

Investigation of Mechanical Properties and In Vitro Corrosion of Bulk Nanostructured Metal Produced by Equal Channel Angular Pressing

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Abstract. ECAP(Equal Channel Angular Pressing) process on 316L stainless steel was done in this study using two different channel angles 120° and 126° after all samples were heat treated. There were three experiments ran in this study optical microscope analysis, hardness test and electrochemical measurement for three conditions samples which are before ECAP (BE), 120° ECAP and 126° ECAP. Metallurgical optical microscope was used to analyse the changing in grain size. The hardness test is examined using Wilson Vickers Hardness Test Machine with 100 gf load subjected on the samples about 10 seconds. Electrochemical measurements are done to observe the corrosion behavior of the samples. Two electrolytes were used during the test which are 0.9%NaCl and E-MEM+10%NCS cell culture medium solution. An incubator is used during the experiment for the samples experience a real human body environment (37°C) in two conditions which is for 0.9%NaCl and 5% CO₂ for cell culture medium on 316L stainless steel. As a result, optical analysis shows that the grain size for both 120° ECAP and 126° ECAP samples had refined with an elongated grain compared to BE for both materials. However, 120° ECAP shows a slightly better refinement grain size than 126° ECAP. Besides, in hardness test results, the 126° ECAP shows the increment value of Vickers hardness from others. 120° ECAP and 126° ECAP has 27.67% and 28.84% hardness increment, respectively. Meanwhile, for electrochemical tests show that ECAP influences the corrosion properties of 316L stainless steel. Current density(I_{corr}) is reduced by 120° ECAP (24.6±4.9 nA/cm² and 37.6±24.3 nA/cm²) and 126° ECAP (107.0±82.0 nA/cm² and 56.6±27.2 nA/cm²) in both conditions tested (0.9%NaCl and E-MEM+10%NCS) , but 120° ECAP improves better than 126° ECAP for both conditions(lower results values). The reduction of I_{corr} by ECAP process is smaller in cell culture medium than 0.9% NaCl. As a conclusion, 120° ECAP shows the best performance in these three testing but almost to 126° ECAP results. Therefore, by increasing small value of ECAP die angle will not obviously change the mechanical properties and corrosion behavior outcomes in fact the ECAP pressing force become lower.

INTRODUCTION

The refinement of grain size in bulk nanostructured of metal and alloys may improve its mechanical properties and corrosion resistance. Recent studies showed severe plastic deformation (SPD) process is capable to produced ultrafine grains on the metals and alloys due to very large plastic strain (Valiev & Langdon, 2006). The SPD process such as equal-channel angular pressing (ECAP), high pressure torsion (HPT) or accumulative roll-bonding (ARB) impose high strain on the materials inducing dislocate in grains, producing sub-grain and finally refine the grain size. Small

grain size with high density of grain boundaries compare to course-grained materials is better in mechanical properties and corrosion behavior (Shri, Tsuchiya, & Yamamoto, 2017).

ECAP is one of the common SPD process that used to refine the microstructure. The process improves the mechanical properties of the materials by initiate high plastic strain into the materials without changing its cross-sectional area (Srinivas, Srinivasu, Mahesh, & Aqheel, 2013). ECAP process assists the material in maintain the shape and dimension of the sample with superior mechanical properties (Zahari, Sh'ri, Hassan, & Harun, 2019). Fortunately, ECAP no need a high cost as it can be done in room temperature (Sabirov, Murashkin, & Valiev, 2013). ECAP process refines the microstructure and corrosion behavior simultaneously.

Corrosion resistance can be improved after through ECAP process (Hosaka, Yoshihara, Amanina, & MacDonald, 2017). There are studies show corrosion give the terrible effect on materials. The materials will be eroded and last with weary. There are methods to avoid the corrosion phenomena and refine the microstructure is one of it (Nene, Kashyap, Prabhu, Estrin, & Al-Samman, 2014).

Biomaterial's corrosion resistance plays a major role on metal biocompatibility (Shri et al., 2017). Besides, grain size that produced by ECAP highly important in improve the surface biocompatibility of materials. It shown when the surface increases the cell-substrate response (Hoseini et al., 2014). There is a study shows microstructure of the material improve the corrosion rate range (Kannan, Shanmugam, Rajkumar, & Vishnukumar, 2020). To improve the biocompatibility of material, the corrosion resistance must be upgraded, and microstructure refinement is one of the main factors to achieve the target. The lower the current density (I_{corr}), the better the corrosion resistance (Nair et al., 2018).

Stainless steel 316L is widely used in biomaterials. The metal used for restoring or replacing the part of human body must be high biocompatible (Morsiya, 2020). Good mechanical properties (Hossain, Ghouse, Nai, & Jeffers, 2021) and good corrosion resistance on SS316L lead to the application in biomaterial (Kartikasari & Aziz, 2017).

In this study, the electrochemical behavior of SS316L is evaluated when it connected to 0.9% NaCl and cell culture by using electrochemical circuit. Three conditions of SS316L; 120° ECAP-ed, 126° ECAP-ed and before ECAP, were tested by discussing the value of current density(I_{corr}), corrosion potential(E_{corr}) and critical pitting potential(E_{pit}). The mechanical properties and microstructure observation also considered in explaining the behaviors.

METHODOLOGY

Material Preparation

Common use SS316L was ready in 9.5 mm diameter and 10 cm length then heat treated in furnace about 790°C for an hour. All samples condition were through these processes to ensure the uniform initial of all samples' mechanical properties before ECAP process will take part.

ECAP

The ECAP die was made in two channels, equal in cross-section, intersecting at an angle near the center of the die. To fit within the channels, the specimens were machined and use the plunger to press it through the die. Two magnitudes of channel angles were examined in this project, which are 120° and 126°. The higher the channel angle, the lower the pressure needed to successfully complete the process (Valiev & Langdon, 2006). The samples were pressed by one pass of ECAP at 1160.3 psi. To reduce the friction between the rods and the channel walls, a lubricant with molybdenum disulfide (MoS_2) was used. A hydraulic press machine was used to carry out ECAP process at room temperature. Figure 1 shows the schematic illustration of ECAP with 120° of angle.

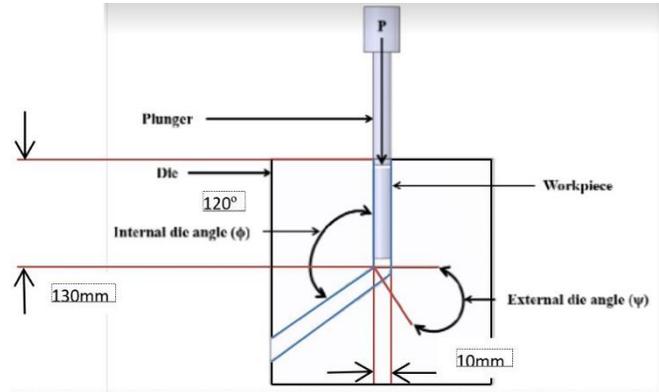


FIGURE 1. Schematic illustration of ECAP.

Microstructure Analysis

For microstructure analysis, a metallurgical microscope was used. All surfaces of samples in 6~9 mm in diameter and 4~5 mm in thickness were polished by SiC paper up to UF-1200 (6.5 μ m). The image of the microstructure appears after etched using Carpenters stainless steel etch as in Table 1 3 condition of samples' grain size could be measured from this analysis. Only one of each condition was tested. Toupview software was used to further the analysis on grain size and particles area.

TABLE 1. Carpenters Stainless Steel Etch composition.

Element	Composition
Iron(III) chloride, FeCl ₃	4.25g
Copper(II) chloride, CuCl ₂	2.4g
Hydrochloric acid, HCl	61mL
Nitric acid, HNO ₃	3mL
Ethanol, C ₂ H ₅ OH	61mL

Hardness Test

The ECAP-processed specimens' hardness was investigated using Vickers hardness machine. The specimens were subjected to load of 100 gf for 10 seconds. The testing taken from 7 point horizontally and 3 points vertically to check the hardness distribution across the samples. All values were divided to 3 groups which were top, middle, and bottom. For every line, the average was calculated to be representing as groups' value. All groups for all samples were tested on the samples' surfaces from left to right, from top bottom and horizontally. The value can be taken randomly, but to avoid the parallax error, the testing was standardized for all samples. Each point in each group located 1mm from other point horizontally. Figure 2 shows the hardness testing distribution points used in this study.

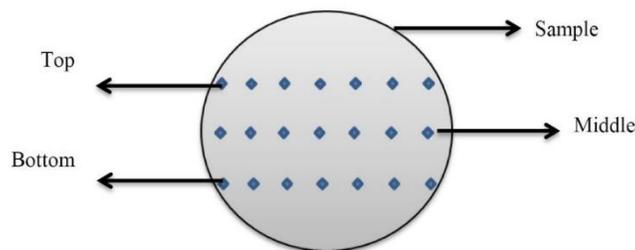


FIGURE 2. Hardness testing distribution points.

Electrochemical Test

SS316L polished samples were sterilized by ethylene oxide gas in prior to the electrochemical test which is mandatory for the test in cell culture medium. The test is performed using a typical three electrode system consisting of a platinum wire as a counter electrode, saturated Ag/AgCl (3 M NaCl) electrode as a reference electrode, and an SS316L sample (exposed area of 0.264 cm^2) as a working electrode. The electrodes setup was connected to a potentiostat (AMETEK VersaSTAT 4). A 5 ml portion of an electrolyte was poured. During electrochemical measurements, the chamber was placed in an incubator at a certain temperature. Approximately, about two hours needed to complete the measurement and a stabilized potential is used as the open-circuit potential (OCP). After 2h of incubation, potentiodynamic (PD) measurement was performed at a scanning rate of 0.16 mV/s with the potential range from -0.25 V vs open circuit potential (OCP) to the potential giving the current over 1 mA/cm^2 using a potentiostat (VersaSTAT3, Princeton Applied Research). Parameters such as corrosion potential (E_{corr}) and corrosion rate (I_{corr}) were decided from polarization curves by the Tafel method using VersaStudio software (Princeton Applied Research). There are testing conditions are as follows:

- In 0.9% NaCl at $37 \text{ }^\circ\text{C}$ with N_2 flow at 100 mL/min ,
- In cell culture medium at $37 \text{ }^\circ\text{C}$ under the atmosphere of 5% CO_2 in humidified air.

As a cell culture medium, Eagle's minimum essential medium supplemented with 10% newborn calf serum (E-MEM+10%NCS) was employed with pre-conditioning overnight at the same condition to the test. At least 3 samples were tested for each condition.

RESULT AND DISCUSSION

Microstructure analysis

Figure 3 shows the optical microstructure of SS316L before and after ECAP. For BE sample, the grain was observed to be coarse grain with average grain size of $\sim 12.5 \mu\text{m}$. However, for both ECAP-ed results, finer grain size with elongated shape and smaller size with some sub-grains were observed. In addition, 120° ECAP shows a slightly better refinement grain size than 126° ECAP. 120° ECAP grain size is about $\sim 2.71 \mu\text{m}$ while 126° ECAP grain size is about $\sim 2.83 \mu\text{m}$. The elongated shape happened due to ECAP process with high strain induced. The grain refinement in the ECAP-ed samples is attributed to the high strain experienced during the process.

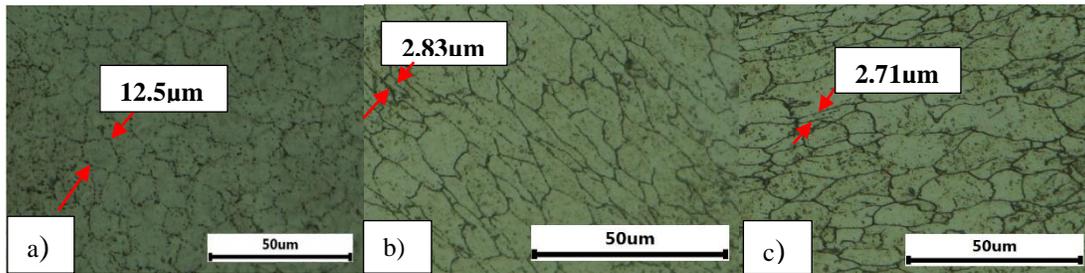


FIGURE 3. Grain sizes microstructure analysis for (a) before-ECAP (b) 120° ECAP-ed condition and (c) 126° ECAP-ed condition.

Hardness Result

ECAP process has changed the mechanical properties of SS316L specifically in hardness test. Figure 4 shows the hardness results of three condition of SS316L. The ECAP-ed sample hardness value increase 27.67% and 28.84% on 120° ECAP and 126° ECAP compared to BE, respectively. The ECAP process boosts the hardness value on the sample. Standard deviation for 120° ECAP is 17.5 while 126° ECAP is 21.47. The highest value of hardness is on point 2mm from center for 126° ECAP which is 480.2HV while the lowest value of hardness is on point 1mm from center for BE which is 333.07HV. The closest hardness value between 120° ECAP and 126° ECAP is at point -1mm from center which are 444.13HV and 428.73HV, respectively. The farthest hardness value between 120° ECAP and 126° ECAP

is at point 3mm from center which are 409.63HV and 461.27HV, respectively. The percentage for 126° ECAP is higher than 120° ECAP.

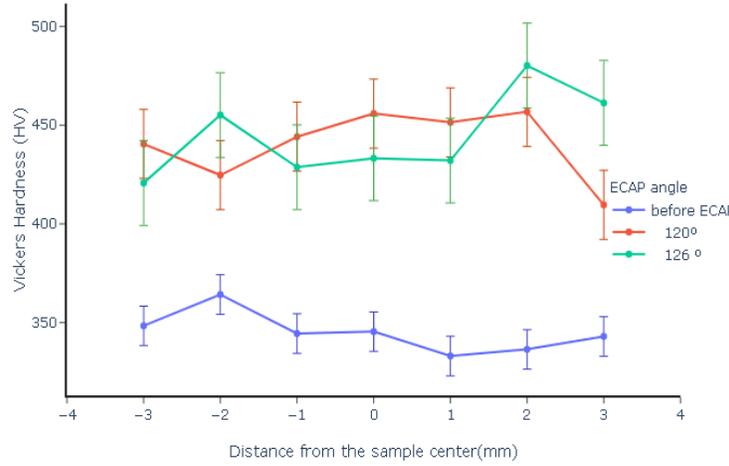


FIGURE 4. Vickers hardness profile across sample between angle of 120°, 126° and BE.

Electrochemical Test Results

Electrochemical Test in 0.9% NaCl

Electrochemical test results of SS316L are shown in Fig. 5 and Table 2. In 0.9% NaCl, before ECAP sample has the noblest E_{corr} and E_{pit} among three samples tested (3.54 ± 31.11 mV and 337.0 ± 35.0 mV), but 120° ECAP sample has the smallest I_{corr} which is 24.6 ± 4.9 nA/cm². 120° and 126° ECAP samples show similar E_{corr} and E_{pit} , where both are lower (120° ECAP; -52.23 ± 49.3 mV and 205.0 ± 90.0 mV, 126° ECAP; -17.9 ± 11.0 mV and 186.0 ± 96.0) than those of before ECAP sample (3.54 ± 31.11 mV and 337.0 ± 35.0). However, the I_{corr} of 126° ECAP sample (107 ± 82.0 nA/cm²) is larger than that of 120° ECAP sample (24.6 ± 4.9 nA/cm²). These facts indicate that ECAP process influences the corrosion property of SS316L and that 120° ECAP sample has slightly better corrosion resistance than 126° ECAP sample.

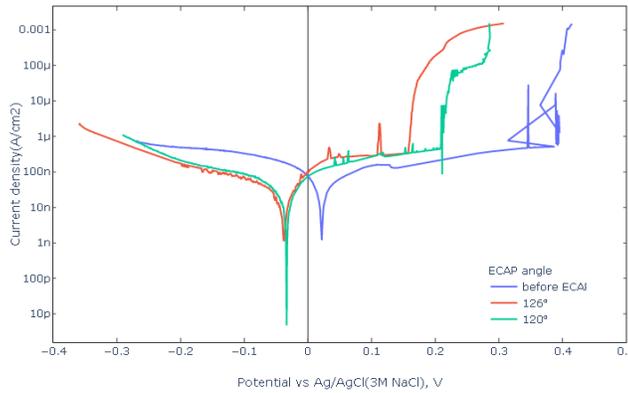


FIGURE 5. The potentiodynamic curves of SS316L in 0.9% NaCl.

TABLE 2. Corrosion parameter of SS316L samples in 0.9% NaCl (mean \pm sd).

ECAP angles	E_{corr} (mV)	I_{corr} (nA/cm ²)	E_{pit} (mV)
BE	3.54 ± 31.11	146.8 ± 100.3	337.0 ± 35.0
120°	-52.23 ± 49.3	24.6 ± 4.9	205.0 ± 90.0
126°	-17.9 ± 11.0	107 ± 82.0	186.0 ± 96.0

Electrochemical Test in E-MEM+10%NCS

Electrochemical tests in E-MEM+10% NCS are shown in Fig. 6 and Table 3. Before ECAP sample has the nobler E_{corr} which is -31.5 ± 43.3 mV but the larger I_{corr} than ECAP samples which is 126.7 ± 92.4 nA/cm², as like those in 0.9% NaCl. Concerning the E_{pit} , 120° ECAP sample is the highest at 348.0 ± 16.0 mV, but the difference is much smaller than those in 0.9% NaCl. The 120° ECAP sample has slightly better I_{corr} (37.6 ± 24.3 nA/cm²) than that of 126° ECAP sample (56.6 ± 27.2 nA/cm²). These facts indicate that the effect of ECAP on corrosion behaviour is much smaller in E-MEM+10%NCS than that in 0.9% NaCl, and that ECAP at 120° gives slightly better suppression of corrosion rate than that of ECAP at 126°.

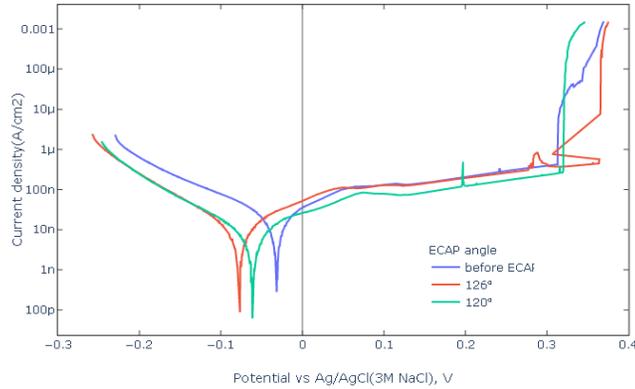


FIGURE 6. The potentiodynamic polarization of SS316L in E-MEM+10%NCS.

TABLE 3. Corrosion parameter of SS316L samples in E-MEM+10%NCS(mean±sd).

ECAP angles	E_{corr} (mV)	I_{corr} (nA/cm ²)	E_{pit} (mV)
BE	-31.5 ± 43.3	126.7 ± 92.4	311.0 ± 99.0
120°	-59.4 ± 22.0	37.6 ± 24.3	348.0 ± 16.0
126°	-56.0 ± 26.9	56.6 ± 27.2	307.0 ± 74.0

All ECAP samples show the microstructure refinement which lead to the better mechanical properties especially material hardness as found by Alateyah et. al. (Alateyah et al., 2021). Electrochemical tests show that ECAP influences the corrosion properties of SS316L. As stated by Nair et. al., this study found the lower value of I_{corr} , the better the corrosion resistance (Nair et al., 2018). I_{corr} is reduced by ECAP in both conditions tested, but 120° ECAP improves better than 126° ECAP for both conditions. The reduction of I_{corr} by ECAP process is smaller in cell culture medium than 0.9% NaCl. Conclusion, 126° ECAP can replace 120° ECAP as the results do not show the big gap.

CONCLUSION

This project shows that the die angle is an important factor in improvement on the mechanical properties and corrosion behavior of SS316L. Due to the grain refinement in microstructure evaluation, both ECAP-ed samples improve in the hardness value 27.67% and 28.84% on 120° ECAP and 126° ECAP compared to BE, respectively. Lower current density (I_{corr}) deformed after the sample through ECAP process compared to BE and it enhances the better corrosion resistance behavior of SS316L. Alternatively, more uniform strain distribution can be achieved at lower pressing force by small increment of die angle instead of low die angle that needed more force during the process which led to high strain magnitude. Its possibility that ECAP at 126° can replace that at 120°.

ACKNOWLEDGMENTS

This paper was fully supported by facilities and resources from Universiti Malaysia Pahang. The authors would like to acknowledge the support of grants from Universiti Malaysia Pahang No. RDU190110, Masters Research Scheme and PGRS1903162.

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