

博士学位論文審査要旨

2015年2月17日

論文題目： Mechanical and corrosion properties of ultrafine-grained low C, N Fe-20%Cr steel produced by equal channel angular pressing (E C A P法により作製した超微細結晶組織を有する極低 C, N Fe-20%Cr 合金の機械的性質と耐食性)

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要 旨：

金属材料の高強度化は自動車や船舶、航空機などの構造体の軽量化に寄与するため、省資源、省エネルギーの観点から今後、ますます重要な課題となる。金属材料の高強度化にはこれまで固溶強化や析出・分散強化、加工強化、結晶粒微細化強化などが利用されてきたが、中でも結晶粒微細化強化は合金元素が不要な強化方法であり、かつ単純組成や純金属にも適用が可能で、使用後のリサイクル性が優れている。結晶粒径をサブミクロンまたはナノオーダーまで微細化した組織を超微細結晶組織またはナノ結晶組織と呼ばれ、同一成分で従来組織の3～5倍まで強度を高めることが可能である。近年、加工ひずみを極限まで高めてバルクの材料に対して、超微細化またはナノ結晶化させる方法が開発され、強ひずみ加工法と呼ばれている。この方法ではバルク材に適用できるため、これまで薄膜が中心であったナノ結晶材料の研究が、機械構造材料を視野に入れた研究が可能になった。強ひずみ加工法の中でも Equal-Channel Angular Pressing (ECAP) 法は別名、側方押し出し加工または等径角度付き押し出しと呼ばれて、棒材ピレットに強度のせん断変形を加えつつ、初期の形状を変えないで押し出す方法で、繰返し加工することが可能である。これまで、比較的加工が容易なアルミニウム（合金）や銅、ニッケルなどの面心立方格子の金属、あるいは炭素鋼などが研究対象であり、結晶粒微細化のメカニズムや機械的性質等に注目した研究が多く発表されてきた。一方、構造材料への適用を考えた場合、強度など機械的性質だけでなく耐食性も重要な性質となる。一般的な構造用の耐食材料は Cr を含有する Fe-Cr 合金が広く利用されているが、本材料は強度が高く、これまで ECAP による微細化は困難であった。また、これまで面心立方格子の金属が主に研究されてきて、炭素鋼以外の体心立方格子の金属に関する研究は十分とは言えない。鉄などの体心立方格子の金属は侵入型元素である炭素や窒素の力学挙動に及ぼす影響が大きく、結晶構造に由来する本質的な面心立方金属との差異を明らかにするためには極力これらの元素を除去した材料で研究する必要がある。

このような背景から本研究では、強ひずみ加工法の一つである ECAP 法により、高強度・高耐食材料である極低 C, N の Fe-20%Cr 合金の結晶粒超微細化を試みて、世界で初めて成功した。微細化や力学挙動への影響が強い材料中の炭素、窒素を極力低減して、結晶構造を考慮した金属物理学的な観点から微細化の機構を明らかにした。また、これまであまり研究されなかった耐食性に及ぼす超微細化の影響を明らかにした。

第1章では、研究の背景と概要について述べている。

第2章では結晶構造の異なる Fe-20%Cr 合金と純銅を E C A P 法により加工して、結晶構造に由来するマイクロ組織の微細化過程の差異を明らかにしている。前者は後者に比べて大角粒界の形成が早く、この違いを転位の性質の違いから考察した。

第3章では、結晶粒微細化に及ぼす加工ルートの影響を明らかにしている。E C A P 法では各パスごとにビレットの入れる方向による加工ルートを変えることができる。面心立方格子の金属については研究が多く報告されているが、C, N の影響の無い、純度の高い体心立方格子の金属は研究例が少ない。その結果、微細化に効率的な加工ルートの存在を明らかにした。

第4章では E C A P 法により作製した超微細結晶組織の熱的安定性および粒成長挙動について明らかにしている。強ひずみ加工で形成した超微細組織は加工組織の性質も有することが予想されている。面心立方格子である銅や銅合金と異なり、本合金は短時間の熱処理での回復過程により、結晶粒径が維持されつつ、加工ひずみの無い平衡組織が得られることを明らかにした。また、結晶粒は均一的に成長している。

第5章では超微細化材の機械的性質に及ぼす熱処理の影響を明らかにしている。強ひずみ加工により微細化した材料は第4章でも述べたように同時に加工組織の性格を有している。これを熱処理により、結晶粒を極力変化させずに加工ひずみを取り除いたときの変形挙動への影響を調べ、その説明を与えている。

第6章では第3章の成果にもとづき、繰返し変形下での変形挙動や疲労強度に及ぼす加工ルートの影響を明らかにしている。

第7章では耐食性とくに孔食に及ぼす微細化と熱処理の影響について検証し、熱処理温度の上昇により、結晶粒径が増加するとともに耐孔食性が低下することを明らかにしている。また、結晶粒径が変化しない程度の短時間熱処理により耐孔食性が大きく低下した。これは結晶粒界が非平衡から平衡粒界に遷移して、Cr 原子の表面への拡散性が低下したためであると考察している。

第8章では腐食環境における疲労強度について、超微細化材と熱処理材について、第7章の結果を考慮しながら検証している。

第9章では本論文の成果を簡潔にまとめている。

本論文は、強ひずみ加工法による超微細結晶を有する極低 C, N の Fe-20%Cr 合金の機械的性質と耐食性に関する先駆的な研究であり、これらの成果はこの分野の発展に多大なる貢献をなすものである。

よって本論文は博士（工学）（同志社大学）の学位論文として十分な価値を有するものと認められる。

総合試験結果の要旨

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論文題目： Mechanical and corrosion properties of ultrafine-grained low C, N Fe-20%Cr steel produced by equal channel angular pressing (E C A P法により作製した超微細結晶組織を有する極低 C, N Fe-20%Cr 合金の機械的性質と耐食性)

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要 旨：

博士論文提出者は立命館大学大学院理工学研究科博士課程（前期課程）を2011年9月に修了し、本学大学院理工学研究科博士課程（後期課程）に在学中である。

本論文の主たる内容はMaterials Science and Applications, Metals, International Journal of Corrosions, Proc. 8th Pacific RIM International Congress on Advanced Materials and Processing, IOP Conference Series:Materials Science and Engineering,に掲載され十分な評価を得ている。

2015年1月31日午前10時より2時間にわたり、提出論文に関する学術講演会が開かれ、種々の質疑・討論が行われたが、提出者の説明により十分な理解が得られた。

さらに、講演会修了後、審査委員により学位論文に関連した諸問題につき口頭試問を実施した結果、十分な学力を確認できた。なお、提出者は本論文を英語で執筆しており、またその他多数の英語による論文発表や学会での発表を行っていることから、十分な語学能力を有すると認められる。

よって総合試験の結果は合格であると認められる。

博士學位論文要旨

論文題目 : Mechanical and corrosion properties of ultrafine-grained low C, N Fe-20%Cr steel produced by equal channel angular pressing
(ECAP法により作製した超微細結晶組織を有する極低 C, N Fe-20%Cr 合金の機械的性質と耐食性)

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要旨 :

In Chapter 1, equal-channel angular pressing (ECAP) is one of the severe plastic deformation (SPD) to produce ultra-fine grain (UFG) material, and its principle and microstructural developments have intensively been studied for the last two decades. In the overall SPD processing, ECAP is unique in that the deformation proceeds by incremental shear restricted to the narrow zone parallel to the intersecting plane of the two channels. The amount of plastic strain imposed in one pass is important as well as the total amount of plastic strain by several passes to obtain UFG materials. On account of the aforementioned unique deformation mode in ECAP, microstructural evolution is influenced by deformation routes or strain path, such as the so-called routes A, Bc and C, and has been studied with a special interest from the academic and industrial perspective. However, the majority of papers on SPD materials have been devoted to the face centered cubic (FCC) materials such as Al, Cu and Ni, little have been reported on body centered cubic (BCC) metals except for low carbon steels. Despite the recent studies on UFG low carbon steels (low carbon, nitrogen (C,N) Fe-20%alloy), the underlying mechanism of deformation and UFG formation is not fully understood, largely due to complexities associated with chemical compositions, especially with solute carbon and cementite. In addition to strength and deformation behavior, corrosion properties are very important for structural application. Most studies have been devoted to aluminum alloys, titanium, copper etc. Although Fe-Cr alloys are one of important structural steels, little study on corrosion properties of UFG Fe-Cr alloys has been reported so far because of technical difficulty for applying Fe-Cr steels to ECAP. The effect of ECAP on corrosion properties may differ from aluminum, copper, titanium alloys because passivating element, namely, Cr is alloying elements in Fe-Cr alloys whereas host elements in other metals. In this respect, Fe-Cr alloys of pure BCC materials should be used in order to obtain the result intrinsic to BCC structure.

In Chapter 2, microstructural development of ultralow C, N Fe-Cr alloy and pure copper processed by ECAP has been examined focusing on the initial stage of the formation of UFG material. Fe-Cr alloys were pressed at 423 K while pure copper at room temperature for 1 to 3 passes via the route Bc to compare at the equivalent homologous temperature. In FCC, the dislocations tend to form pile-up rather than cross slip, then they are accumulated as plastic strain rather than absorbed in the grain boundaries and they are hard to be restructured as grain boundary dislocation. This may explain the reason why the fraction high angle grain boundary (HAGB) is lower after three passes in pure copper in spite of comparable low-angle sub grain/cell size with Fe-Cr alloy. In this case, dislocation density should be higher in pure copper than Fe-Cr alloy at the same strain level. Dislocation density of Cu shows lower than Fe-Cr alloys and it seems

inconsistent with the explanation mentioned above. Possible explanation of lower dislocation of pure copper is dynamic recrystallization, which may occur during ECAP. Inhomogeneous microstructures with large and small grains may be originated from the dynamic recrystallization.

In Chapter 3, the effect of the deformation route on the microstructure, and the mechanical and electrochemical properties of this alloy by ECAP have been investigated focusing on the anisotropy of the microstructure. This alloy was pressed at 423 K from one to eight passes via routes A, Bc and C, and the microstructure was observed in three orthogonal planes in terms of pressing direction. As has been acknowledged, overall grain fragmentation proceeded most effectively in route Bc. However, the degree of anisotropy of microstructural development was different among the three deformation routes. The fractions of the HAGB and mean grain boundary misorientation were high and nearly isotropic in route Bc, whereas they were considerably low in one direction and highly anisotropic in routes A and C. The anisotropy of microstructure in route A and C were higher than those of FCC metals. The anisotropy of microstructural evolution can be explained rationally in terms of crystal slips that are intrinsic to BCC materials. The Peierls barrier of screw dislocations is higher than that of edge dislocation in BCC crystals; thus, slip by screw character is more predominant than by edge dislocation. When plastic straining increases by the formation and extension of dislocation loops, edge dislocation characters with high mobility slip faster than screw dislocation, resulting in extended lines of screw dislocations. Therefore, the nature of the slip of predominant cross-slip, which is intrinsic to screw dislocation, has an influence on the dislocation microstructures and macroscopic behavior of plastic deformation. The micro hardness exhibited an increase by ECAP as was reported before in many metals and alloys. However, the degree of hardening of the ECAPed sample was different among three orthogonal planes in different routes. This anisotropic strain hardening seems to be a characteristic of BCC metals. The isotropic hardening in the material processed by route Bc was reflected the isotropic configuration of HAGB. Namely, this isotropic hardening tendency was observed due to high dislocation density in route Bc. This hardening was suggested that the 45° rotation of billets in route Bc, which resulted in cross hardening. Since screw dislocations are predominant in BCC metals, positive and negative screw dislocation pairs tend to meet by cross-slip and disappear in both the forward-forward and forward-reverse shear in successive passes.

In Chapter 4, the post-ECAP annealing process was carried out from 473 until 1373 K for one hour after eight passes route Bc ECAP. The microstructure were then analyzed by electron back-scattering (EBSD), a transmission electron microscope (TEM), and X-ray diffractometer (XRD). Hardness tests after post-ECAP annealing showed typical three stages softening comprising the first stage of relatively constant hardness, followed by the second stage of significant softening and final stage of constant hardness. In the second stage, grains grew uniformly, which differ from typical nucleation-and-growth mode of discontinuous recrystallization. It was found by X-ray line broadening analysis that strain was released in early stage prior to the significant softening stage. It was suggested that the homogeneous grain growth was led by the uniform grain distribution with a HAGB fraction. Grain growth on the annealing process may be divided into two types, normal grain growth and abnormal grain growth or secondary recrystallization. Normal grain growth, in which the microstructure coarsens uniformly, is classified as a continuous process and result in a relatively narrow range of grain sizes and

shapes. On other hand, in abnormal grain growth, which is a discontinuous process, a few grains in the microstructure grow and consume the matrix of other smaller grains and a bimodal grain size distribution develops. During the annealing, material softening occurred gradually and uniformly in a fixed time. This behavior was different from the softening behavior of aluminum alloys which inhibits discontinuous recrystallization by extended recovery stage. Strain energy stored as dislocations can be released in recovery process easily prior to recrystallization. Therefore, strain energy stored in UFG structures in as-ECAP state may be released prior to the next stage, resulting in the formation of UFG structure with less stored strain energy. Homogeneous grain size distribution with high fraction of HAGB (81%) may lead to homogeneous and normal grain growth whose driving force is solely grain boundary energy, rather than recrystallization which requires strain energy as driving force.

In Chapter 5, the ECAP processed and post-ECAP annealed sample was also characterized by tensile testing. After one, two, four and eight passes, the tensile strength increases while the elongation drastically. After the annealing, the tensile strength of the samples of one, two, four and eight passes decreases, while the elongation increases due to the recovery and grain growth. It was found that annealed samples show higher strength than 8 passes as-ECAPed samples when the strength was plotted as function of grain size. In other words, as-ECAPed UFG samples and annealed samples are in different slope in Hall-Petch relationship. Hardening by post-ECAP annealing was suggested that non-equilibrium grain boundary is a source of dislocations which lower the yield stress.

In Chapter 6, the microstructural evolution at low cycle fatigue (LCF) behavior of UFG Fe-Cr alloys was investigated. It was found that the fatigue life of the ECAP processed via route Bc specimens is much shorter than that of routes A. This result is not unexpected in view of their lower ductility. LCF behavior of iron chromium steel after ECAP for up to four passes shows that the deformation microstructure remained fine and stable after cyclic deformation. However, the LCF life decreased along with the limited ductility, as is commonly observed for materials manufactured by ECAP.

In Chapter 7, effect of annealing on pitting corrosion of UFG structure material has been investigated in term effect of strain energy and grain size reduction. UFG structures of initial grain size of 140 nm exhibited the typical three stage softening comprising recovery, recrystallization and grain growth. Pitting potential in $1000 \text{ mol}\cdot\text{m}^{-3}$ NaCl solution was higher in UFG state, but it started to decrease monotonously at lower temperature than hardness. The degradation of corrosion resistance in the early stage of annealing is attributed to stability change of passivation by recovery of dislocations structures inside grains and in non-equilibrium grain boundaries. The resistance to corrosion of stainless steel was enhanced by UFG formation by SPD. This is often explained by the higher diffusion of Cr enhanced by high density of grain boundaries. The higher diffusion of Cr is considered that the passive film form by selective dissolution of Fe atoms into the solution and resultant enrichment of Cr at the surface. The linear relation between residual strain and (pitting potential) E_p can be interpreted by the faster diffusion Cr along the stored dislocations inside the grains or/and non-equilibrium grain boundaries. Indeed, the result has been shown that the grain boundary diffusivities in nanostructured metals processed by means of SPD in the temperature range of 398–448 K are 4–5 orders of magnitude higher relative to the same materials in a coarse-grained state. Namely, early reduction of E_p by the annealing can be caused

by diminish of dislocations or transformation from non-equilibrium to equilibrium grain boundaries. It was suggested that dislocation arrangements during the strain hardening stages could better explain this trend according to electrochemical approaches.

In Chapter 8, the corrosion fatigue life of the ECAP processed and post-ECAP annealed sample was examined focusing on the effect of grain boundary state (equilibrium and nonequilibrium) on corrosion fatigue. Annealed samples have a little lower tensile strength with a lower ductility as compare with as-ECAPed samples. It was found that corrosion fatigue life was longer in annealed samples. The crack initiation started from corrosion pits and propagated in both the samples. It was suggested that the resistance to crack propagation at annealed samples override the lower pitting resistance so that the fatigue life was longer in annealed samples.