Effect of stored energy on corrosion fatigue properties of ultrafine grained Fe-20%Cr steel by equal channel angular pressing

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Abstract. Corrosion fatigue properties of ultrafine grained (UFG) Fe-20%Cr steel by equal channel angular pressing was investigated in term of grain refinement and stored energy. The corrosion fatigue life of the ECAP processed and the post-ECAP annealed sample was analysed. Under annealing temperature of 773 K, due to the recrystallization stage, there was a little difference in microstructure from the four passes ECAP. After the annealing process, the strength of the samples pressed four passes decreases, while the elongation showed more ductile. Two mechanisms for crack propagation have been well recognized for stainless steel. One is slipping step dissolution mode. In this model, the slip step formed by active dislocation at a crack tip is anodic dissolution reaction, so that crack tip advance to further distance. The other is stress adsorption mechanism. The corrosion fatigue cracks initiation and cracks propagation process of iron-chromium alloy can be characterized by corrosion pits and intergranular fracture, respectively. The corrosion fatigue behaviour of non-equilibrium and equilibrium grain boundary of iron-chromium alloy was occupied by crack initiation.

1. Introduction
The application of biomaterials as implant material has been widely investigated in medical application. In general, the requirements of implant material should have adequate mechanical strength for a precise period until tissue healing happens. The biomaterial implant needs to have a biodegradation rate which has excellent biocompatibility and safety in human body tissues. In metallic materials, they have good mechanical properties and poor corrosion resistance. Stainless steel also has many disadvantages as an implant material, but it has very fast degradation in specific environment, causing stainless steel implants to degrade and lose mechanical strength. Several studies have been conducted to overcome these limitations, including grain refinement.

Equal-channel angular pressing (ECAP) is a technique grain refinement using simple shear to produce bulk metallic materials with sub-microcrystalline and high mechanical properties [1,2]. A considerable plastic deformation leads to the formation of inhomogeneous structures resulting in different corrosion properties such as corrosion fatigue and stress-corrosion cracking (SCC) [3-6]. SCC is cracking that occurred by synchronized behavior of corrosion and tensile stress. This cracking excludes reduced corrosion, which fails by rapid fracture. SCC is related to three parameters, such as [7]: (1) vulnerable material, (2) environment, and (3) tensile stress. On the other hand, corrosion fatigue...
is a fatigue test which carried out in the corrosive environment. The corrosive environment is a significant role in the fatigue limit. Fatigue corrosion is considered to be the leading research topic of degradation metal mechanism in a corrosive environment. The fatigue life is limited due to pit formation on the metal surface, which is causing the crack initiation from pitting corrosion. Characterization of corrosion fatigue of materials with the ultra-fine grain (UFG) size is essential to be observed. The corrosion behavior of ECAP material has reported in limited intention. The rate of dissolution of the UFG is higher in comparison with coarse-grained material, as discussed in our previous publication [8,9]. The behavior of ECAP materials immersed in a corrosive environment under stress has not been investigated yet in term grain boundary state.

2. Experimental Procedure

The material used in this experiment had a chemical composition of low CN Fe-20%Cr alloy with Cr 19.97, C 0.0020, N 0.0015, and Fe balance (in mass percent). This material was machined with dimensions of 8 mm × 8 mm × 120 mm for ECAP pressing. ECAP was carried out using a split die with two channels intersecting at an inner angle of 90°, and an outer angle of 0° at 423 K. The samples were lubricated with high-temperature fluorine lubricating grease and pressed for four passes via route Bc. Annealing process was carried out at 773 K for one hour. A TEM (JEM 2100F) was used to examine the microstructures. Thin foils for TEM were polished using abrasive papers to about 100 µm thick and then thinned by a twin-jet polishing Tenupol 5 facility using a solution of 40% acetic acid, 30% phosphoric acid, 20% nitric acid and 10% distilled water. Mechanical and electrochemical properties were measured by microhardness and pitting corrosion. The microhardness experiments were performed on a Vickers hardness testing machine at room temperature. Corrosion fatigue testing was carried out at ambient temperature in a flat polarization cell, using platinum counter electrodes and SCE reference electrodes to measure the corrosion current and corrosion potential. The corrosion fatigue characteristic was obtained in neutral solutions 1 M NaCl, under stress amplitude of 200MPa. Corrosion fatigue sample and testing machine arrangement can be seen in figure 1 and 2.

3. Result and discussion

The grain refinement process using ECAP by route C can be seen in figure 3 in three dimensions. The microstructure shows an equiaxed grain shape due to redundant stress during ECAP process. In this study, the grain boundary status as non-equilibrium and equilibrium grain boundary can be investigated in detail by comparing the ECAP processed sample and the post ECAP annealing. The microhardness of ECAP processed shows higher than post-ECAP annealing due to effect from the slight recrystallization accompanying with softening, as shown in Figure 4. The microstructure of TEM was also observed on ECAP and after post-ECAP annealing at 773 K for one hour, as shown in figure 5. Under annealing temperature of 773 K, due to the recrystallization stage, there was a little difference in microstructure from the four passes ECAP. The microstructure of ECAP processed sample exhibited a
dark contrast and smaller grain size compared to that of the post-ECAP annealing. The dark contrast indicates that the dislocation was kept inside the UFG structure. The light difference appeared at the TEM micrograph of the post-ECAP annealing due to the releasing of dislocation in grains.

**Figure 3.** The misorientation image of ECAP processed by route C in three dimension (a) one pass, (b) two passes, (c) three passes, and (d) four passes.

**Figure 4.** Micro hardness of ECAP processed and post-ECAP annealed sample.

**Figure 5.** TEM micrograph of ECAP processed and post-ECAP annealed sample. Observed from transverse direction.

**Figure 6.** XRD of as ECAP processed and post-ECAP annealed
Figure 6 shows XRD after ECAP and the post-ECAP annealing. In the as-ECAP processed sample, line broadening can be seen clearly, and this line broadening is a result of non-equilibrium grain boundaries having a high density of extrinsic defects in their structure and elastic stresses [8,9].

Dislocation density and crystallite size can be identified by X-Ray broadening analysis. The crystallite size increased with the annealing process. However, dislocation density decreased with the annealing process, as seen in figure 7. Grain boundary misorientation maps on ECAP and after post-ECAP annealing are represented in figure 8. HAGB fraction on ECAP processed microstructure is predominant with a little fraction of LAGB. Because of low orientation resolution, boundaries with misorientation smaller than 2° was omitted. Homogeneous microstructure evolution with small equiaxed grains and high HAGB fraction was exhibited on post-ECAP annealing sample until 698 K. However, grain size increased gradually until the annealing temperature of 1373 K, but HAGB fraction almost remained constant. The grain in ECAP processed sample are finely subdivided in the first pressing compare to as-annealed sample.

Stress-strain curves as ECAP processed and post ECAP annealed sample can be seen in figure 9. Work hardening is observed after ECAP, although the ductility is limited, as is commonly found in SPD metals. Four passes, the tensile strength increases while the elongation drastically compares to post-ECAP annealed sample. After the annealing process, the tensile strength of the post-annealing ECAP processed samples decreases, while the elongation shows more ductile. Figure 10 (a) exhibited post necking elongation at Fe-Cr alloys post-ECAP annealed sample. Post necking elongation can be influence by the grain structure, which is equiaxed. The post necking elongation of the post-ECAP annealed sample was more significant than an as-ECAP sample. HAGB can affect post necking elongation of equiaxed grain sample. Figure 10 (b) shows the SEM micrograph of the fracture surface on as ECAP processed and post-ECAP annealed sample after tensile testing. The observation with high magnification on as ECAP processed and the post-ECAP annealed sample had been done to understand dimple appearance on the fracture surface. Dimple appearance of post-ECAP processed annealed was distributed homogeneously, as shown in figure 10 (c) From the observation above, it can be explained that post-ECAP annealed sample has excellent elongation with ductile fracture appearance. But as-ECAP processed sample, fracture mode is transformed from ductile to brittle. It can be confirmed with the decreasing elongation of ECAP-processed sample.

![Figure 7](image_url) Dislocation density and crystallite size of as ECAP processed and post-ECAP annealed.
Figure 8. EBSD analysis of before and after corrosion fatigue (a) as-ECAP processed sample and (b) post-ECAP annealed sample. Observed from transverse direction.

Figure 9. Stress and strain curve of as-ECAP processed and post-ECAP annealed sample.

Figure 10. (a) Laser microscope observation of as-ECAP processed and post-ECAP annealed sample, and Dimple appearance of (b) as-ECAP processed and (c) post-ECAP annealed sample.

It was often reported that resistance to pitting corrosion resistance of iron chromium alloy was improve by UFG structure formation [10-12]. This is usually explained by the higher diffusion of Cr increased by a high density of grain boundaries [13-15]. It is considered that the passive film form by selective dissolution of Fe atoms into the solution and resultant condensation of Cr at the surface [16,17]. It is pitting corrosion resistance of as ECAP processed, and post-ECAP annealed sample can be seen in figure 11. UFG structure seems having more chromium diffusion on the pitting sites [18,19]. The value decrease of $E_{pit}$ versus Ag/AgCl by the annealing can be caused by the diminishing of dislocations or
transformation from non-equilibrium to equilibrium grain boundaries (grain boundary state transformation).

Figure 11. (a) Pitting corrosion resistance, (b) pitting appearance of as-ECAP processed and (c) post-ECAP annealed sample.

Figure 12. Cyclic deformation of (a) as-ECAP processed and (b) post-ECAP annealed sample.

Figure 13. Fracture surface appearance on fatigue test of as-ECAP processed and post-ECAP annealed sample.

Corrosion fatigue test on ECAP processed and post-ECAP annealed sample was clarified that crack initiation started from corrosion pits and propagated. Cyclic deformation of as ECAP processed and annealed sample can be seen in figure 12. Crack initiation and propagation on corrosion fatigue can be observed clearly. Crack propagation occurred at the corrosion fatigue crack tip. This crack propagation is characteristics in corrosion fatigue process. It can be determined that corrosion fatigue behavior of iron-chromium alloy is managed by the initiation and growth of corrosion pits. After corrosion fatigue tests, the sample was observed by an electron microscope which corrosion pits can be seen on the surface of the sample, as shown in figure 13. The fatigue fracture image by SEM of iron-chromium alloy manufactured by ECAP and post-ECAP annealing, which can be seen as less pronounced and microcracks.
4. Conclusion
Corrosion fatigue cracks initiation process of UFG iron-chromium alloy was briefly reviewed on experimental results. The corrosion fatigue cracks initiation and cracks propagation process of iron-chromium alloy can be characterized by corrosion pits and intergranular fracture, respectively. The corrosion fatigue behavior of iron-chromium alloy is occurred by crack initiation. Under annealing temperature of 773 K, due to the recrystallization stage, there was a little difference in microstructure from the four passes ECAP. After the annealing process, the strength of ECAP processed sample drop off, while the elongation shows more ductile. Both corrosion and stress can affect the rate of crack advance in corrosion fatigue. The unique phenomena of UFG structure material can be explained by the grain boundary transformation from non-equilibrium into equilibrium grain boundary state.

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