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Pre-irradiation Characterization and Thermal Stability Analysis of Stainless Steel Processed

through Severe Plastic Deformation

by

Ishtiaque Karim Robin

A thesis

submitted in partial fulfillment

of the requirements for the degree of

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To the Graduate Faculty:

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Pre-irradiation Characterization and Thermal Stability Analysis of Stainless Steel Processed

through Severe Plastic Deformation

Thesis Abstract – Idaho State University (2018)

Stainless steel 304 and 316 are mostly used as the structural materials for light water reactors and stainless steel is also a potential candidate material for future generation reactors. As an attempt to enhance the mechanical properties and irradiation resistance of the stainless steel, severe plastic deformation techniques like high pressure torsion (HPT) and equal channel angular pressing (ECAP) has been used to refine the grain size and increase grain boundary volume. Microstructure of these pre-irradiated steels have been characterized through transmission electron microscopy, scanning electron microscopy, X-ray diffraction, energy dispersive spectroscopy and microhardness testing. Annealing was carried out in different temperature and time to find out the thermal stability of these steel. Here in this research, an attempt has been made to investigate how HPT and ECAP process changed the microstructure to result in better mechanical properties and how stable they are in elevated temperature for a prolonged period.

Key Words: SPD, ECAP, HPT, TEM, SEM, XRD, Thermal Stability.

Chapter 1: Introduction

1.1 Objective

The main objective of this study is to do microstructure characterization of the stainless steel 304 and 316 which are processed through severe plastic deformation techniques of high pressure torsion and equal channel angular pressing. The intension of this characterization is to look into the microstructure and how it is influencing the mechanical properties as the microstructure is changed through the severe plastic deformation processes. Also, up to which temperature these materials can be used safely without losing the better mechanical properties was determined by thermal stability analysis. These materials will be neutron irradiated at the Advanced Test Reactor of Idaho National Laboratory and will be characterized again after the irradiation. This current study of pre-irradiation characterization will be compared to the post irradiation characterization and conclusion will be made on how these severe plastic deformation techniques are influencing the materials to be more radiation tolerant and if these techniques can be incorporated into bulk manufacturing for future generation reactor materials.

1.2 Motivation and Background

Nuclear industry is now embarking into the fourth-generation reactors and further improvement of structural and cladding materials is a matter of paramount importance. A development in the nuclear materials to extend the lifetime of the reactors from 40-60 to 60-80 years can ultimately lead towards a very strong stand for the nuclear industry compared to the other available power generating sectors. A development of roadmap for robust science-based technology is necessary for the development of nuclear materials with respect to modeling and life prediction, manufacturing, fabrication, testing and evaluation which will result in matching the expectations of performance in increased temperature, pressure, chemical and other physical constraints required for the future generation reactors.

Stainless steel has been used for the structural materials for nuclear reactors for a very long time. Changing the microstructure through severe plastic deformation manufacturing process can enhance the mechanical property of the stainless steel and also result in better irradiation resistance. This can eventually result in lifetime increase of nuclear reactors while providing the advantage of operating the reactors at higher temperature and pressure. Degradation of the structural and cladding materials is the primary reason for the lifetime limitation of a nuclear reactor. An attempt has been made here through the severe plastic deformation processes like high pressure torsion and equal channel angular pressing to overcome this limitation by enhancing the mechanical properties and rendering the materials more radiation tolerant.

Chapter 2: Literature Review

2.1 Stainless Steels 304 & 316 in Nuclear Reactors

Stainless steels (SS) are one of the vastly used materials in modern times contributing to the sectors of architecture and construction, automotive and transportation, medical, energy and heavy industries, and so on. Austenitic stainless steel has superior corrosion resistance and excellent mechanical properties at elevated temperatures which make it a good candidate material in different fields [1, 2]. Higher degree of plasticity between the proof strength and ultimate tensile strength stress, very good low temperature toughness and relatively higher degree of anisotropy make the stainless steel the major structural materials for a lot of the applications [3, 4]. In nuclear field, the necessity of stainless steel becomes significantly more important due to the high neutron fluence, elevated temperature, corrosive environment, different transmutation phenomena and overall very harsh environment within the reactor. All these phenomena make it very difficult for the reactor materials to survive with optimal mechanical properties. Corrosive environment, complex chemical and radio-chemical situation, minimization of maintenance requirement and very long-term waste management expectations are some of the deciding factors for choosing the suitable materials in nuclear reactors. Stainless steels are vastly used here due to its superior properties like higher work hardening rate, superior strength and hardness, good corrosion resistance, higher tensile and yield strength, good ductility and formability and good machinability.

SS304 and SS316 are very similar outwardly and not distinguishable to naked eyes. Property wise, they are also non-magnetic, austenitic and non-hardenable through heat treatment. Both steels

have good corrosion resistance property, superior durability and these are easily formed and fabricated. In general, the difference lies in their chemical compositions. There is a total of 18% chromium and 8% nickel in SS304. SS316 is made up of 16% chromium, 10% nickel and 2% molybdenum. So, the basic difference between these two steels lies in the presence of molybdenum. Molybdenum gives extra corrosion resistance in SS316 in the acidic environment. Corrosion is often caused by the formation of chromium depletion zone when chromium is oxidized, and the extra molybdenum gives a protection against this. Thus, SS316 provides extra protection against chlorides and chlorinated solutions and for this reason, it is desirable in the applications where exposure to salt environment is an issue. But addition of extra Molybdenum comes with some extra cost. On the other hand, SS304 is relatively less expensive compared to SS316 and that is the reason SS304 is the most versatile and widely used austenitic stainless steel in the world.

SS304 and SS316 are widely used in nuclear field and some of its applications include end fittings of fuel channels for fuel pellet, pressure vessel, intermediate and secondary heat exchangers, steam pipes and so on. SS304 and SS316 are integral parts of nuclear fuel transportation and it is also a good storage material for spent nuclear fuel.

The use of stainless steel in first generation water based nuclear power plants was observed in early 70's and SS304 and SS316 were recommended for structural and core application in fast spectrum reactors (SFR) and other future generation reactors. On an attempt to minimize the failure of these steels and to improve the mechanical property and resistance to sensitization and intergranular corrosion resulted in the development of SS304 and SS316. The reactor core

applications in intense radiation environments pushed the improvements of stainless steel to yield a significant extension of lifetime of the core components in the fast reactors [5].

2.2 Severe Plastic Deformation (SPD)

2.2.1 Why SPD?

As the attempt to improve the mechanical property of materials scientists have devoted a lot of researches to come up with different manufacturing process. Nanocrystalline (NC) and UFG materials have shown better tolerance to irradiation induced swelling and hardening/ embrittlement which can lead to materials degradation and failure [6, 7]. NC and UFG are associated with superior mechanical properties and this behavior can be accurately predicted most of the times from the microstructural analysis of these materials. Conversion of a coarsegrained (CG) materials to NC and UFG results in higher volume fraction of interfaces. For example, for a 5 nm grain, the volume fraction of interfaces can be as high as 50%. But it comes down to 30% and 3% when the grain size becomes 10 nm and 100 nm respectively [8]. A significant portion of the atoms lies in the interfaces in NC and UFG materials for which high density interfaces are responsible. Grain boundary (GB) acts as a defect sink. From fig.1 it can be shown that the dislocation loops and segments are drawn towards GB and eventually get sucked in GB defect sink [26]. More GB volume results in more defect sink in the materials, which can result in superior radiation tolerance. In this way, by converting the CG structure into UFG and NC structure we can potentially increase the radiation tolerance. In comparison to conventional polycrystalline materials, some of the superior mechanical properties present in NC and UFG materials are increased strength/ hardness [10-12], improved toughness, reduced elastic

modulus and ductility, enhanced diffusivity [13], higher specific heat, enhanced thermal expansion coefficient, and superior soft magnetic properties. As it is shown in fig.2, higher void swelling capacity can result in UFG materials [14].

There are two main ways of producing NC and UFG materials from conventional coarse-grained materials. They are known as bottom-up and top-down approach. In the bottom-up approach, NC materials are assembled from individual atoms; through the consolidation of small cluster to from nanoscale building block. On the other hand, top-down approach starts with a bulk material and break down the structure into a nanostructure. Techniques such as inert gas condensation [15], electrodeposition [16], chemical and physical deposition [15] are some of the "bottom-up" approaches. Severe plastic deformation (SPD) is the most successful top-down approach. It is beneficial because through this process CG structure can be converted into NC without changing the cross section of the materials. Equal Channel Angular Pressing (ECAP) [18, 19], high pressure torsion (HPT) [20, 21], accumulative roll bonding [22, 23], repetitive corrugation and strengthening [24, 25], friction stir processing [26, 27] are some of the SPD techniques.



Fig:1. In-situ TEM imaging during ion-irradiation of NC Ni films showing GB as sinks for irradiation induced dislocation loops and segments [9].

For this particular study, ECAP and HPT process are considered. In both cases, enormous amount of strain is introduced into the microstructure, which is responsible for the conversion of CG structure into the NC and UFG structures.

2.2.2 ECAP

Schematic of ECAP process is shown in the fig 3. Samples are pressed through a cross-section with a die and as it moves through two intersecting channel, it is sheared in the intersection and exits through the exit-channel. As the channel is symmetric, the sample can be rotated after every pass. If the sample is not rotated before the re-entry then it is called route-A and if it is rotated 180 degree then it is called route C. If the sample is rotated 90 degree, then it is called route-B. If the rotation is in the same direction, then it is called route B_C and if the direction 90 degree rotation is changed alternatively then it is called B_A route. For this particular research route B_C is used to produced UFG structure. From fig. 4 it can be seen that element abcd gets transformed

to a'b'c'd'. The amount of strain introduced here can be calculated from the following equation [28]:

$$\epsilon_{\rm eff} = \frac{1}{\sqrt{3}} \left[2 \cot(\frac{\phi + \psi}{2}) + \psi \csc(\frac{\phi + \psi}{2}) \right]$$
(2.1)

Here ' φ' and ' ψ' ' are described in the figure 4. From the equation, we find that when φ = 90 degree and ψ = 0 degree then ϵ_{eff} becomes $\frac{2}{\sqrt{3}}$. [29-36] are some of the comprehensive reviews for ECAP process. ECAP was first introduced by Segal et al. [37]. Some work done on ECAP materials are Armco iron [38, 39], Al alloys and their composites [40-44], Mg alloys [40], Cu alloys [45, 46], pure Ni [38], low carbon steel [47-49], Ti alloys [50, 51], Zn-22% Al [52] and so on. ECAP is an effective way of producing relatively larger bulk Samples [53, 54] and it has also been incorporated with conventional rolling mills and form a continuous manufacturing process for ultrafine grained materials [55, 56]. To move the nanocrystalline materials from laboratory to widespread use in commercial sector depends on a successful combination of superior performance and relatively cheaper cost of production. The cost associated with ECAP process is comparable to other intensive thermomechanical size reductions of grain size in conventional metals [57]. Thus, ECAP has a significant potential to be employed commercially as a solution for several important sectors where superior mechanical property is a must for technological advancement.

2.2.3 HPT

For high pressure torsion (HPT) a thin disk is taken and is subjected to torsion and high pressure simultaneously as it is shown in fig. 5. In this particular set up, the sample is constrained from all the surrounding directions. Torsional strain is applied to the sample while rotating the plunger. The frictional force generated between the plunger and the sample and the sample and the anvil are responsible for generating shear within the sample. The dimension of the sample is usually about 20 mm in diameter and about 0.2 to 0.5 mm in thickness. The normal pressure that is applied to the material ranges from 5 to 7 GPa.

For N rotations the shear strain γ is achieved by the following equation [29, 58-60]:

$$\gamma = \frac{2\pi r N}{l\sqrt{3}} \tag{2.2}$$

Where 'r' is the radius and 'l' is the thickness of the of the disk. Increasing number of rotations creates homogenization within microstructure. Ref [61] is a comprehensive review for HPT process.



CG 304L SS

(a)

(b)





Fig 2. Comparison of CG and UFG; ion irradiation resistance for SS304 steel [14]. Higher void swelling capacity and higher engineering stress are found in UFG structure.



Fig 3. (a) Schematic of Equal Channel Angular Pressing (ECAP) showing the sample on the top before insertion into die and the pressed sample horizontally exiting from the die [29, 30]. (b) Different techniques in which the samples can be re-entered after one pass. Route A entry without any change in orientation, route B rotation by 90 degrees, and route C rotation by 180 degrees [31].



Fig 4: Schematic of the shear strain experienced by a material element as it passes through the channels of an ECAP die. Φ is the angle the channels meet at, ψ is the angle of curvature at the outer point of contact of the channels. (a) For $\psi = 0$, (b) for $\psi > 0$



Fig 5. Schematic diagram of the high-pressure torsion setup [32]

2.2.4 Major Properties Resulted from SPD Process

Conversion of coarse grained materials into NC and UFG results in some superior mechanical properties of the materials. Some of the major properties are discussed below:

2.2.4.1 Yield Strength

Strength of the materials is directly related to grain size which can be predicted from the Hall-Patch (H-P) relationship:

$$\sigma_y = \sigma_o + \frac{k}{\sqrt{d}} \tag{2.3}$$

Where d = grain size, σ_v = yield strength, σ_o = friction stress. This equation can be theoretically explained based on the dislocation piling up on grain boundaries which acts as a barrier to dislocation motion. This causes stress concentration in the grain boundary. The smaller the grain size the less pile up and the higher stress required to penetrate the boundary. But this equation is only valid up to certain extent. When the grain size comes below a critical size, dislocation pile up may no longer be able to form and this physical model of pile up at GB breaks down. Nano twinned Cu with twin boundary spacing lower than ~20 nm produced through electrodeposition showed decreased strength as grain size is decreased, resulting in a negative H-P relation [62]. At such grain sizes the usual dislocation-dislocation interaction and pile up of dislocations normally found in micrometer-sized grains most likely do not exist. Though the mechanism in such small-scale microstructure level is not fully understood, it can be assumed that at such level grain boundary mediated activities start [29]. It can be noted that in general boundary spacing less than 10s of nm cannot be produced through SPD. Also, the strength of the materials does not depend on the grain size only. Dislocation density within the grain can also contribute to the overall strength of the materials. The following equation includes this effect of dislocation density [63, 64]:

$$\sigma_y = \sigma_o + \frac{k}{\sqrt{d}} + \alpha M G b \sqrt{\rho} \tag{2.4}$$

Where $\alpha = 0.25$, M is Taylors Factor, G is the shear modulus, b is the magnitude of Burgers vector, and ρ is the total dislocation density. So, it can be expected that SPD processed materials would be stronger than the prediction of the H-P equation. In fact, some of the studies done on SPD materials showed that the second term of equation 2.4 is major contributor to the strength

than the grain boundary strengthening term [65, 66]. The dislocation loop within the microstructure itself acts as a barrier to dislocation motion, making the materials stronger. Thus, materials with higher dislocation density result in a positive deviation from the H-P relation.

2.2.4.2 Ductility

It is expected that the reduction of grain size leads to an increase of ductility in conventional grain size regime. However, when the grain size is reduced to nanoscale a drop of ductility is observed. Three major sources responsible for the reduction of ductility is observed by Koch [67]. They are (1) artifacts from the processing like pores, etc. ;(2) tensile instability; (3) crack nucleation or shear instability. From the investigations, it is generally agreed that there are three regimes for plastic deformation mechanism. (a) $d > 1 \mu m$; when plasticity is controlled by dislocation and plasticity; (b) d < 10 nm; at this point intragranular dislocation activity and grain boundary shear act as the main mechanism for deformation (c) intermediate grain size (10 nm to 1 μ m) is less well understood. SPD process is known to introduce a lot of non-equilibrium grain boundaries, which can be acting as a mechanism to improve the ductility [68]. This non-equilibrium GBs can act as a source for excess dislocations which help to initiate slip in the system and in the room temperature it can even slide or rotate the GB to increase strain hardening component. Three major factors: the work hardening, the strain rate sensitivity and thermal softening are the major contributor to determining ductility. Higher strain rate sensitivity is related to smaller activation volume. So, it is connected to the nanostructure (presence of twins). It can be predicted that ductility, strain rate sensitivity and deformation mechanisms are connected, and ductility can be engineered through the manipulation of these variables as Zhu and Liao [69] were able to increase the ductility of NC metals through the growth of twins. Synthesis process of UFG and NC

materials often introduce porosity and contaminates, which can be detrimental to ductility. As a result, reduction of ductility in NC materials is often observed given that there is no porosity and bonding was complete during the synthesis.

2.2.4.3 Strain Hardening

Nanocrystalline materials show very little to zero strain hardening after the initial stage of rapid strain hardening over small plastic strain regime. Plastic deformation causes dynamic recovery at room temperature. It is possible that there is annihilation of the dislocations or dynamic recovery which cause the dislocation density to reach a saturation point. Severe plastic deformation requires dynamic recovery. Materials produced through ECAP has shown very small strain hardening behavior [70]. Localized deformation can be caused from low strain hardening, which results in low ductility of materials. In most of these cases, necking is observed and shear band form. Competition between the origin of dislocation through SPD process and annihilation of dislocation due to dynamic recovery determines the steady state of dislocation density. Some of the previous studies mentioned that dislocations are generated from grain boundary. This is debatable because grain boundary also acts as defect sink. Dislocations are generated in large number and also disappear very fast due to the presence of higher volume of grain boundary, which makes it very difficult to determine the contribution of dislocations in deformation mechanism.

2.2.4.4 Strain-rate Sensitivity

Previous studies on strain-rate sensitivity reported both increase and decrease of strain-rate sensitivity with the decrease of grain size. Strain rate exponent m (defined as $m = \frac{\delta \ln \sigma}{\delta \ln \epsilon} \text{ or } \frac{1}{\sigma_y} \frac{\delta \sigma}{\delta \ln \epsilon}$)

for iron goes down to 0.004 from 0.04 when the grain size is 80 nm. Melow et al. [71] reported the value of m= ~0.006 at d~ 20 nm for Fe processed through ball milling and consolidation. Some of the studies reported that the strain rate sensitivity depends on the strain rate [71]. Gray et al. in their study [72] mentioned that this higher strain rate sensitivity is caused by the higher preexistent dislocation density. Some other study showed an increase of strain-rate sensitivity is increased when grain size falls below a critical value [73]. Same kind of result is reported for Al [74] where the strain rate sensitivity increased for smaller grain size. This increment of strain rate sensitivity is directly related to the change in the rate of controlling mechanism for plastic deformation. Strain rate sensitivity is related to activation volume, where m is inversely proportional to activation volume. So smaller activation volume would result in higher strain rate sensitivity. Strain rate sensitivity also depends on the number of passes during the ECAP process [75]. Higher number of passes results in higher strain rate sensitivity. But this is not attributed to a change in the mechanism to grain boundary sliding, but rather to the switch to thermally activated dislocation annihilation in the grain boundaries. This hypothesis can be supported by the deactivation of forest dislocation in ultrafine grained materials because of the scale effect.

2.2.4.5 Creep

Creep study of nanocrystalline materials is complicated because of the introduction of different defects like porosity and impurities and the existence of higher fraction of grain boundary volume including triple lines and quadruple junctions. Also, grain growth phenomena which occurs in nanocrystalline materials in much lower temperature compared to the coarse-grained materials makes it very hard to determine the mechanism responsible for creep. Due to the presence of higher grain boundary volume, diffusion creep is considered to be significant. Diffusion creep mechanism includes Nabarro-Herring creep where vacancy flows through the lattice and Coble creep where vacancy diffuses through the grain boundary. Different equations are present to predict the diffusion creep within the microstructure. Wang et al [76, 77] reported different mechanisms for creep in ultrafine grained and coarse-grained materials. A combined mechanism of dislocation creep and grain-boundary diffusion governs the deformation in CG materials while grain boundary diffusion is operating mechanism in nanocrystalline creep. Another study from Snaders et al. [78] reported that the prevalence of low energy grain boundary together with inhibition of dislocation activity caused by small grain size is responsible for low strain rate and creep resistance is also increased due to this. The study from Wang et. AI [79] reported that at high level stress, grain-boundary sliding becomes the major deformation mechanism at room temperature. Some other study from Grabovestskaya et al [80] for creep of nanostructured materials (Cu, Ni, and Cu-Al₂O₃ composite) produced by SPD at temperature T< 0.3 T_m reported that the steady state creep rate of nanostructured materials is well described by a power law where the exponent n is close to 5.5 for copper and 8 for nickel. They estimated the activation energy for creep in nanostructured copper and nickel in the temperature range of 0.2-0.3 T_m is 2.5 times lower than the coarse-grained counterpart. Grain boundary sliding controlled by grain boundary diffusion is the main contributor to the difference of the activation energy. From simulation study of Yamakov et. AI [81] conducted at higher temperature reported that the distinct effect of grain boundary diffusion is significant. Direct observation of grain boundary sliding was reported as a mechanism for Coble creep. Grain growth is supposed to decrease the creep rate because of the increase of the grain size. However, in molecular dynamics (MD) study by Estrin et al [82], it was showed that the creep rate increased with the grain growth. The enhanced creep rate was a result from the topological changes during initial grain growth phases, which also happens to act as a contributor of grain boundary diffusion fluxes and grain boundary sliding. Dislocation generated from grain rotation induced grain coalescence and grain boundary decomposition in the vicinity of certain triple point junctions were also shown to contribute to the deformation. Grain boundary segregation has been shown to slow down the creep rate. Study from Yin et al. [83] reported that the increase of doping nanostructured buckle with boron and addition of Sulphur significantly decrease the creep rate. Here the interstitials in grain boundary retard the movement of grain boundary sliding, resulting in lower creep rate.

2.2.4.6 Fatigue

Materials processed through SPD have higher yield strength and for that reason the fatigue life of NC and UFG materials are also enhanced. From the study of Yan et al [84] it was shown that the localized superplastic deformation of the grains was present near the fatigue fracture surfaces while equiaxed grains were visible in submicron sized grains. Other than grain boundary diffusion, dislocation climb and multiplication were associated with this behavior. Vinogradov et al. [85] reported that ECAP processed Ti demonstrated better fatigue resistance compared to coarse grained counterpart while being subjected to constant load testing. The investigation of Pelloux [86] showed no reduction of fatigue performance under constant plastic strain cyclic testing. SPD resulted in grain refinement and work hardening in materials through the increment of dislocation density which is responsible for this fatigue performance. Fatigue performance for 6061 Al was found to be superior for both high and low cycles after one pass in ECAP process but as the number of passes was increased, the improvement was eliminated. From this Chung et al. [87] reported that the reason behind this is the fine-grained microstructure with low-grain boundary misorientational angle which is typically resulted from one pass during the ECAP process. Therefore, if fatigue life improvement is the primary intention, then one pass during ECAP process is the best way to achieve that. Same result was found for low carbon steel [88] while doing fatigue testing. The result was a gradual decrease of tension and compression peak with the increase of number of cycles. Kim et al. and Chapetti et al. [89, 90] observed a beneficial effect on fatigue behavior of low carbon steel as the grain size is decreased. From these studies, it can be concluded that the finer grain size is helpful for increasing the resistance against fatigue. Enhanced ductility due to grain refinement resulted in increasing crack growth resistance because of the ability to accommodate the plastic strains during cycling, which ultimately leads to superior fatigue resistance for NC and UFG materials.

2.3 Grain Boundary (GB) Evolution and Related Phenomena

The process of SPD introduces non-equilibrium grain boundaries which have higher internal energy and long-range stress. The extinction of contours inside the grain boundary also occurs from the elastic stress originated from GB [90]. High resolution microscopy studies showed that there is existence of dislocation in the vicinity of the GB. Non-equilibrium grain boundaries are result of the interaction between these dislocations and grain boundaries. These non-equilibrium GB have higher energy and long-range stress fields. If this structure is subjected to additional energy from annealing, we see that the rate of the extinction of contours goes down. The crystallographic width of a GB is around 1 nm, which is determined by the degree of the nonequilibrium state in the GB structure while the elastically distorted layer closer to grain boundary is 10 nm where the elastic strains are relatively high and is 3-5%. This elastically distorted layer contains a high dynamic activity of atoms. When the grain size comes down below 10 nm, the GB thickness becomes very close to the crystalline size and high dynamic properties can be manifested [41]. When the grain size comes to 1 nm, theoretically there is no crystal structure is present in the material and it essentially becomes an amorphous material.

During SPD, plastic deformation takes place by movement and interaction of dislocation. Due to imposed plastic strains by SPD there is usually a large increase of defect density including dislocations, vacancies, new grain boundaries. The dislocations are grouped together to form a substructure. Under the influence of increasing stress, the substructure of configuration of dislocation arranged in the cells. These walls contain most of the dislocation whereas the interior cell has a very few dislocations. There have been some studies on evolution of microstructure with increased strains [91-99].

During the ECAP process, after the first pass, elongated grains are generated with a lot of dislocations. During the second pass there is formation of deformation bands which intersect with the with the earlier elongated grains and as a result, smaller sub-grains are formed. As the number of passes go higher, this fragmentation process goes on and result in finer grain sizes till it reaches an equilibrium when well defined and equiaxed grains are visible. These grain boundaries have increased fraction of high-angle boundary. Normally the first few passes are most effective for grain refinement, after that only the fraction of high angle boundaries increases, and more defined grain structure become visible. Microstructure investigation from previous studies reported that these refined grain structure completely replace the previous grains. This finer grain replacing the previous coarse grain is a dynamic recrystallization process.

For the HPT due to high hydrostatic stress from SPD process, the vacancy concentration goes very high and it is close to the vacancy concentration during the near melting point. Vacancy plays a very important role in the annellation of point defects. But if the imposed condition is not favorable for the diffusion, dislocation annihilation slows down and as a result, strain hardening increases [100]. It is observed from the in-situ experiment that with the removal of hydrostatic pressure the dislocation density reduces significantly [101]. It is very important to gather the important information related to this grain boundary evolution in microstructure and how the deformation takes place during this process. Some of the major deformation mechanism and microstructure evolution is discussed below:

2.3.1. Dislocation Pile-up

As strain is introduced to the materials, dislocation is generated. Through the SPD process as the grain size grows smaller, the number of dislocations pile up against a grain boundary decreases for a constant stress level. If we want to keep the amount of dislocation constant within a grain boundary, we need to increase the stress level as the grain size is growing smaller. If the microstructure goes into nanocrystalline regime, the number of dislocation pile-up eventually reduced to one, so the stress field can no longer be multiplied [102]. In this state, the individual grain in a polycrystal can no longer support more than one dislocation [103]. From this idea, we can come up with the concept a minimum grain size below which no dislocation pile-up will occur. This is known as the critical grain size. Below this, the Hall-Patch relationship no longer works.

2.3.2. Grain Boundary Sliding

For the smaller grain size in nanocrystalline materials (d< 50nm), grain boundary sliding act as the major deformation mechanism. When stress is applied to a material, one set of grain boundary starts to slide towards the direction of applied stress while the neighboring grains remain still in their position, thus causing grain boundary sliding. For Cu Corand [104] proposed three distinct regions based on grain size for flow stress. Region (i) $d > 1 \mu m$; where grain size is relatively bigger and here dislocation pile-up is the main deformation mechanism. Region (ii) 1 μ m >d > 10 nm; grain boundary shear is the main deformation mechanism. Dislocation pile up is the reason for this grain boundary shearing. Region (iii) d< 10 nm; where the grain size is very small and in this regime grain boundary sliding is the major deformation mechanism. Molecular dynamic studies have been done on deformation mechanism in nanocrystalline materials by Van Swygenhoven [105-108] which concluded that grain boundary sliding during the deformation causes the build up of stress across the neighboring grains. This extra stress is relieved through grain boundary and triple point migration. This phenomenon is determined by the grain size and other hindrance towards grain boundary sliding. Atomic shuffling and stress-assisted free volume migration facilitate this grain boundary sliding. All the deformation is stored in the in grain boundaries cause the grain boundary sliding for nanocrystalline materials. While in larger grain size intragrain deformation is observed through the presence of stacking fault energy. Raj and Ashby [109] predicted that plastic accommodation between adjacent grains occurs by diffusion alone.

2.3.3. Core and Mantle Models

The basic idea of the core and mantle model is comprised of two parts: (i) the core or the grain interior, which is subjected to more homogeneous stress and (ii) the mantle, or grain boundary region, which is responsible for resistance to plastic flow and work hardening. When the materials are subjected to stress, the applied shear stress in the grain boundary is 2 or 3 times greater than the stress in the core region. So, it is logical to assume that the origin of plastic flow is generated from the grain boundaries. Grain boundary ledges and dislocations in grain boundary are responsible for this plastic flow. Grain boundary may have segregation and other impurities and different mechanical properties compared to grain interior. Normally grain boundaries show much faster rise in the dislocation density and hardening rate. Gray [110] predicted that the higher hardening occurs on the region adjacent to the grain boundaries and triple points. As the applied stress is increased, there is a formation of work hardened layer along the grain boundary. Once this work hardened layer is formed, the stress within the polycrystalline aggregate homogenizes. For all strains rates, the stress first increased and then decreased as the grain size is reduced. Dislocations, boundary diffusions and the lattice diffusion mechanisms contribute to these strain rates.

2.3.4. Grain Boundary Rotation

Another interesting mechanism for the deformation mechanism is grain boundary rotation and grain coalescence. During the plastic deformation grain can rotated and can coalesce along the direction of shear. As plastic deformation takes place, two neighboring grains can rotate in such a way to bring their orientation closer together. That lead to the elimination of barrier that was

previously present by the boundary. So, dislocations have more extended path of migration. This mechanism can potentially induce softening and localization. This is one of the reasons attributed to the limited ductility of nanocrystalline materials.

Another way of grain rotation can be accompanied by the disclination motion [111]. A disclination motion can be characterized by a crystalline lattice rotating around its line. Generation of partial dislocation defects can provide an alternative mechanism to grain boundary sliding. Through this partial dislocation, instead of sliding grain boundaries rotate to accommodate the stress applied by the SPD process. There is a large stress field associated with the partial dislocations. This large stress field makes it very difficult for the other defects to move through, thus making the strength higher. The interaction between partial dislocations can also break down the grain. Thus, disclination can contribute to both deformation and strengthening of the materials and is considered an alternate mechanism to grain boundary sliding.

2.3.5. Shear-band Formation

Immediately after the onset of plastic deformation, the shear band development is observed. This corresponds with the strain hardening behavior of those grains as the ability to work harden by the increase in dislocation density is lost. This shear band formation is generally not observed in the conventionally processed materials. From previous studies, it was determined that the shear banding does not appear to change between low-rate and high-rate loading and the failure mechanism is governed by the grain size rather than strain rate. During the plastic deformation rotational recrystallization occurs and dislocation rearrange itself into elongated dislocation cells. As the deformation process continues, the cells become elongated sub-grains and eventually they break up into approximately equiaxed grains. The breakdown of sub-grains into an equiaxed micro-crystalline structure can occur by minor rotation of the grain boundaries lying along the original elongated boundaries.

2.3.6. Twinning

Mechanical twinning and growth twinning (recrystallization) are the two types of twin considered here.

2.3.6.1 Mechanical Twinning

Mechanical twinning and slip are two competing processes. This mechanical twinning is directly related to the stacking fault energy. There is an increase in twinning stress with increasing stacking fault energy and decreased grain size [112]. So as the grain size of the material goes down, the mechanical twinning also decreases and eventually disappears. Normally heterogeneous nucleation of twins is observed in grain boundary areas while homogenous nucleation of twin lamellae are observed in grain interior. Growth of twin lamella eventually results in new grains. These twins react with dislocations to form coherent twin boundaries. In nanocrystalline materials the critical nucleus approach for twinning becomes impossible. There can be three probable reasons for that: (i) conventional nucleation mechanism breaks down in nanoscale. (ii) higher fraction of local stress concentration points like triple points, etc raise the stress significantly. (iii) partial dislocation separation increases in nanoscale domain.
2.3.6.2 Growth Twinning

Growth twin can be formed through controlled heat treatment. Growth twin can be engineered in the microstructure to introduce proper mechanical properties within materials. These growth twins normally form in the larger grains. Lu et. Al [113] was able to initiate good mechanical strength and electrical conductivity in Cu through the formation of high density growth twins.

2.3.7. Grain Boundary Dislocation Creation and Annihilation

When the grain size becomes very small, deformation structure changes within the microstructure. The generation of dislocation in the grain boundary becomes very limited. So instead of cross slipping and generating work hardening, the dislocations run freely until they reach the opposite end of grain boundary. When the grain boundary becomes significantly small in nanocrystalline regimes, the GB becomes virtually ledge free and intrinsic and extrinsic grain boundary dislocations pushed out into the grain core. Because the mean free path of dislocations become limited, the normal phenomena associated with dislocation like dislocation reaction and annihilation, cross slip, dislocation multiplication can no longer occur. Some of the simulation work done reported that with the decreasing grain size plasticity related to dislocation activity towards a plasticity that is primarily accommodated in the grain boundary. Nonoindentation experiment done on the materials showed that dislocations can be emitted, absorbed and reflected from grain boundaries. After one indentation, a dislocation is generated under the indenter and moves towards the grain boundary. On further indentation, another dislocation is created while the leading partial of the dislocation is completely absorbed. This absorption of dislocation happens within the grain boundary and the grain boundary structure is changed. If a

large number of dislocation is generated during plastic deformation, some of the dislocation are absorbed within grain boundary while some of them are reflected back to plastic zone. So, it can be assumed that both the local stress and the coherency of grain boundary play a combined role in the interaction between the grain boundary and incoming dislocations.

2.3.8 Dynamic Recrystallization During SPD

Dynamic recrystallization (DRX) process is the renewal of new grains while the material is going through plastic deformation. There are two kinds of DRX: Continuous (CDRX) and discontinuous (DDRX). In DDRX involves the movement of existing grain boundary and new grains are also created from nuclei. On the other hand, CDRX does not involve any grain boundary movement and creation of new grains are facilitated through the geometrically necessary dislocation (GND). The difference between statistical dislocation and GND is the misorientation angle. When statistical dislocations are grouped, there is not a significant mis-orientational angle change. But GND results in mis-orientational angle change and this can be further increased by pumping further dislocations into the wall. During the SPD process, in the grain boundary area, the lattice rotation is slowed down because of the neighboring grains. In this way, a lattice curvature is created which requires a large number of GND. But there is a critical point for this lattice curvature after which the GNDs form sub grains. This is called the steady state. The initial stages of refinement can cause the GND density as high as statistical dislocation. But once it reached the steady state, the GND density becomes very small.

2.3.8.1 Texture Induced DRX

This process is similar to grain rotation and coalescence process, while the orientation difference between decreases continuously and eventually both of the cells reaches the ideal orientation thus the grain boundary disappears. This process can also be referred to as texture induced DRX or TDRX.

2.4 Thermal Stability

SPD process causes the grain refinement and increases the grain boundary volume through the increase of densities of defects like dislocations, stacking faults, and vacancies. The defects increase the driving force for recrystallization and the nucleation of new defect free grains. Putting increased strain in the materials causes long range internal stress. These stresses may influence the annihilation of dislocations. It can be anticipated that the annihilation of lattice defects starts at relatively lower temperature in the grains which have much higher defect densities. From the general rule of recrystallization, the higher the dislocation density and lower the crystalline size, the lower is the onset temperature of recovery and recrystallization. So, we can predict that the thermal stability decreases when the SPD process is applied due to the reduction in grain size and the increase in dislocation density. From previous studies, it was concluded that for the majority of the materials the activation energy is about $0.5 \pm 0.1 \times Q_{self}$ and here Q_{self} is the activation energy for self-diffusion. It does not depend on the type of materials or how it was processed. The activation energy of diffusion along grain boundaries and dislocation is about half of that for self-diffusion [114-118]. This activation energy of recovery and recrystallization is the reason for the dislocation and grain boundaries to act as diffusion

paths during annealing. If the pressure is very large during SPD process, it can hinder the vacancies to form cluster. Also, in the places where the dislocation density is higher, the number of glide obstacles is larger and that is favorable for twinning activity. Larger twin fault probability makes the materials thermally less stable. This effect is attributed to very low energy of twin boundaries. In the volume where twin boundaries were formed at the expense of dislocations, the stored energy decreased locally by comparison with the neighboring regions. The volumes act as nuclei of defect free grains when there is necessary energy available. This acts as a favorable variable for accelerated recrystallization. Also, for the low SFE materials, the thermal stability is relatively low because the smaller the SFE, the larger the distance between partials in the dissociated dislocations. The high degree of dislocation density during grain refinement by SPD. Grain refinement process is responsible for superior mechanical properties of materials. In order to take the advantage of these advantages, it is needed to make sure that the material does not lose it thermal stability during the working conditions.

Chapter 3: Materials and Experimental Methods

3.1 Materials

Materials used for this experiment are Stainless Steel (SS) 304 and 316. The chemical compositions of the 304 and 316 are given in the table 1.

Table 1: Chemical Composition of SS304 and SS316

	Cr	Ni	С	Mn	Ti	Si	Cu	Мо	V	W	Р	Fe
SS 316	16.18	12.24	.03	.34	.32	.37	.23	2.47	.06	.04	.03	blnc
SS 304	17.22	9.56	.02	.53	.26	.24	.16	.14	.05	.04	.03	blnc

Both SS304 and SS316 were processed through equal channel angular pressing (ECAP) and high pressure torsion (HPT). For the ECAP process route B_c was chosen for grain refinement which is known to result in the most equiaxed grains. The temperature used for ECAP SS304 during processing was 450°C and for ECAP SS316 it was 380°C. Number of passes was 6 for both of ECAP SS304 and SS316. This particular number of passes were chosen because dynamic recrystallization starts to occur normally after 6 passes. Temperature was chosen so that the materials do not break during the ECAP process. Inner contact angle used for ECAP process was 120°. For HPT process, temperature used was 300°C for both of the steels. Total number of passes used for the high pressure torsion was used 10. The parameters are summarized in the table 2.

Table 2: Processing Temperature and Parameters

Materials	Techniques	Temp(°C)	No of turns/passes		
SS304	НРТ	300	10		
SS316	НРТ	300	10		
SS304	ECAP	450	6		
SS316	ECAP	380	6		

3.2 Experimental Process

The experimental process involves sample preparation and characterization. Sample preparation is a matter of great importance because characterization of the microstructure depends greatly on the sample preparation. Characterization may result in producing non-usable data if the sample is not prepared well. Once the sample preparation is done, the materials are subjected to various characterization methods. These characterizations are useful to get important information on the microstructure of the materials. Here an attempt has been made to look into the microstructure change of severe plastic deformed steels through these characterization methods and to find out how ECAP and HPT is changing the microstructure of the materials to produce good mechanical property.

3.2.1 Sample Preparation

Sample preparation was done at the Advanced Materials Laboratory (AML) at Center for Advanced Energy Studies (CAES). BUEHLER Isomet low speed saw and BUEHLER Isomet 100 precision saw were used to cut the samples. ECAP samples came as rod bar, from which diskshaped slice is cut. HPT samples came as disks. Due to grain refinement and dislocation strengthening, HPT and ECAP processed materials have higher hardness and yield strength. As a result, these are a lot harder than conventional coarse grain samples, which makes it harder to cut the samples. Cutting speed and weight on the sample against the blade were chosen carefully for the optimum cutting. Water was used as the cooling fluid during cutting. Crystal bonding was used to attach the samples with pucks and hot plate with the model number GATAN 623-40 was used for this purpose. For the sample polishing, Leco Spectrum System 1000 automated polisher and Vibromet 2 vibratory polisher were used. Acetone and methanol were used in ultrasonic bath (model: 1510 BRANSON) to clean the samples.

3.2.2 Annealing

Annealing was conducted in argon environment within glovebox at AML. Furnace used for annealing has the model number FB1315M (serial no: 1256100150269) with the specification: volts 120, amps 8.9, watts 1060, hz 50/60, phase-1. Annealing temperature and time were strictly maintained to observe their influence on the microstructure.

3.2.3 Mechanical Property Determination: Microhardness Testing

Hardness of a material indicates the microstructure change of a material. If the hardness goes down, that could be an indication of recovery, recrystallization and grain growth of the materials. Vickers hardness value was determined for the hardness value of materials. Microhardness tester with the model number AMH43 Automatic Micro/ Macro Indentation was used to find out this Vickers hardness value. Amount of force chosen for the indentation was 300-gram force and dwell time for the indentation was 13 seconds. Software Amh43-1.71 was used to draw the pattern along the radial direction where three sets of data were collected to find the average Vickers hardness value with standard deviation.

3.2.4 Characterization Methods

3.2.4.1 Scanning Electron Microscope

Scanning electron microscopy was carried out through JEOL JSM 6610 LV. Bulk samples were put inside the vacuum chamber after being polished. All samples were coated with carbon to overcome the charging due to the presence of epoxy around the mounted sample. The layer was of very small thickness. It is just thick enough to eliminate charging.

Several modes were used during SEM data collection. Secondary electron imaging mode was used to take the images of bulk samples. Back scattering mode was leveraged to observe different phases within the microstructure. Different contrast in the image shows different phases present in the bulk material. Energy dispersive spectroscopy (EDS) was used to find out chemical composition of the bulk material. The Oxford Aztec software was used for all SEM EDS analysis. TSL OIM was used to analyze data from the SEM back scattering images.

3.2.4.2 Transmission Electron Microscope (TEM)

TEM used for this experiment is with the model number Tecnai TF30-FED STwin STEM. Dual focused ion beam (FIB) at the Microscopy and Characterization Suits (MaCS) at CAES was used to prepare the TEM lamella. The FIB used here was of the model number Quanta 3D FEG (maker: FEI from Portland, OR). The advantage of using FIB techniques over ion milling or jet polishing is that it can be useful to lift out the sample from the interesting regions like grain boundaries or precipitates. Before that samples are polished very carefully and put inside the vacuum chamber of FIB. Back scattering mode can be used to look into the different phases to find out interesting regions for TEM lamella. When the lamella is done it is put in a desiccator to preserve it in a vacuum to avoid contamination.

Sample and beam alignment were done very carefully to obtain TEM images. Images were taken throughout the sample to determine the grain size. Image J software was used for this purpose. High resolution TEM (HRTEM) images were also obtained. Objective apertures were used to include contrast within the image. Objective aperture was removed during taking diffraction image. These diffraction images were associated with the other TEM images and HRTEM images to get the microstructural morphology. Inverse fast furrier transformation (IFFT) was used in Digital Micrograph software to find out dislocation density of the materials.

Scanning transmission electron microscope (STEM) mode was used to do energy dispersive spectroscopy (EDS) from the interesting regions. Point scans and line scans were taken. Line scan is especially helpful to get chemical composition along a line, which can indicate the change in

chemical composition in grain boundaries. EDS mapping is also done on interesting regions to get chemical composition in that particular area.

Software James was used to do diffraction pattern indexing. Both converge beam electron diffraction and selected area diffraction can be indexed with this software. Pearson's Database is used to get crystallographic information of materials. Interesting regions are tried to be determined morphologically by combining the diffraction indexing, HRTEM, chemical composition from EDS scanning alltogether.

3.2.4.3 X-Ray Diffraction (XRD)

X-ray diffraction was performed on the sample in Rigaku Smartlab Diffractometer with Cu- α radiation. Bragg-Brentano focusing was used with the D/tex detector for collecting the spectrum. For general measurement the following parameters were used: Speed duration time 4.0 degree/ minute, step size 0.012-degree, voltage 40 kv, current 44 mA. Slit with a size of 2.0 mm and kbeta filter method were used. Volume fraction of α -ferrite was found out from the following equation [119, 120]:

$$V_{\alpha} = \frac{I_{\alpha}}{I_{\alpha} + 1.4I_{\gamma}}$$

Where I_{γ} and I_{α} are the average integrated intensity obtained from the austenite and ferrite peaks respectively. Full-width half-maximum (FWHM) of peaks was obtained as a measure of peak broadening. The true peak broadening was calculated from the equation $B = \sqrt{b^2}_{\rm obs} - b^2_{\rm inst}$ for Gaussian distribution and $B = b_{\rm obs} - b_{\rm inst}$ was used for Lorentzian distribution, where $b_{\rm obs}$ is the observed peak and $b_{\rm inst}$ is the instrumental broadening. Williamson-Hall plot is generated from the collected peaks of XRD scanning. Crystalline size,

macrostrain and dislocation density were calculated from the curve of this plot.

Chapter 4: Results and Discussion

4.1 Pre-irradiation Characterization

Pre-irradiation characterization includes Vickers hardness value determination, X-ray diffraction analysis and transmission electron microscope observation.



4.1.1 Initial Hardness After SPD Process

Fig 6: Hardness Value (Before and After SPD)

Vickers hardness value was measured after the SPD processing using microhardness tester. It can be seen that the hardness value and yield strength of the materials almost doubled after ECAP and almost tripled after HPT compared to the coarse-grained materials. The Vickers hardness value of HPT and ECAP are ~540 and ~350 respectively while the coarse-grained steel has a hardness value of ~180. As a conclusion, it can be said that the both ECAP and HPT processes were highly effective in increasing the mechanical properties of the materials. The reason behind this hardness and yield stress increase can be assumed as a result of grain refinement through the ECAP and HPT processes. From the Hall-Patch relationship, it is known that the smaller the grain size the higher the yield strength. Also, it can be assumed that the SPD processes introduced a lot of dislocation within microstructure. This is responsible for dislocation strengthening. Hardness value can be used as a tool to predict the microstructure change. Other than the Hall-Patch strengthening and dislocation strengthening, another reason for the increase of hardness can be caused by the formation of precipitates and secondary phase particles. Another important thing that can be seen here is the difference in hardness value of ECAP 304 and ECAP 316. The reason behind this could be the difference of processing temperature. ECAP 304 was processed at 450°C while ECAP 316 was processed at 380°C. Therefore, it can be also assumed that initial processing parameters influence the grain refinement process in the materials.

4.1.2 X-Ray Diffraction (XRD)

XRD scans were conducted on coarse-grained, ECAP and HPT processed steels. The scans are presented in the figure 7. More peak broadening can be observed in HPT 304 compared to the coarse-grained (CG) 304. The reason behind this could be the higher strains present within the microstructure. Same trend is also present in HPT 316. Higher strains are responsible for grain refinement. ECAP 304 has significant texture present within the microstructure when compared to the CG 304. There is a very strong austenite (γ) 220 peak present here. No such trend is present in ECAP 316, as γ -220 peak present here is less significant. Another very important data that can be interpreted from the XRD scans is that there is no phase change in 316 steels. All of the peaks

correspond with the austenite peaks. There is a presence of martensite phase in the 304 steels. No martensite peak was found in 316 steels.



Williamson-Hall plot was generated from the XRD scans. This is shown in the figure 8. Williamson-Hall plot is especially helpful for calculating micro strain and crystalline size of the microstructure. For 304 steel the micro strain found for CG, ECAP and HPT are 0.12, 0.24 and 0.29 respectively. For 316 steel the micro strain found for CG, ECAP and HPT are 0.12, 0.16 and 0.47 respectively. For 304 steel the crystalline size found for CG, ECAP and HPT are 152, 125 and 26 nm respectively. For 316 steel the crystalline size found for CG, ECAP and HPT are 274, 98 and 53 nm respectively. Dislocation density was also calculated from the Williamson-Hall plot for both the steels. For 304 steel, the dislocation density found for CG, ECAP and HPT samples are 1.1*10^(14), 3.9*10^(14) and 1.5*10^(15) per square meter respectively. For 316 steel, the dislocation density found for CG, ECAP and HPT samples are 6.0*10^(13), 2.2*10^(14) and 1.2*10^(15) per square meter respectively. Micro strain, crystalline size and dislocation density of 304 and 316 steels are summarized in the table 3. As we can see from the table, HPT 316 has the highest strain and also the highest dislocation density compared to other samples. ECAP 316 has the least strains and dislocation density among the SPD processed steels. In general HPT samples have smaller crystalline size, higher strains and higher dislocation density compared to other samples.



Table 3: Willamson-Hall Plot Summary

			Dislocation
Sample	Strain (%)	Size (nm)	
			ρ (m^-2)
HPT 316	0.47	53	1.2 x 10^15
HPT 304	0.29	26	1.5 x 10^15
ECAP 304	0.24	125	3.9 x 10^14
ECAP 316	0.16	98	2.2 x 10^14
CG 316	0.12	274	6.0 x 10^13
CG 304	0.12	152	1.1 x 10^14

4.1.3 Transmission Electron Microscope (TEM)

4.1.3.1 ECAP 304

Figure 9 shows the grain structure of ECAP 304. A lot of dislocation networks and cells can be observed from this. The existence of a lot of dislocation cells and possibly very low angle grain boundaries make it harder to estimate the grain size from TEM images.



Secondary phases could be observed from the TEM images. In fig 10, (b) is the selected area electron diffraction pattern from the circular portion of (a). Diffraction pattern indexing indicates the presence of Martensite and M₂₃C₆ phases present within the microstructure. Also, another notable thing here is the rings of the diffraction pattern. The rings are not full, which could be an indication of the presence of texture within the microstructure. From (c) and (d), high resolution TEM (HRTEM) image was obtained. Inverse Fast Fourier transformation (IFFT) was conducted on this and d-spacing found out of here too large to be from iron structure. Normally carbides have such big d-spacing.



4.1.3.2 HPT 304

Microstructure of HPT 304 was observed through TEM. Figure 11 is showing the microstructure of HPT 304. Compared to the ECAP 304, it has more defined grain boundaries. The grain boundaries are more equiaxed in HPT 304. There are less dislocation cells and it appears to have more high angle grain boundaries compared to ECAP 304.

Figure 12 shows the presence of martensite in HPT 304. Selected area diffraction pattern (b) has been collected from the circular area shown in (a). The main phase present here is austenite. But the presence of Martensite in the microstructure is also noticeable. A bright field image of HPT 304 microstructure is shown in image (c). Converge beam electron diffraction (CBED) of the circular portion of (c) is shown (d). The zone axis here is [111]. It corresponds with the martensitic structure.





Figure 13 shows the presence of Ti precipitates within the microstructure. In (a) the bright field image of Ti₂C is shown. The size is also determined of this particular particle. The circular area in (a) is the area chosen for selected area diffraction pattern which is shown in (b). From SAED, the pattern also corresponds with the Ti₂C spot. STEM images were also obtained for this particular potion, which is presented in (c). This STEM image including the two EDS point scan location of same particle indicates the stoichiometry of Ti₂C. (d) is the bright field image of another Ti₂C particle. STEM image of this particular spot from (d) is shown in (e) with the annotation of EDS points. A large selected area diffraction pattern is collected from this area. This is shown in (f) where it can be seen that the primary structure is austenite.



4.1.3.3 ECAP 316



Figure 14 has the TEM micrograph of the ECAP 316 steel. There is presence of dislocation cells and networks within the microstructure. The grain boundaries are not as defined as the HPT materials. A lot of the dislocation cells make it harder to estimate the grain size for this material.





Figure 16 shows the TEM and STEM micrograph ins (a) and (b) respectively. Corresponding EDS scans are shown in (c). Uniform composition is noticeable in this region. The whole region mainly includes iron, chromium and nickel. HRTEM is shown in (d) while (e) corresponds to the IFFT. D-spacing calculated from here shows 1.86 Å which corresponds with Austenite (220). Figure 16 also shows the composition of ECAP 316. Here the EDS scans from the marked points corresponds with the primary phase Fe(Cr, Ni). No other secondary phases were seen here. This might be an indication that other precipitates and secondary phases have lower density in ECAP processed materials.

4.1.3.4 HPT 316

Microstructure of HPT 316 was observed through TEM. Figure 17 is showing the microstructure of HPT 316. Compared to the other ECAP samples, it has more defined grain boundaries. The

grain boundaries are more equiaxed in HPT 316. There are less dislocation networks and it appears to have more high angle grain boundaries.





On figure 18 both elongated and equiaxed grains of HPT 316 were observed. (a) shows the elongated grain region. (b) is the converged beam electron diffraction pattern from the smaller circular portion showen in (a). The zone axis here is [111]. Indexing of the diffraction pattern shows austenitic structure. Selected area diffraction pattern is also collected from the larger circular portion shown in (a). Indexing of this selected area diffraction pattern also shows austenitic structure. On the figure (d), small equiaxed grain is observed. Converge beam electron diffraction and selected area electron diffraction is taken from the smaller and larger ring respectively and are presented in (e) and (f) respectively. From (e) the CBED shows austenitic FCC structure. The presence of cementite is observed in SAED rings. This might be an indication that the smaller equiaxed grains have cementite.



Figure 19, (a) shows another equiaxed grain of HPT 316. Both CBED and SAED are taken from (a) which are shown in (b) and (c) respectively. CBED shows BCC structure with [001] zone axis. SAED shows the rings which corresponds to the presence of carbides. (d) is a chromium rich region. HRTEM is taken from this region and that is presented in (e). d-spacing here is 2.3 Å which corresponds with the Cr. SAED of this area shows the presences of carbides. The bulk matrix is austenite.

In figure 20, the EDS scans show the presence of chromium in the microstructure. From SAED analysis, this area is found to be rich in carbides. So, it can be assumed that here the area has a lot of chromium carbide precipitates.



					Atom	nic %				
										Phase
#	Fe	Cr	Ni	Мо	Si	Mn	Cu	V	w	Composition
1	31.95	61.47				4.83	2.98			Cr(Fe)
2	65.74	19.44	11.86				2.98			Fe(Cr, Ni)
3	10.94	78.02	1.67		0.96	3.19	3.63	0.89		Cr(Fe)
4	2	69.91			0.73	25.1	2.24			Cr
5	4	92.51	0.25		0.4		2.59		0.09	Cr
6	66.32	29.15	1.3				2.94	0.56		Fe(Cr)
7	77.5	17.8			0.88	0.26	3.13			Fe(Cr)
8	16.94	3.09	0.24		79.22					Si(Fe)
9	3.38	93.22			0.45		2.92			Ċr
10	3.21	93.47	0.13				3	0.02		Cr
11	3.22	93.26					2.97	0.36		Cr
12	73.62	16.01	7.46	0.72	0.4		1.58			Fe (Cr, Ni)
13	69.89	14.42	12.16		0.32		3.18			Fe (Cr, Ni)

Fig 20: Presence of Chromium in HPT 316

4.1.3.5 TEM Grain Size Measurement

Grain size is measured from the TEM images. The grain size analysis summary is presented in figure 21. In general, the HPT samples have lower grain size than the ECAP ones. HPT 304 has a grain diameter of 155nm with a standard deviation of 59nm while HPT 316 has a grain diameter of 135nm with a standard deviation of 74nm. On the other hand, ECAP 304 has a grain diameter of 281.3nm with a standard deviation of 85.42nm while ECAP 316 has a grain diameter of 394.2nm with 92.77nm standard deviation. Both HPT samples have similar grain size. But ECAP 316 seems to have bigger grain size than ECAP 304. Different processing temperature may have influence on different grain size. However, from the hardness value, we saw that ECAP 316 has higher hardness than ECAP 304. It is possible that the dislocation density of ECAP 316 is higher than ECAP 304 and for that reason, the dislocation strengthening caused higher hardness in ECAP 316. However, it is to be noted that the dislocation density found in XRD measurement showed ECAP 304 has higher dislocation density compared to ECAP 316.



From the above TEM observation, it can be interpreted that the grain refinement process through SPD was successful. The grain size was reduced with the introduction of a dislocation density. Strain introduced by the HPT and ECAP process is responsible for reducing the grain size and introducing the dislocations within microstructure. For the ECAP process, after one pass there is a lot of shear bands introduced in one direction. Since the path used here during ECAP process was B_c route, the material was rotated 90 degree in every subsequent pass and as a result in every subsequent pass, the shear band was formed in a 90 degree rotation. These shear bands intersect one another, and these intersecting points act as nucleation sites for new grains. As it

was observed from the TEM images, there was a lot of dislocation cells and dislocation network introduced within the ECAP processed materials. For the HPT process, rotational recrystallization occurs and dislocation rearrange themselves into elongated dislocation cells. As the deformation process carried on, the dislocation cells became elongated. Eventually, these elongated cells break up into smaller equiaxed grains. The breakdown of sub-grains into an equiaxed microcrystalline structure can occur by minor rotation of the grain boundaries lying along the original elongated boundaries.

Both grain size reduction and dislocation density enhance the mechanical properties of materials. The smaller the grain size the less the pileup and the higher stress required to penetrate the boundary, so the yield stress of the material increases. Also, when there is a lot of dislocation within the microstructure, that dislocation loop itself act as a barrier to dislocation motion, making the materials stronger. Also, from TEM images a lot of non-equilibrium grain boundary is observed. Presence of non-equilibrium grain boundary is known to increase the ductility of the material [68]. On the other hand, SPD process sometimes introduces porosity and crack within materials, which can be detrimental for the ductility. Due to increase of grain boundary volume, creep can be a potential problem for SPD process materials. More grain boundary volume will have a positive influence on Coble creep. But as it was observed, with the SPD process there has been introduction of precipitated and secondary phase particles, which are known to pin down the grain boundary and increase the creep resistance. Also, neutron irradiation on these materials is going to introduce a lot more precipitates as it was observed in various previous studies. This is going to help in pinning down the grain boundary and increase the creep resistance of the materials.

4.2 Thermal Stability

Thermal stability determination is a very important aspect for the SPD processed materials. The main reason for SPD process is to enhance the mechanical properties of materials. But as the materials go through SPD process, better mechanical properties are resulted but at the same time, there is a lot of strain energy introduced within microstructure. The more strain energy stored within the materials, the more drive it has to release that extra energy to go back to lower energy state which often results in the annihilation of dislocations, recovery, recrystallization and finally grain growth. It has to be made sure that the SPD processed materials do not lose their thermal stability in the real life working conditions.

When subjected to higher temperature, a few microstructure changes occur within materials. A lot of the time higher temperature is associated with the introduction of precipitates and secondary phase particles. These precipitates and secondary phase particles are favorable in keeping the materials thermally stable. Often times they pin down the grain boundary so the grain growth is resisted. Introduction of precipitates and secondary phase particles are helpful in enhancing the mechanical properties of materials. The hardness value and yield strength of the material are increased with precipitates and secondary phase particles. On the other hand, when extra energy is added to the materials through higher temperature, diffusion within material is increased. The result is the annihilation of dislocation while a positive and negative dislocation meet and annihilate themselves. This is the recovery process. With the recovery process in progress, materials start to lose it hardness and yield strength as the dislocation strengthening is

no longer in play. As the temperature is further increased, nucleation of new grains is initiated, and recrystallization starts to occur which result in strain free new grains. With further increase of temperature, grain growth starts to occur, and all the good mechanical property resulted from SPD process is eliminated.

Here hardness value is determined after head treatment/ annealing to find out the thermal stability of the ECAP and HPT processed materials.

4.2.1 ECAP 304

The hardness value of ECAP 304 is shown in figure 22 with time at different temperature. As it can be seen here, for 500°C and 600°C the hardness increased slightly compared to the unannealed samples. So, it can be assumed that there is formation of precipitates and secondary phase particles while annealed at 500°C and 600°C. Time does not have any significant impact in these temperatures. But at 700°C the hardness value dropped. The reason behind this could be recovery, recrystallization and grain growth that occur at this temperature.



As it can be seen in figure 23, Hardness value of ECAP 304 drops at 700°C. The amount of time during the annealing has some effect on the materials. It can be seen that as the time increases the hardness value goes down. It keeps on happening up to 24 hours. After this, time does not have a significant effect on hardness change. So, it can be assumed that after 24 hours at 700°C the recrystallization and grain growth saturate. From this annealing experiment, the thermal stability can be determined. Up to 600°C ECAP 304 is thermally stable. After this temperature, it is no longer stable and after 24 hours at 700°C recrystallization and grain growth saturates.



4.2.2 ECAP 316

The hardness value of ECAP 316 is shown in figure 24 with time at different temperature. As it can be seen here, for 500°C and 600°C the hardness increased a little bit compared to the unannealed samples. So, it can be assumed that there is formation of precipitates and secondary phase particles while annealed at 500°C and 600°C. Time does not have any significant impact in these temperatures. But at 700°C the hardness value dropped. The reason behind this could be recovery, recrystallization and grain growth that occur at this temperature.



As it can be seen in figure 24, hardness value of ECAP 316 drops at 700°C. The amount of time during the annealing has a great effect on the materials. It can be seen that as the time increases the hardness value goes down. It keeps on happening up to 72 hours. After this time the hardness value was still going down. So, the recrystallization and grain growth process are still in play and do not reach saturation after 72 hours. From this annealing experiment, the thermal stability is determined. Up to 600°C ECAP 316 is thermally stable. After this temperature ECAP 316 is no longer stable and at 700°C the recrystallization and grain growth process are still active.


4.2.3 HPT 304

In figure 22, the hardness value of HPT 304 is summarized. At 500°C the hardness value increased a little bit compared to the unannealed sample. Formation of precipitates and secondary phase particles could be responsible for this. At 550°C the hardness value decreased slightly. So, it can be assumed that at this temperature recovery occurs and it brings down the dislocation density through recovery so that dislocation strengthening resulted from HPT processing is no longer in play. But recrystallization and grain growth may not be occurring yet as the hardness value is still very close to the unannealed sample. Time has some impact at 550°C as the hardness value is the lowest after 24 hours at this temperature.



Figure 27 summarizes the hardness value of HPT 304 at 600°C with time. As it can be seen here, hardness value dropped significantly after 600°C. So, there might be significant amount of

recrystallization and grain growth are occurring at this temperature. Time also has a significant effect on hardness value at this temperature. With the increment of time, the hardness value tends to go down. And after 24 hours, the hardness value is still going down. So, the recrystallization and grain growth process do not saturate at this temperature. From this, the thermal stability is also determined. HPT 304 is fully stable thermally at 500°C. It is also stable 550°C but there is some form of recovery occurring at this temperature. But it completely loses thermal stability at 600°C.



4.2.4 HPT 316

The hardness value of HPT 316 is shown in figure 28 with time at different temperature. As it can be seen here, for 500°C and 600°C the hardness increased a little bit compared to the unannealed samples. So, it can be assumed that there is formation of precipitates and secondary phase particles while annealed at 500°C and 600°C. Time does not have any significant impact in these temperatures. But at 700°C the hardness value dropped. The reason behind this could be recovery, recrystallization and grain growth that occur at this temperature.



Figure 29 summarizes the hardness value of HPT 316 at 700°C with time. As it can be seen here, hardness value dropped significantly after 700°C. So, there might be significant amount of recrystallization and grain growth are occurring at this temperature. Time does not have a significant effect on hardness value at this temperature. With the increment of time, the

hardness value tends to remain same. So, the recrystallization and grain growth process might be saturated at this temperature. From this, the thermal stability is also determined. HPT 304 is fully stable thermally up to 600°C. But it completely loses thermal stability at 700°C.



Chapter 5: Conclusion

An attempt has been made to do pre-irradiation characterization and thermal stability determination of stainless steel 304 and 316 which have been processed through high pressure torsion and equal channel angular pressing techniques.

Initial characterization shows that the severe plastic deformation techniques of HPT and ECAP were successful for grain refinement and the grain boundary volume increased significantly compared to the coarse-grained sample. This could be observed directly from the initial hardness value and estimated yield stress value after SPD processing. Due to grain refinement, Hall-Patch strengthening occurred. At the same time, due to the introduction of lot of dislocation, dislocation strengthening impart a significant effect on hardness value and yield strength.

XRD characterization showed peak broadening in HPT 304 compared to CG 304 while texture was found in ECAP 304 as an austenite 220 peak. No such peaks or texture was found in 316 samples. However, the peak broadening is evident in HPT 316 samples compared to the CG and ECAP 316 samples. Williamson-Hall graph showed similar pattern for both 304 and 316 steels. Crystalline size is smallest while microstrain and dislocation density is highest in HPT samples compared to ECAP and CG samples for both 304 and 316 steels. ECAP samples have smaller crystalline size, higher dislocation density and microstrain compared to CG samples for both the 304 and 316 steels.

TEM characterization showed a lot of dislocations cell and network in ECAP samples for both the steels while HPT samples have relatively defined grain structure which included both equiaxed and elongated grains. Secondary phases like martensite and carbides were found in ECAP 304.

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HPT 304 had some martensite and Ti precipitates in its microstructure. ECAP 316 microstructure was very homogenized and initial TEM analysis did not find any other phases, which might be an indication that the amount of precipitates and secondary phase particles have very low density within the structure. HPT 304 had a very austenitic structure in elongated grains while in equiaxed grains some precipitates with larger d-spacing were found which could be carbides. EDS scans showed some Cr rich regions which could be an indication of chromium carbide formation. Grain size is also measured from TEM images. HPT samples had smaller grain size with 135nm and 155 nm average grain size for 316 and 304 steels respectively while ECAP samples had an average grain size of 394nm and 281nm for 316 and 304 steels respectively. So, ECAP and HPT process both were successful in grain refining.

Thermal stability was determined for both ECAP and HPT steels. ECAP 304 is stable up to 600°C but it loses it stability at 700°C. Grain growth and recrystallization saturate after 24 hour of annealing at 700°C.

ECAP 316 is also thermally stable up to 600°C and it loses its stability at 700°C. For ECAP 316 stainless steel, the recrystallization and grain growth process do not reach saturation even after 72 hours of annealing at 700°C.

HPT 304 has thermal stability up to 500°C and recovery starts to occur significantly after 550°C. It completely loses its stability after 600°C. Annealing up to 24 hours at 600°C does not saturate the materials for recrystallization and grain growth as the hardness in this temperature still had a negative slope after 24 hours.

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HPT 316 has thermal stability up to 600°C. It completely loses its stability at 700°C. Recrystallization and grain growth seem to be saturated after annealing at 700°C and time does not have a significant influence on changing the hardness value of the sample.



Chapter 6: Future Work

More pre-irradiation characterization through TEM, SEM and XRD is needed to look into microstructure evolution of SPD processed steels in order to find out microstructure changes as the materials are subjected to higher temperature for prolonged period of time. Once the pre-

irradiation characterization is done, the materials will be put into Advanced Test Reactor at Idaho National Laboratory for neutron irradiation. The capsules for holding the materials are already manufactured and a schematic of the setup is shown in the figure 30.

Specific dimensions are required for the materials to be put inside this capsule. These materials are already machined through wire electrical discharge machining (EDM) at Wirecut Co. in California to attain the specific dimension for the capsules. Once the setup is complete, these materials will be irradiated at ATR in four different capsules for two different temperatures and two different DPAs (displacement per atom). Capsule 1 will be irradiated at 300°C to 2 DPA. Capsule 2 will be irradiated at 300°C to 6 DPA. Capsule 3 will be irradiated at 500°C to 2 DPA and Capsule 4 will be irradiated at 500°C to 6 DPA. Melt wire and SiC will be used to monitor the temperature and flux wire will be used to monitor the fluxes. Neutron irradiation takes much longer time to attain the required DPA compared to the ion irradiation. Once the required DPA is attained, the materials will be characterized again through TEM, SEM, XRD and atom probe tomography. It will be compared to the pre-irradiated characterization and conclusion will be made on how severe plastic deformation through high pressure torsion and equal channel angular pressing can enhance the mechanical property of the materials to tolerate the irradiation and how these SPD steels can be deployed in real life nuclear reactors.

Reference

- 1 Rui Guo, Yifu Shen, Guoqiang Huang, Wei Zhang & Wei Guan; Journal of Adhesion Science and Technology, ISSN: 0169-4243 (Print) 1568-5616.
- 2 Committee AIH, Davis JR, Abel LA. Properties and selection: irons, steels, and highperformance alloys. Vol. 1, Metals Handbook. Ohio (OH): ASM International; 1990.

- 3 Ben Young, "Experimental and numerical investigation of high strength stainless steel structures", Journal of Constructional Steel Research 64 (2008) 1225-1230.
- 4 Minakshi Vaghani, Dr. S.A. Vasanwala, Dr. A.K. Desai Journal of Engineering Research and Applications ISSN : 2248-9622, Vol. 4, Issue 3(Version 1).
- 5 Baldev Raja, U. Kamachi Mudalib, M. Vijayalakshmic, M.D. Mathewd, A.K. Bhadurie, P. Chellapandif, S. Venugopalg, C.S. Sundarh, B.P.C. Raoi, B. Venkataramanj; Development of Stainless Steels in Nuclear Industry: with Emphasis on Sodium Cooled Fast Spectrum Reactors: History, Technology and Foresight.
- 6 Was, G. S. (2017); Fundamentals of radiation materials science: metals and alloys. New York: Springer.
- 7 S. J. Zinkle (2016); Advanced irradiation-resistant materials for Generation IV nuclear reactors.
- 8 M.A. Meyers, A. Mishra, D.J. Benson; Progress in Materials Science 51 (2006) 427–556.
- 9 Sun C, et al., Metall Mater Trans A 44 (2013) 1966.
- 10 Hall EO. Proc Phys Soc B 1951;64:747.
- 11 Petch NJ. J Iron Steel Inst 1953;174:25.
- 12 Ashby MF. Philos Mag A 1982;46:737.
- 13 Wurschum R, Herth S, Brossmann U. Adv Eng Mater 2003;5:365–72.
- 14 Sun C, et al., Scientific Reports 5 (2015) 7801.
- 15 Gleiter H. Prog Mater Sci 1989;33:223.
- 16 Yang NYC, Headley TJ, Kelly JJ, Hruby JM. Scripta Mat, this issue (same view point set).
- 17 Suryanarayana C, editor. Non-equilibrium processing of materials. Amsterdam: Pergamon; 1999.
- 18 Valiev RZ, Islamgaliev RK, Alexandrov IV. Prog Mater Sci 2000;45:103.
- 19 Segal VM. Mater Sci Eng A2002;338:331.
- 20 Jiang H, Zhu YT, Butt DP, Alexandrov IV, Lowe TC. Mater Sci Eng A2000;290:128.
- 21 Zhilyaev AP, Nurislamova GV, Kim B-K, Baro MD, Szpunar JA, Langdon TG. Acta Mater 2003;51:753.
- 22 Saito Y, Tsuji N, Utsunomiya H, Sakai T, Hong RG. ScriptaMater 1998;39:1221.
- 23 Tsuji N, Salto Y, Utsunomiya H, Tanigawa S. Scripta Mater 1999;40:795.
- 24 Huang JY, Zhu YT, Jiang H, Lowe TC. Acta Mater 2001;49:1497.
- 25 Zhu YT, Jiang H, Huang J, Lowe TC. Metall Mater Trans A 2001;32:1559.
- 26 Mishra RS, Mahoney MW, McFadden SX, Mara NA, Mukherjee AK. Scripta Mater 1999;42:163.
- 27 Su J-Q, Nelson TW, Sterling CJ. J Mater Res 2003;18:1757.

- 28 Y. Iwahashi, J. Wang, Z. Horita, M. Nemoto, T.G. Langdon, Scr. Mater. 35 (1996) 143-146.
- 29 R Kapoor, Chapter 20: Severe Plastic Deformation of Materials.
- 30 P.B. Berbon, M. Furukawa, Z. Horita, M. Nemoto, T.G. Langdon, Metall. Mater. Trans. A 30 (1999) 1989-1997.
- 31 V. Sklenicka, J. Dvorak, M. Svoboda, P. Kral, M. Kvapilova, Equal-channel angular pressing and creep in ultrafine-grained aluminium and its alloys, in: Z. Ahmad (Ed.), Aluminium Alloys e New Trends in Fabrication and Applications, InTech, 2013, http://dx.doi.org/10.5772/51242.
- 32 A.P. Zhilyaev, G.V. Nurislamova, B.K. Kim, M.D. Baro[´], J.A. Szpunar, T.G. Langdon, Acta Mater. 51 (2003) 753-765.
- 33 R.Z. Valiev, R.K. Islamgaliev, I.V. Alexandrov, Prog. Mater. Sci. 45 (2000) 103-189.
- 34 R.Z. Valiev, T.G. Langdon, Prog. Mater. Sci. 51 (2006) 881 -981.
- 35 Y. Estrin, A. Vinogradov, Acta Mater. 61 (2013) 782-817.
- 36 I. Sabirov, M.Y. Murashkin, R.Z. Valiev, Mater. Sci. Eng. A 560 (2013) 1-24.
- 37 Segal, V. M., Reznikov, V. I., Drobyshevskiy, A. D. and Kopylov, V. I., Russ. Metall., 1981, 1, 99.
- 38 Segal, V. M., Mater. Sci. Engng, 1995, A197, 157.
- 39 Valiev, R. Z., Ivanisenko, Yu. V., Rauch, E. F. and Baudelet, B., Acta mater., 1996, 44, 4705.
- 40 Valiev, R. Z., Korznikov, A. V. and Mulyukov, R. R., Mater. Sci. Eng, 1993, A168, 141.
- 41 Markshev, M. V., Bampton, C. C., Murashkin, M. Yu. and Hardwick, D. A., Mater. Sci. Engng, 1997, A234–236, 927.
- 42 Berbon, P. B., Tsenev, N. K., Valiev, R. Z., Furukawa, M., Horita, Z., Nemoto, M. and Langdon, T. G., Metall. Mater. Trans., 1998, 29A, 2237.
- 43 Iwahashi, Y., Furukawa, M., Horita, Z., Nemoto, M. and Langdon, T. G., Metall. Mater. Trans., 1998, 29A, 2245.
- Valiev, R. Z., Islamgaliev, R. K., Kuzmina, N. F., Li, Y. and Langdon, T. G., Scripta mater., 1999, 40, 117.
- 45 Valiev, R. Z. and Alexandrov, I. V., Nanostruct. Mater., 1999, 12, 35.
- 46 Alexandrov, I. V. and Valiev, R. Z., Nanostruct. Mater., 1999, 12, 709.
- 47 Shin, D. H., Oh, K. H., Kim, W. J., Lee, S. W. and Choo, W. Y., J. Korean Inst. Metall. Mater., 1999,37, 1048.
- 48 Shin, D. H., Kim, W. J. and Choo, W. Y., Scripta mater., 1999, 41, 259.
- 49 Shin, D. H., Seo, C. W., Kim, J. R., Park, K.-T. and Choo, W. Y., Scripta mater., 2000, 42, 695.

- 50 Semiatin, S. L., Segal, V. M., Goforth, R. E., Frey, N. D. and DeLo, D. P., Metall. Mater. Trans., 1999, 30A, 1425.
- 51 DeLo, D. P. and Semiatin, S. L., Metall. Mater. Trans., 1999, 30A, 2473.
- 52 Furukawa, M., Ma, Y., Horita, Z., Nemoto, M., Valiev, R. Z. and Langdon, T. G., Mater. Sci. Engng, 1998, A241, 122.
- 53 Horita Z, Fujinami T, Langdon TG. Mater Sci Eng A 2001;318:34.
- 54 Valiev RZ, Stolyarov VV, Zhu YT [unpublished data].
- 55 Raabe GJ, Valiev RZ, Lowe TC, Zhu YT. Continuous processing of ultrafine grained Al by ECAPconform. Mater Sci Eng A.
- 56 Schiøtz J, Di Tolla FD, Jacobson KW. Nature 1998;391:561.
- 57 Yuntian T. Zhu, Terry C. Lowe, Terence G. Langdon. Scripta Materialia 51 (2004) 825–830.
- 58 R.Z. Valiev, et al. Acta Mater. 44 (1996) 4705.
- 59 F. Wetscher, et al. Mater. Sci. Eng. A387–389 (2004) 809.
- 60 F. Wetscher, et al. Metall. Mater. Trans. A 37A (2006) 1963.
- 61 A.P. Zhilyaev, T.G. Langdon, Prog. Mater. Sci. 53 (2008) 893-979.
- 62 L. Lu, X. Chen, X. Huang, K. Lu, Science 323 (2009) 607-610.
- 63 N. Kamikawa, X. Huang, N. Tsuji, N. Hansen, Acta Mater. 57 (2009) 4198-4208.
- 64 N. Hansen, Scr. Mater. 51 (2004) 801-806.
- 65 R. Kapoor, A. Sarkar, R. Yogi, S.K. Shekhawat, I. Samajdar, J.K. Chakravartty, Mater. Sci. Eng. A 560 (2013) 404-412.
- 66 R. Kapoor, A. Sarkar, R. Yogi, S.K. Shekhawat, I. Samajdar, J.K. Chakravartty, Mater. Sci. Eng. A 560 (2013) 404-412.
- 67 A.P. Zhilyaev, T.G. Langdon, Prog. Mater. Sci. 53 (2008) 893-979.
- 68 Valiev RZ, Alexandrov IV, Zhu YT, Lowe TC. J Mater Res 2002;17:5–8.
- 69 Zhu YT, Liao X. Nature Mater 2004;4:351.
- 70 Jia D, Wang YM, Ramesh KT, Ma E, Zhu YT, Valiev RZ. Appl Phys Lett 2001;79:611–3.
- 71 Malow TR, Koch CC, Miraglia PQ, Murty KL. Mater Sci Eng A 1998;252:36.
- 72 Gray GT, Lowe TC, Cady CM, Valiev RZ, Aleksandrov IV. Nanostruct Mater 1997;9:477–80.
- 73 Wei Q, Cheng S, Ramesh KT, Ma E. Mater Sci Eng A 2004;381:71.
- 74 May J, Ho"ppel HW, Go"ken M. Scripta Mater, in press.
- 75 Ho"ppel HW, May J, Go"ken M. Adv Eng Mat 2004;6:781.
- 76 Wang DL, Kong QP, Shui JP. Scripta Metall Mater 1994;31:47–51.
- 77 Deng J, Wang DL, Kong QP, Shui JP. Scripta Metall Mater 1995;32:349–52.
- 78 Sanders PG, Rittner M, Kiedaisch E, Weertman JR, Kung H, Lu YC. Nanostruct Mater 1997;9:433–40.

- 79 Wang N, Wang Z, Aust KT, Erb U. Mater Sci Eng A 1997;237:150–8.
- 80 Grabovetskaya GP, Ivanov KV, Kolobov YR. Ann Chim Sci Mater 2002;27:89–98.
- 81 Yamakov V, Wolf D, Phillipot SR, Gleiter H. Acta Mater 2002;50:61–73.
- 82 Estrin Y, Gottstein G, Shvindlerman LS. Scripta Mater 2004;50:993–7.
- 83 Yin WM, Whang SH, Mirshams RA. Acta Mater 2005;53:383–92.
- 84 Yan DS, Qiu HB, Zheng YS, Gao L. Nanostruct Mater 1997;9:441–50.
- 85 Vinogradov AY, Stolyarov VV, Hashimoto S, Valiev RZ. Mater Sci Eng A 2001;318:163–73.
- 86 Pelloux RM. In: Burke JJ, Weiss V, editors. Ultrafine-grain metals. Syracuse University Press; 1970. p. 231.
- 87 Chung CS, Kim JK, Kim HK, Kim WJ. Mater Sci Eng A 2002;337:39–44.
- 88 Kim HK, Choi ML, Chung CS, Shin DH. Mater Sci Eng A 2003;340:243–50.
- 89 Schino AD, Kenny JM. Mater Lett 2003;57:3182–5.
- 90 R. Z. Valiev, V. Yu. Gertsman and O. A. Kaibyshev, Phys. Status Solidi A, 97(1986) 11.
- 91 Y. Iwahashi, Z. Horito, M. Nemoto, T.G. Langdon, Metall. Mater. Trans. A 29 (1998) 2503-2510.
- 92 Y. Iwahashi, Z. Horito, M. Nemoto, T.G. Langdon, Metall. Mater. Trans. A 29 (1998) 2503-2510.
- 93 W.Q. Cao, A. Godfrey, Q. Liu, Mater. Sci. Eng. A 361 (2003) 9-14.
- 94 Y. Huang, P.B. Prangnell, Scr. Mater. 56 (2007) 333-336.
- 95 A. Mishra, B.K. Kad, F. Gregori, M.A. Meyers, Acta Mater. 55 (2007) 13-28.
- 96 M. Cabibbo, W. Blum, E. Evangelista, M.E. Kassner, M.A. Meyers, Metall. Mater. Trans. A 39 (2008) 181-189.
- 97 E.A. El-Danaf, Mater. Sci. Eng. A 487 (2008) 189-200.
- 98 I. Nikulin, Y. Motohashi, R. Kaibyshev, Mater. Sci. Forum 584-586 (2008) 691-696.
- 99 I. Saxl, A. Kalousova', L. Ilucova', V. Sklenicka, Mater. Charact. 60 (2009) 1163-1167.
- 100 M. Kawasaki, Z. Horita, T.G. Langdon, Mater. Sci. Eng. A 524 (2009) 143-150.
- 101 Laszlo S. Toth, Chengfan Gu Tutorial review: Ultrafine-grain metals by severe plastic deformation.
- 102 M.J. Zehetbauer, H.P. Stüwe, A. Vorhauer, E. Schafler, J. Kohout, Adv Eng Mater 2003:5:330-7.
- 103 Pande CS, Masumura RA, Armstrong RW. Nanostruct Mater 1993;2:323–31.
- 104 Nieh TG, Wadsworth J. Scripta Metall Mater 1991;25:955–8.
- 105 Conrad H. Met Mater Trans 2004;35A:2541.
- 106 Van Swygenhoven H, Derlet PM. Phys Rev B 2001;64.
- 107 Van Swygenhoven H, Spaczer M, Caro A. Acta Mater 1999;47:561.
- 108 Kim HS, Hong SI. Acta Mater 1999;47:2059.
- 109 Yamakov V, Wolf D, Phillpot SR, Gleiter H. Acta Mater 2003;51:4135.
- 110 Li JCM. Trans Met Soc 1963;227:239.

- 111 Gray GT. Nanostruct Mater 1997;9:477.
- 112 Murayama M, Howe JM, Hidaka H, Takaki S. Science 2002;295:2433–5.
- 113 Huang B, Perez RJ, Lavernia EJ. Mater Sci Eng A 1998;255:124.
- 114 Lu L, Shen Y, Chen X, Qian L, Lu K. Science 2004;304:422.
- 115 J. Lian, R.Z. Valiev, B. Baudelet, On the enhanced grain growth in ultrafine grained metals, Acta Metallurgica et Materialia 43 (1995) 4165- 4170.
- 116 S.C. Tjong, H. Chen, Nanocrystalline materials and coatings, Materials Science and Engineering, R45 (2004) 1-88.
- 117 C.M. Kuo, C.-S. Lin, Static recovery activation energy of pure copper at room temperature, Scripta Materialia 57 (2007) 667-670.
- 118 S. Divinski, J. Ribbe, G. Schmitz, C. Herzig, Grain boundary diffusion and segregation of Ni in Cu, Acta Materialia 55 (2007) 3337-3346.
- 119 Z.J.ZhengabY.GaoaY. Guia M.Zhu, Corros. Sci. 54 (2012) 60-67.
- 120 120. Z.J.ZhengabY.GaoaY. Guia M.Zhu, Mater. Sci. Forum 667-669 (2011) 937-942.