, S. J., Lai, J. J.,"The effects of electropolishing (EP) process parameters on corrosion resistance of 304L stainless steel", J. Mater. Process. Tech. 140 , 2003, 206–210
4. Hryniewicz, T., Rokosz, K., Rokicki, R., "Electrochemical and XPS studies of AISI 304L stainless steel after electropolishing in a magnetic field", Corros. Sci. 50, 2008, 2676–2681
5. Pardo, A., Merino, M. C.,Coy, A. E., Viejo, F., Arrabal, R., Matykina, E.,"Pitting corrosion behavior of austenitic stainless steels – combining effects of Mn and Mo additions", Corros. Sci. 50 , 2008, 1796–1806
6. Hryniewicz, T.,"Concept of microsmoothing in the electropolishing process", Surf. Coat. Tech. 64 , 1994, 75-80.
7. Nawrat, G., Marciniak, J., Paszenda, Z., Korczyjski, A., "Electrolytic surface processing of implants used in surgery", J. Appl. Chem. 39 , 1995, 477–480.
8. Baron, A., Simka, W., Nawrat, G., Szewieczek, D., Krzyzak, A.,"Influence of electrolytic polishing on electrochemical behavior of austenitic steel", J. Achiev. Mater. Manufac. Eng. 18 , 2006, 55–58.
9. SEMI F19-95, Specification for the Finish of the Wetted Surface of Electropolished 304L Stainless Steel Components.
10. Qvarfort, R., " Some observations regarding the influence of molybdenum on the pitting corrosion resistance of stainless steels", Corros. Sci., 40 , 1998, 215–223.
11. Ilevbare, G. O., Burstein, G. T., "The role of alloyed molybdenum in the inhibition of pitting corrosion in stainless steels", Corros. Sci., 43 , 2001, 485–513.
12. Moayed, M. H., "Deterioration of pitting corrosion of 316 stainless steel by sensitization heat treatment", IJMSE 2 , 2005, 9-15.
13. Laycok, N. J., Newman, R. C., "Localized dissolution kinetics, salt films and pitting potentials", Corros. Sci., 39 ,1997, 1771–1790.
14. Baroux, B., "Further insights on the pitting corrosion of stainless steels", in: Ph. Marcus (Ed.), Corrosion Mechanisms in Theory and Practice, Marcel Dekker, New York, 2002, pp. 311–347 (Chapter 10).
15. Ziemniak, S. E., Hanson, M., Sander, P. C., "Electropolishing effects on corrosion behavior of 304 stainless steel in high temperature", hydrogenated water, Corros. Sci. 50 , 2008, 2465–2477
16. Lin, C. C., Hu, C. C., "Electropolishing of 304

stainless steel: Surface roughness control using experimental design strategies and a summarized electropolishing model", Electrochim. Acta 53 , 2008, 3356–3363

17. Huang, C. A., Chen, Y. C., "The effect of water content on the electropolishing behavior of Inconel 718 alloy in perchloric–acetic acid mixtures", Corros. Sci. 51, 2009, 1901–1906
18. Moayed, M. H., Laycock, N. J., Newman, R. C., "Dependence of the Critical Pitting Temperature on surface roughness", Corros. Sci. 45 , 2003, 1203–1216
19. Asami, K., Hashimoto, K., "Importance of initial surface film in the degradation of stainless steels by atmospheric exposure", Corros. Sci. 45, 2003, 2263-2283
20. Hilbert, L. R., Bagge-Ravn, D., Kold, J., Gram, L., "Influence of surface roughness of stainless steel on microbial adhesion and corrosion resistance", Int. Biodeter. Biodeg. 52 , 2003, 175-185
21. Uno, Y., Okada, A., Uemura, K.,Raharjo, P., Sano, S., Yu, Z., Mishima, S., "A new polishing method of metal mold with large-area electron beam irradiation", J. Mater. Process. Tech. 187-188 , 2007, 77-80
22. Arthur, H., Tuthill, P. E., "stainless steel: surface cleanliness", Pharma. Eng. 14 , 1994, 35-44