Microstructure evolution and mechanical properties of electroformed nano-grained nickel upon annealing

by

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Abstract

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Nano-grained nickel produced by electroforming technique was investigated for its microstructure evolution and mechanical properties upon annealing. The thermal behaviour was studied using DSC, and a major exothermic reaction and a minor endothermic reaction were detected at 320 °C and 528 °C, respectively. It was found that during low temperature annealing (<250 °C), electroformed nano-grained nickel showed scattered and isolated abnormal grain growth. A major abnormal grain growth was observed after reaching the major heat release peak at 320 °C. A secondary abnormal grain growth, featuring faceted grain boundaries, was observed at a higher annealing temperature (528 °C). A semi-in-situ observation using optical microscopy was conducted to track the movement of the faceted grain boundaries, and it was found that these boundaries were mostly stable. The mechanical properties under various annealing conditions were studies using hardness and tensile testing. The hardness was observed to decrease with increasing annealing temperature. The material became very brittle after annealing at 320 °C or higher temperatures. Fractography investigation showed that the brittleness is caused by intergranular fracture.
I would like to take this opportunity to acknowledge all those people who have supported me throughout the work. First and foremost, I wish to express my deepest gratitude to my supervisor Professor Zhirui Wang. This thesis would not have been possible without his guidance and encouragement. I would also like to show my gratitude to Dr. Zhi Mei for his helpful suggestions and technical supports during my experiments. Furthermore, I would like to extend my many thanks to my colleagues for their support and company. The material supply from Beijing University and Science and Technology is greatly appreciated. Finally, I would like to thank the University of Toronto Open Fellowship for financial support.
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1 Introduction

During the past few decades, the field of nanotechnology has attracted considering interest due to the exceptional mechanical properties provided by nanostructured materials [1]. According to the Hall-Petch relation, the strength and hardness of a material increases with finer microstructure, i.e. decreasing grain size. However, such microstructure is associated with extremely high internal energy raised from grain boundaries and triple junctions. As a consequence, the microstructure tends to evolve upon activation. Therefore, it is crucial to study the stability of nanostructured materials.

Numerous manufacturing methods have been developed to produce materials with nanostructures [2]. Some examples include powder compaction, mechanical milling, and deposition techniques. Among these techniques, electrodeposition is shown to be a cost effective methods to produce fully dense, three-dimensional nano-structured materials which are ideal for theoretical studies. Nanocrystalline nickel produced by electrodeposition has been found to exhibit excellent strength and corrosion properties. Its thermal stability and microstructure evolution have been systematically investigated by a number of researchers. The mechanical properties obtained for nanocrystalline nickel were mainly based on hardness measurements. This is due to the limitation of the electrodeposition technique in producing thick samples. Electroforming, on the other hand, is a well developed process in producing free-standing articles. In the present study, it has been employed to produce nanocrystalline nickel having an approximate thickness of 1.5 mm. The objectives of this study are listed as follows:

1. To find out the thermal stability and microstructure evolution of electroformed nano-grained nickel upon annealing.
2. To find out the mechanical properties using conventional tensile and hardness testing.

Background knowledge on nanocrystalline materials, electroforming technique, and up-to-date thermal stability and mechanical properties of nanocrystalline nickel will be provided in detail in Chapter 1. The material used in the present study and experimental procedures will be introduced in Chapter 2. Results will be presented in Chapter 3, followed by discussions in Chapter 4. Chapter 5 summarizes the key findings, and Chapter 6 suggests possible future works.
1.1 Nanocrystalline Materials

1.1.1 Definition

Nanocrystalline materials belong to a new class of disordered solid generated by introducing a high density of defects such as grain boundaries, interphase boundaries, and dislocations [3]. Depending on the type of defects, nanocrystalline materials with different structures may be produced. By far, the most common nanocrystalline materials are obtained through introducing a high density of grain boundaries (Figure 1.1). Nevertheless, all nanocrystalline materials exhibit the following common features: their atomic domains are spatially confined to less than 100 nm and a large fraction of atoms (50% or more) are situated within the defected regions [3]. The crystalline lattice surrounding these defects is highly distorted, hence contains a significant amount of elastic strain. Upon thermal and/or mechanical activation, grain growth in a nanocrystalline material can easily occur, transforming into conventional polycrystalline materials with lowered internal strain.

*Figure 1.1. Atomic structure of a two-dimensional nanocrystalline material [3]. White open circles represent atoms associated with interphase regions i.e. grain boundaries, whereas black circles represent atoms within perfect crystalline lattices. For nanocrystalline materials, atoms from the interphase region occupy a large percentage of the whole.*
1.1.2 Classification of Nanocrystalline Materials

Depending on the fabrication technique, nanocrystalline materials with different geometrical forms can be produced. They can be classified into four categories based on the dimensionality of the structural elements that the materials possess [4]. Zero-dimensional nanocrystalline material refers to clusters and powders; one-dimensional refer to fibrous materials such as nanotubes and whiskers; two-dimensional nanocrystalline materials are films and layers; and three-dimensional materials are polycrystalline with nanometre-scaled grains (Figure 1.2). In order to investigate the fundamental structure and properties of nanocrystalline materials, three-dimensional bulk specimens are required. The following section will focus on the fabrication techniques of bulk nanocrystalline materials only.

*Fig. 1.2. Schematic illustration of the dimensionality of nanocrystalline materials [4]. The four categories are: zero-dimensional nanocrystalline powders; one-dimensional nanotubes; two-dimensional layers; and three-dimensional polycrystalline material.*
1.1.3 Fabrication of Bulk Nanocrystalline Materials

A number of fabrication techniques have been developed to produce bulk nanocrystalline materials. Based on the processing conditions, these techniques can be classified into four main classes: powder compaction, severe plastic deformation, crystallization from amorphous state, and deposition of films and coatings [5]. The chemistry and processes behind each method will be briefly discussed in the following section.

1.1.3.1 Powder Compaction

Up to the early 1990’s, most of the nanocrystalline materials were produced by consolidation and sintering of nanocrystalline particles. A detailed review on such synthesis methods were thoroughly discussed by Gleiter [3]. In general, precursor nanocrystalline particles were first synthesized and then compacted to form the bulk material. A large number of methods exist for the production of nanocrystalline particles. Some examples of these techniques are plasma chemical, precipitation from colloid solutions, and mechanical milling. The main concern with powder compaction method is the porosity of the final bulk material. During compaction, both pressure and temperature are needed in order to obtain a fully dense material. The sintering time and temperature are crucial operating conditions. Relatively high temperatures and longer times results in grain growth, while lower temperatures and shorter times lead to low densities of bulk materials. In addition, the initial size of nanoparticles also plays an important role in determining the properties of the final bulk. On the whole, it has been shown that powder compaction is a promising technique in producing nano-ceramics having densities up to 98% [5].

1.1.3.2 Severe Plastic Deformation

Severe plastic deformation refers to the class of fabrication techniques that produce nanocrystalline materials by means of plastic deformation often under high pressure and relatively low temperatures [6]. The most common methods of severe plastic deformation are Equal Channel Angular Pressing (ECAP) and severe torsion straining under high pressure, though other methods such as Accumulative Roll Bonding (ARB) have also been used. Only materials with certain potential to plastic deformation can be manufactured using these methods.
Hence they are often limited to producing metals and alloys. The basic mechanisms behind these techniques are to increase the dislocation density within the original material through intense plastic deformation. In order to reduce the strain field associated with dislocation structure, they recover into cell wall structures and deformation shear bands. Through room temperature recovery-recrystallization, these microstructures can further transform into low-angle and high-angle grain boundaries [7]. A large number of elemental and alloy systems (nickel, copper, aluminum, and magnesium) have been produced by severe plastic deformation methods. It has been shown that the grain sizes of these bulk systems are in the order of 100 nm.

*Figure 1.3 Severe plastic deformation techniques used to produce nanocrystalline materials [6]. (a) Severe torsion under high pressure. (b) ECAP produces billets under pure shear.*

1.1.3.3 Crystallization of Amorphous Alloys

Crystallization of amorphous alloys has been shown to be a promising technique for the manufacturing of certain alloys. A number of alloys such as Ni-P, intermetallic NiAl, iron based ferromagnetic alloys have been successfully produced [5]. In general, this method employs controlled crystallization of alloys from the amorphous state. The amorphous alloys are often produced by a rapid cooling process known as melt spinning. Then, the amorphous alloy is heat
treated under conditions that maximize crystallization rate and minimize grain growth. In some cases, it was shown that preliminary deformation by rolling and low-temperature annealing could enable a reduction in grain size [5].

1.1.3.4 Deposition of Film and Coating

Deposition can be used to produce continuous and porosity-free bulk nanocrystalline materials. It is commonly used to produce coatings. However, by controlling the thickness of deposit, free-standing bulk materials can be produced by stripping away the substrate. During deposition, layers of nanoparticles form directly and continuously on the surface of a substrate by means of electrolytic or vapour processes [4, 5]. Some examples of deposition techniques include Chemical Vapour Deposition (CVD), Physical Vapour Deposition (PVD), and electrodeposition.

Electrodeposition is a well developed and versatile coating technique that can be used to produce a large number of metals, alloys, and composites. It is an electrolytic process which involves the dissolution of a metallic anode and the deposition of metal ions onto a cathode under an applied current in an electrolyte [8]. The microstructure of the deposit can also be manipulated by changing deposition conditions. The material employed in this study is produced through electroforming, which is extremely similar to electrodeposition. Therefore, a more detailed review on electroforming is presented in the next section.
1.2 Electroforming of Nickel

1.2.1 Methodology

Electroforming is an electrochemical process similar to electrodeposition, except the metal deposit is subsequently separated from its substrate (Figure 1.4). Hence it is an application of electrodeposition to produce or reproduce free-standing articles that are used as finished or semi-finished products [9-16]. The major difference between the two processes lies in the cathode. Electroforming briefly involves the following procedures:

- fabrication and preparation of a suitable mandrel (also acts as the cathode),
- suspending the mandrel into an appropriate electroplating solution or electrolyte,
- electrodeposition of the metal onto the mandrel by electrolysis,
- removing the metal-covered mandrel from the solution upon requiring the desired thickness, and
- separation between the deposit (or electroform) and the mandrel by mechanical means or heating/cooling cycles.

After obtaining the parted electroform, the metal component may be further machined or surface polished. The anode material and plating conditions such as bath composition, pH, and temperature for electroforming are similar to electrodeposition.

Figure 1.4. Manufacturing of an electroformed article [16].
Nickel is an attractive material due to its many sounding mechanical properties. It can be electroplated in a low stress state with excellent wear, corrosion, and erosion resistance [12-14]. For this reason, it is often utilized in decorative and protective coatings. Likewise, electrodeposited nickel can be strong and tough, i.e. having both moderate hardness and ductility. The mechanical properties of nickel electroforms can be closely controlled by changing the deposition conditions, alloying with other elements, and/or incorporating particles and fibres within the electrodeposited nickel matrix [12, 13]. In addition, a wide selection of known nickel plating solutions is readily available in market.

1.2.1.1 Anode Material for Electroforming of Nickel

Anode is the electrode whereby nickel dissolves and replenishes the plating solution, i.e. \( \text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^{-} \). There are two types of primary nickel available for electroplating/electroforming, activated (sulphur-containing) and non-activated (sulphur-free) [13]. Activated nickel retains small amounts of sulphur (0.01 to 0.04 %), usually in the form of sulphides, during refining. It is found that the anode dissolution potential for sulphur-containing nickel is approximately 0.4 volt lower than for sulphur-free ones. Sulphur also prevents surface oxidation of nickel, thus allowing smooth dissolution of the anode. Titanium anode baskets, introduced in the 1960s, are often utilized to hold the primary nickel of selected size and shape [8]. The use of titanium basket allows simple refilling, a constant anode area and current distribution, and material conservation.

1.2.1.2 Cathode Material for Electroforming of Nickel

The mandrel not only serves as the cathode where nickel ions deposit out of the solution and reduce to the metallic form, but also forms the shape, dimension, and surface texture of the finished or semi-finished metal objects. The design and fabrication of the mandrel are critical to the electroforming process as well as the quality of the produced electroforms [10]. Some of the basic requirements for mandrels include minimum shape change (thermal expansion) in warm electrolytes, chemically inert to the acidic electrolyte, deformation resistant (rigidity) to stress-containing electroforms, electrically conductive, and providing easy separation from electroforms [12].
The most commonly used mandrels are made of pure metal or alloys of metals such as stainless steel, copper, brass, Invar, Kovar, titanium, nickel, and chromium. Most of these materials are also conductive. Stainless steel is by far the most popular material. It can be machined to high surface finish and close tolerance [10]. Austenitic stainless steel readily forms a passive film on the surface that is inert to the chemical solution and prevents adhesion of the electrodeposit to the mandrel. Copper and brass are less costly than stainless steel and are relatively easy to machine. Often the mandrel is electroplated with a thin film of nickel and/or chromium to facilitate separation and prevent attack by the electrolyte. Invar and Kovar are the more expansive mandrel materials. They have low coefficients of thermal expansion and are used in critical cases where dimensional accuracy is the major concern.

1.2.1.3 The Watts Bath

The most common nickel electroplating solution is the Watts bath which was developed by Professor O. P. Watts of the University of Wisconsin in 1916 [14]. Table 1.1 shows the original Watts bath compositions. The Watts bath is composed of double nickel salt: nickel sulphate and nickel chloride. Nickel sulphate is the main source of nickel ions in the electrolyte. The presence of nickel chloride has two purposes: increase solution conductivity and act as anode corrodant. The beneficial effect from nickel chloride is the uniformity of metal distribution at the cathode [12-14]. However chloride is also the primary stress raiser. Boric acid acts as a buffering agent in the solution to maintain the pH at the cathode-solution interface.

<table>
<thead>
<tr>
<th>Table 1.1. Composition of the original Watts bath.</th>
</tr>
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<tbody>
<tr>
<td>Nickel sulphate NiSO₄·7H₂O</td>
</tr>
<tr>
<td>Nickel chloride NiCl₂·6H₂O</td>
</tr>
<tr>
<td>Boric acid H₃BO₃</td>
</tr>
</tbody>
</table>

The Watts bath yields nickel deposits containing tensile stress [12, 13]. Excessive internal stress results in distortion of electroform, difficulty of separating electroform from the mandrel, and occurring of micro cracks or buckling. The accepted method of stress reduction in nickel
deposits is by adding organic agents. These agents are sulphur-containing compounds such as saccharin, paratoluene sulphonamide, benzene disulphonate, and 1-3-6 sodium naphthalene trisulphonate [13, 14]. All of the above stress reducers will decompose over time. Thus regular replenishment is needed for close control of internal stress. Saccharin is the most effective stress reducer since it decomposes slowly and permits stress-free operation at moderate current densities for several weeks. These organic stress reducers invariably introduce sulphur into nickel deposits. As a result, the hardness and strength are increased, but ductility is reduced. The electroforms also become embrittled when exposed to temperatures above 200 °C [14].

1.2.1.4 Nickel Sulphamate Bath

In a conventional nickel sulphamate bath, nickel sulphate is simply replaced with nickel sulphamate. The metal deposits from a nickel sulphamate bath possess lower internal stress comparing to that from a Watts solution [12 -14]. Therefore, it is preferable for electroforming since the deposits are relatively thick. The drawback of this solution is the occurrence of anodic oxidation of sulphamate anions, which co-deposit sulphur onto the cathode. The incorporated sulphur usually leads to lower stressed and brighter nickel deposit. However the ductility and other mechanical properties are also affected [13].

Ni-Speed, a concentrated sulphamate process, was developed by Inco Europe Limited [13]. It contains 550 to 650 g/L of nickel sulphamate, 5 to 15 g/L of nickel chloride, and 30 to 40 g/L of boric acid [8]. Use of activated anode materials can reduce the amount of nickel chloride, and the stress of deposit can be kept low without organic addition agents. The process is often carried out at a pH of 4.0, a temperature of 60 to 70 °C, and high current densities (~900 mA/cm²). These operating conditions and the high nickel concentration permit high deposition rates. Hence Ni-Speed is used specifically for electroforming.

1.2.2 Microstructure of Electroformed Nickel

The microstructure depends on many operation conditions including, but not limited to, type of plating solution, solution temperature and pH, thickness of deposits, current density, rotational velocity, and type of substrates [14]. All these parameters induce different modes of electro-
crystallization, hence microstructures. The grain size and shape depend on the relative rates of nuclei formation and grain growth. During the electro-crystallization process, a metallic ion can either nucleate a new grain or join an existing grain upon reduction [16]. If the process is nucleation controlled, i.e. formations of nuclei are favourable, fine-grained deposits are formed. On the other hand, if the process is growth controlled, coarse-grained and/or columnar structure will be produced. Deposits made from conventional Watts baths without any grain-refining agents usually result in low-strength nickel having columnar structures [16, 17]. Normally, fine-grained deposits are smoother, brighter, harder, and more corrosion/wear resistant. Therefore they are preferable to coarse-grained deposits for many applications. In the following section, the dependence of microstructure on deposit thickness and the methodologies taken to produce ultra fine grained nickel deposits will be briefly discussed.

Figure 1.5 shows the change in surface morphology with current density and film thickness in nickel deposits grown from a modified Watts bath [17]. It is observed that as the film thickness increases or current density decreases while maintaining other parameters constant, the grain size and surface irregularity increase. It is believed that the initial smooth and fine grained deposit results from an immediate reduction of the metal ions in close contact of the substrate [18]. At the same time, a metal ion denuded layer (MIDL) is created immediately above the substrate surface, suppressing further nucleation. As the deposition progresses, surface irregularity increases as a result of varying MIDL thickness over the substrate surface which subsequently results in localized deposition and film thickness.

One of the most generally accepted methodology for minimizing the MIDL is pulse current plating [18, 19]. The most commonly employed pulse current is of a square wave form consist of T_{on} and T_{off} (Figure 1.6). During T_{on}, extremely high overpotentials are achieved, and during T_{off}, the current is completely cut-off allowing replenishment of metal ions into the MIDL. High overpotentials results in a large number of metal ions arriving at the substrate. In addition, the metal ions and free electrons are distributed evenly over the substrate surface. Thus high nucleation rate and smooth deposition are accomplished. The optimum pulse plating conditions leading to ultra-fine grained nickel have been thoroughly studied by El-Sherik [18], and are summarized in Figure 1.6. By electrodeposition from a modified Watts bath and applying these conditions, nickel deposits having grain size ranging from 10 to 40 nm have been produced.
Figure 1.5. A surface morphology change with current density and deposit thickness in nickel films from a modified Watts bath [17].

![Surface Morphology Change](image)

Figure 1.6. Optimum current conditions for pulse plating [18].

![Current Conditions](image)

As mentioned previously, additives are often introduced to lower the internal stress of the deposit, especially in the case of electroforming where thick deposits are often required. Most of the
sulphur-containing additives that are used as stress reducers also act as minor brighteners and grain refiners [12]. In the absence of saccharin, conventional polycrystal nickel is obtained. As shown in Figure 1.7, by increasing the saccharin concentration in a modified Watts bath, the grain size of the nickel deposits decrease [18, 20]. In addition, it was shown that in the presence of saccharin, the reduction potential of nickel ion was lowered by about 0.1 V [20]. As well, the co-deposition of these large molecules can effectively block grain growth and promote nucleation [18, 21]. Other factors such as temperature and pH of the electrolyte also closely control the surface morphology and grain size. It is observed that an increase in temperature results in larger grain size. Higher temperatures results in an increased diffusivity of adatoms and allow them to migrate a long distance over the substrate surface, thus producing large grains. The rotational velocity is also observed to have effect on grain size. It was shown that the grains become finer when the rotational velocity of the mandrel is increased [22].

*Figure 1.7. Dark field electron micrographs showing the relationship between grain size and the saccharin concentration in the plating bath [18].*
1.2.3 Mechanical Properties of Electroformed Nickel

The mechanical properties of nickel deposits vary from solution to solution due to different compositions and additives which affect the amount of metallic impurities in the deposits. Typical properties of conventional polycrystalline nickel electroform from the Watts and sulphate solutions are shown in the following table [11, 13, &14]. The grain size of these deposits is in the range of micrometers.

Table 1.2. Mechanical properties of electroformed nickel produced by different plating solutions [13].

<table>
<thead>
<tr>
<th></th>
<th>Watts Nickel</th>
<th>Conventional Sulphamate</th>
<th>Concentrated Sulphamate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength, MPa</td>
<td>345 – 485</td>
<td>415 – 620</td>
<td>400 – 600</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>15 – 25</td>
<td>10 – 25</td>
<td>10 – 25</td>
</tr>
<tr>
<td>Vickers Hardness, 100</td>
<td>130 – 200</td>
<td>170 – 230</td>
<td>150 – 250</td>
</tr>
<tr>
<td>Internal Stress, MPa</td>
<td>125 – 185 tensile</td>
<td>0 – 55 tensile</td>
<td>0</td>
</tr>
</tbody>
</table>

The strength and ductility are also affected by the thickness of the electroformed nickel. The ductility is observed to increase with increasing thickness up to about 250 micrometers after which it becomes relatively constant [13]. The ultimate tensile strength, similarly, also varies with nickel thickness but becomes stable above 250 micrometers. This occurs because not enough material is available for plastic deformation when the thickness is less than 250 micrometers. Hence the true properties cannot be reflected. The ductility shows greater variation with thickness than does the ultimate tensile strength. The measurements of ultimate tensile strength and percent elongation in the above table are obtained through standard uniaxial tension testing [13].

Grain size is another major factor causing varying mechanical properties. As shown in table 1.3, most of the mechanical properties are greatly improved by a reduction in grain size [23]. Yield strength and ultimate tensile strength increase dramatically, more than 5 times, with a grain size reduction from 10 μm to 10 nm. However, the ductility also decreases significantly from 50% to less than 1%. Typical stress-strain curves of an annealed polycrystalline nickel and several
deposited nickel with varying nanocrystalline sizes are shown in Figure 1.8 [24]. However it must be point out that these properties are thickness dependent, i.e. samples with different size and shape yield different values. Nonetheless, the Hall-Petch relationship is clearly shown. It is interesting to note that, further reduction in grain size from 10 nm produces an opposite effect. It is generally believed that an inverse Hall-Petch effect is a result of changing deformation mechanism. Other mechanical properties such as wear rate and coefficient of friction are also strong dependent of grain size (Figure 1.9).

Table 1.3. Comparisons of mechanical properties between conventional and electrodeposited nanocrystalline nickels [23].

<table>
<thead>
<tr>
<th>Property</th>
<th>Ni 10 µm</th>
<th>Ni 100 nm</th>
<th>Ni 10 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield Strength, MPa</td>
<td>103</td>
<td>690</td>
<td>&gt;900</td>
</tr>
<tr>
<td>Ultimate Tensile Strength, MPa</td>
<td>403</td>
<td>1100</td>
<td>&gt;2000</td>
</tr>
<tr>
<td>Tensile Elongation</td>
<td>50</td>
<td>&gt;15</td>
<td>1</td>
</tr>
<tr>
<td>Modulus of Elasticity, GPa</td>
<td>207</td>
<td>214</td>
<td>204</td>
</tr>
<tr>
<td>Vickers Hardness, kg/mm$^2$</td>
<td>140</td>
<td>300</td>
<td>650</td>
</tr>
<tr>
<td>Work Hardening Coefficient</td>
<td>0.4</td>
<td>0.15</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Figure 1.8. Engineering stress-strain curves for conventional and electrodeposited nanocrystalline nickels [24].
Figure 1.9. Effect of grain size on (a) Vickers hardness, (b) yield strength, (c) wear rate and (d) coefficient of friction in electrodeposited nickel [26].
1.3 Thermal Stability of Nanocrystalline Materials

It is well known that nanocrystalline materials are thermally unstable due to the extreme high energy associated with grain boundaries and triple junctions. Given a certain amount of activation energy either thermally or mechanical, the microstructure of the nanocrystalline material changes through grain growth. This phenomenon is often studied by annealing, which is a common heat treatment. During annealing, a material is exposed to an elevated temperature for an extended period of time and then slowly cooled to room temperature [1]. The microstructure under different annealing conditions can be obtained. In the following sections, microstructure evolution upon annealing for conventional and nanocrystalline materials will be discussed.

1.3.1 Conventionally Deformed Materials

It is a common practice that a material is work-hardened by plastic deformation to achieve desired strength and hardness. Annealing is often performed afterwards in order to reduce internal stress and recover certain ductility. During annealing, conventionally work-hardened materials often experience the following three stages: recovery, recrystallization, and grain growth. Each of these stages will be briefly discussed in the following sub-sections.

1.3.1.1 Recovery

Recovery refers to partial restoration of material’s properties to its undeformed condition by dislocation movements [1]. During this stage, the total energy of the material decreases by either dislocation annihilation or rearrangement of dislocations [25]. In the former case, dislocation density decreases by thermally activated dislocation glide, climb and cross-slip. In the ladder case, dislocations rearrange themselves by formation of dislocation cell walls. Dislocation cell walls are three dimensional structures consisting of dislocation tangles. The number of dislocations in the cell interior may further reduce by dislocation annihilation, forming sub-grains. Further thermal activation results in the growth of subgrains, or subgrain coarsening. The various stages of recovery are summarized in Figure 1.10.
There are two different mechanisms for subgrain coarsening: subgrain boundary migration and subgrain rotation and coalescence [25]. It has been proposed that for two closely oriented subgrains, they might rotate through a boundary diffusional process until similar orientation is reached. Hence, the two smaller grains will coalesce into one larger grain (Figure 1.11). This mechanism is also proposed as one of the growth mechanisms in nanocrystalline nickel.
1.3.1.2 Recrystallization

Recrystallization refers to the formation of new grains that are strain-free [1]. These grains form and grow at the expense of highly deformed/strained grains. Recrystallization can be divided into nucleation and growth [25]. Nucleation refers to the formation of new grains, often at locations with high energy such as triple junctions or sites with impurities. Growth refers to the growth of these new grains and consumption of the parent grain. The process of recrystallization completes upon consuming all the parent grains.

The border line between recovery and recrystallization is not always very clear. For example, sub-grain formation may also be nucleation, while sub-grain growth may be grain growth from recrystallization. Both sub-grain growth and recrystallization may be continuous or discontinuous. Continuous growth exhibits similar growth rates everywhere in the material and results in a uniform microstructure. Whereas varying growth rates result in discontinuous process and non-uniform grain size distribution. This is also the same notion for normal and abnormal grain growths which will be discussed in the following section.
1.3.1.3 Grain growth

As mentioned earlier, grain boundaries are associated with energies. The driving force for grain growth is therefore, reducing the number of grain boundaries and the total amount of energies. Grain growth occurs by the migration of grain boundaries, i.e. short range diffusion of atoms between two adjacent grains.

The mobility of grain boundaries depends on a number of factors. These may include temperature, grain boundary structure, and solutes [25]. It is very straightforward that a higher temperature leads to higher diffusion rates and boundary mobility. Therefore, grain growth is generally faster at higher temperatures. The migration of grain boundaries also depends strongly on the boundary structure. It is commonly known that the mobility of High Angle Grain Boundaries (HABGs) is higher than that of Low Angle Grain Boundaries (LABG). In addition, it was found that the mobility of HABGs also depends on orientation. Studies have shown that special boundaries with high density of coincidence sites often exhibit fast growth rates. The boundary plane may also have significant effect on the boundary mobility. This often leads to very anisotropic growth such as the ones shown in Figure 1.12.

Figure 1.12 (a) Anisotropic growths in Al-0.05%Si [25]. Faces parallel to \(\{111\}\) planes are very immobile, forming plate-shaped grains. (b) Faceted grain growth in Ni-SiO- alloy. The facets are parallel to the \(\{100\}\) planes with no particular orientation relationship to the matrix.
Solutes also have significant effect on the boundary mobility. It is generally realized that at high solute concentration, the mobility decreases with increasing solute concentration. Because of the vacancies and disordered atomic structures associated with the grain boundaries, solutes are likely to segregate at grain boundaries and form an atmosphere of solutes. Hence, the rate of migration depends on the rate of diffusion of these solutes. It is considered that once the boundary breaks free from these impurities, the migration rate will be no longer affected by the solutes. This would be the scenario at low solute concentration, where the mobility is less dependent on the solute concentration.

1.3.2 Nanocrystalline Nickel: Recrystallization and Grain growth

The thermal stability of electrodeposited nanocrystalline (nc) nickel has been investigated systematically [26-32]. It was found that upon annealing, grain growth occurs through a series of stages summarized in Figure 1.13.

Figure. 1.13 Multi-stage grain growth in electrodeposited nanocrystalline nickel upon annealing [30]. Material was annealed at a constant temperature of 420 °C. (a) as-received condition, (b) annealed after 1 second, (c) 30 s, (d) 3.6 ks, (e) 39.6 ks, (f) 432 ks.
Stage I Abnormal Grain Growth (AGG) is initiated at relatively low temperatures, approximately 80 °C [26]. The microstructure evolution can be described by a quasi nucleation-growth process in which certain nanometre-sized grains start to grow preferentially at the expense of the surrounding grains very similar to recrystallization. During Stage I, the microstructure features bimodal grain size distribution where submicron grown grains were embedded in a nanocrystalline matrix (Figure 1.13 b). Upon completion of Stage I, a uniform grain size distribution is established. This marks the beginning of Stage II where further grain growth occurs uniformly and relatively slowly (Figure 1.13 c & d). A secondary AGG, referred as Stage III, was found at higher annealing temperatures [28, 29]. This process is characterized by extremely large faceted grains (~100µm) embedded in the submicron matrix resulted from Stage II (Figure 1.13 e). Detailed investigation on the mechanism leading to Stage III was carried out [30, 31]. A significant amount of sulphur, as high as 5wt%, was detected at the faceted boundaries, and it was suggested that Stage III is initiated by a critical sulphur concentration, whereby wetting of facets occurs enabling a rapid, planar fashion migration of these boundaries. Furthermore, EBSD study has shown that the facets of these grains are parallel to the family of \{100\} planes [32].

1.3.2.1 Stage I Abnormal Grain Growth

Klement [26, 27] have shown based on DSC scans and TEM analysis that nanocrystalline nickel produced by electrodeposition having average grain sizes of 10 and 20 nm became unstable at approximately 80 °C. A broad exothermic reaction was detected on the DSC curve at the onset of 80 °C (Figure 1.14). A dual microstructure was observed in TEM samples with an initial grain size of 10 nm annealed at 220, 250, and 270 °C for 30 min. After annealing at 270°C for 30 min, the matrix grains are in the range of 10 to 20 nm, while the abnormal grown grains are in the range of 200 to 500 nm. This was referred as Stage I Abnormal Grain Growth. The growth mechanism for this stage is believed to be very similar to sub-grain formation during recovery or nucleation during recrystallization. TEM observations have shown abnormally grown grains having irregular shapes, which could be formed by rotation and coalescence of various numbers of the former nanometre sized grains. Once formed, these grains grow rapidly, consuming the nano-matrix, in a way very similar to recrystallization. Hence, the Stage I Abnormal Grain Growth is said to have a quasi-nucleation process.
1.3.2.2 Stage III Faceted Grain Growth

A secondary abnormal grain growth was first reported upon annealing at a higher temperature range, 500 °C to 600 °C [28, 29]. It is characterized by the occurrence of extremely large cube-shaped grains (5 to 50 µm) in a submicron matrix (500 nm). A more detailed investigation was carried out by Hibbard [30, 31] at a constant annealing temperature of 420 °C with different annealing times including 1, 30 s, 1, 11, 120 hr. It was observed that first stage abnormal grain growth was completed after 30 s at 420 °C, and the grain size increased from an initial of 20 nm to 350 nm. Normal grain growth follows, and after 1 hr, a uniform microstructure having a mean grain size of 450 nm is observed. Sometime between 1 hr and 11 hr, second stage abnormal grain growth set in. A duel microstructure with very large planar grains embedded in a submicron scale matrix grains. Investigation by STEM with energy dispersive X-ray spectroscopy (EDS) showed considerable sulphur concentration at grain boundaries between abnormal grains and matrix grains (Figure 1.15). It was suggested that the second stage “runaway” grain growth is initiated by a critical sulphur concentration in which wetting of grain boundaries occurs and rapid migration is triggered. This faceting behaviour is very similar to the one found in Ni-SiO- alloy described in previous section.
1.4 Deformation Behaviour of Nanocrystalline Materials

As introduced in section 1.2.3, the mechanical properties of nanocrystalline nickel are much more superior to its counterpart polycrystalline nickel. Basic deformation mechanisms for both conventional polycrystalline materials and nanocrystalline materials will be briefly explained in the following sections.

1.4.1 Deformation Mechanisms for Polycrystalline Materials

Conventional deformation mechanism in a polycrystalline material is mainly due to dislocation reproduction and dislocation slip through the crystal lattice. A moving dislocation can be impeded by obstacles such as grain boundaries. This creates a pile-up of dislocations in the vicinity of the boundary (Figure 1.16). Due to the strain field surrounding each dislocation core, a back stress which acts in the opposite direction as dislocation slip is induced. In order for the material to further deform, an increase in the applied stress is required, often high enough to activate new dislocation slips in another grain. When the grain size of a polycrystalline material is relatively large, the length of the dislocation pile-up is greater, as well as the back stress. As a consequence, it is easier to activate new dislocation sources at lower stress levels. For polycrystalline materials with smaller grains, the driving force for activation of new dislocation sources is smaller. Hence it is more difficult for dislocation slip in such materials [35].
1.4.2 Hall-Petch and Inverse Hall-Petch Relations

The well known Hall-Petch relation was derived based on dislocation pile-up considerations. In a conventional polycrystalline material, increasing yield stress ($\sigma$) and hardness ($H$) can be obtained by reducing its grain size ($d$), i.e. increasing the number of grain boundaries. Mathematical expressions for Hall-Petch relation are commonly written as:

$$\sigma = \sigma_0 + K_y d^{-n}$$

or

$$H = H_0 + K_H d^{-n}$$

where $K_y$ and $K_H$ are the strengthening coefficients and $n$ typically takes the value of 0.5.

Mathematically, these equations will predict infinite strength of a material when its grain size approaches to zero. However, this is impossible because dislocation pile-ups cannot be formed due to lack of space in very small grains. In fact, deviation was observed for materials with very fine grains (approximately < 50 nm) and decrease in the strength of a material has been observed when the grain size becomes smaller than a critical value (usually 10 nm). This strength reduction with decreasing grain size is known as the inverse Hall-Petch Relation (Figure 1.17). The critical grain size for the transition from classic to inverse Hall-Petch has been derived based...
on the dislocation pile-up formations. By equating the elastic forces between two dislocations and the material strength, the critical grain size \( d_c \) is calculated to be:

\[
d_c = \frac{G b}{\{(1 - v) H\}}
\]

where \( G \) is the shear modulus, \( b \) is the Burgers vector, \( v \) is Poisson’s ratio, and \( H \) is the hardness [33].

*Figure 1.17. The Hall-Petch and inverse Hall-Petch relations. For grain size greater than \( d_c \) (usually around 10 nm for most metals), the strength and hardness of the materials increases with decreasing grain size. If the grain size is smaller than \( d_c \), then the former linear relationship is inversed.*

There are a number of hypothesis for the softening behaviour of extremely small-grained materials. One of the arguments is that grain boundary and triple lines are regions with very low atomic density. The strength of such regions may be considerably smaller than the perfect crystal lattice. Assuming regular fourteen sided tetrakaidecahedron-shaped grains with known grain boundary thickness and grain size, the volume fraction of the intercrystalline component \( V_{ic} \) was derived and expressed as follows [34]:

\[
V_{ic} = 1 - [(d - \Delta)/d]^3
\]

where, \( d \) is the grain size and \( \Delta \) is the grain boundary thickness.

The volume fraction of grain boundary is given by
\[ V_{gb} = \frac{[3\Delta (d - \Delta)]}{d^3} \]
and
\[ V_{ul} = V_{ic} - V_{gb}. \]

If the grain boundary thickness is taken to be 1 nm, it can be seen that the intercrystalline region is negligible (0.3\%) for grain size larger than 1 µm. If the grain size decreases to 100 nm, the intercrystalline region would increase to 3\%, most of which is contributed from grain boundary regions. Upon reaching the critical grain size, 10 nm, the overall intercrystalline volume becomes to 30\% and a considerable amount (5\%) is contributed from triple line components.

**Figure 1.18. Intercrystalline volume as a function of grain size [34].**

1.4.3 Deformation Mechanisms for Nanocrystalline Materials

From the previous section, we saw that at very small grain size, the material contains extremely high density of grain boundaries. For polycrystalline materials, deformation occurs through grain interior mechanisms such as dislocation slip. When the grain size reduces to nanometre range, it is believed that a transition occurs from grain interior dominated deformation to grain boundary denominated deformation [35]. *In situ* TEM observation of nanocrystalline copper during deformation had shown sudden change in contrast in both individual and groups of grains. This indicates the possibility of dislocation activities and grain rotations. Dislocation motion was also observed in grains. However there is no evidence of pile ups.
1.4.3.1 Grain boundary sliding

The rate of deformation during steady-state creep was observed to increase rapidly with decreasing grain size. It was then suggested that Grain Boundary Sliding (GBS) acts as an additional deformation mechanism during creep [36]. Assuming GBS was a result of dislocation movements along or adjacent to grain boundaries, the strain rate due to sliding was found to be proportional to $\sigma^2/d$, where $\sigma$ is the applied stress and $d$ is the average grain diameter [36]. More detailed investigation was carried out on the subject [37]. It was realized that grain boundaries are never perfectly smooth or straight, and was shown that the rate of GBS as well as the extent of plastic strain is controlled by various accommodation processes. These can be purely elastic, diffusional, or plastic flow by dislocation motion.

In the case for nanocrystalline materials, due to the high volume fraction of intercrystalline components, material flow can be significantly greater than its conventional counterpart, and GBS was suggested to be one of the major grain boundary deformation mechanisms. It was proposed that in order for GBS to occur, a mesoscopic planer interphase ($\delta$) must be established. Once a planar interface is formed, sliding can occur along the grain boundaries of many grains [36]. For conventional materials, GBS along a mesoscopic planer interphase would involve the rearrangement of a significant amount of perfect crystal lattice (Figure 1.19a). Hence it is unlikely to occur under homologous temperatures. At very fine grain sizes, however, the number of atoms that needs to be rearranged in order to form a mesoscopic planer interphase becomes very small (Figure 1.19b). Therefore, as grain size decreases into the nanometer-range, GBS appears as an additional deformation mechanism, which leads to lowering of material’s strength.

*Figure 1.19 The mechanism of grain boundary sliding.*
Through Molecular Dynamic investigations, a more recent study had shown the mechanisms of GBS at the atomic level in a model nanocrystalline computer-generated Ni sample [38]. It was found that the accommodation processes include grain boundary and triple junction migration, as well as dislocation glide. Furthermore, a significant amount of discrete atomic activity such as shuffling of individual atoms was observed.

1.4.3.2 Diffusion and Grain Boundary Creep

Another dominating deformation mechanism in nanocrystalline material is Grain Boundary Creep (GBC). Creep is a thermally activated process that involves diffusion of atoms and vacancies. Diffusion may take place either through the grain interior or grain boundaries. Due to the misalignment of atoms around grain boundary regions, grain boundaries are considered to be short circuit diffusion paths. The diffusivity of grain boundary is much greater than that of grain interior. In polycrystalline materials, creep strain depends strongly on the testing temperature and is only noticeable when the deformation temperature is greater than 0.4 of the material’s melting temperature. In the case for nanocrystalline materials, a large volume fracture of grain boundary or diffusion paths are present. Therefore, even at relatively low testing temperatures, GBC may become the dominating deformation mechanism.
2 Experimental

2.1 Material

The material used in the present study is provided by Beijing University of Science and Technology (BUST). It is nanocrystalline nickel produced by electroforming technique. As introduced in chapter 1.2, electroforming is very similar to electrodeposition, often used to manufacture free-standing components. The setup used in producing this material is similar to that described in Ref [39], shown in Figure 2.1. The exact bath solution and plating conditions are unknown. However it is known that there were no intentional added grain refiners such as saccharin. The finishing electroform exhibits a cone shape, measuring approximately 10mm in height (h) and 10 mm in diameter (d). The thickness (t) of the wall of the cone measures approximately 1.5mm as shown in Figure 2.2. This cone is further cut into smaller pieces for the following investigations.

Figure 2.1 Electroforming setup used in producing nanocrystalline nickel [39].

Figure 2.2 Cone-shaped electroform, with a thickness of ~1.5mm.
2.1.1 Thermal Stability Analysis via Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a technique often used to detect the physical and chemical changes in a material [40]. When a material experiences a physical transformation, it will either absorb or give off energy. The amount of energy can be quantified by maintaining the material of interest and a reference material at the same temperature. During a DSC scan, a material of interest is placed into a heating chamber, while a reference material is placed into another chamber. The temperatures of both chambers are increased linearly with time, and the temperatures of the two chambers are maintained nearly the same. If the material of interest experiences a transformation, it will require more or less heat flow into the chamber compared to the reference. Upon performing a DSC scan, a DSC curve of heat flow vs. temperature is obtained. A number of transformations in metals and polymers can be identified using this technique. Some examples include glass transition, melting and boiling points, crystallization and recrystallization.

In this study, the thermal behaviour and phase changes of the as-received material were analyzed by Dupont 910 Differential Scanning Calorimeter purged with argon gas. Disc-shaped samples, each measured 5 mg in weight, were first prepared from the electroform and then heated from room temperature to 600 °C at two different heating rates: 10 °C/minute and 20 °C/minute. Physical transformations such as microstructure changes are reflected by the endothermic and exothermic heat flows in the DSC curves.

2.2 Microstructure Evolution

The microstructure evolution of the material is analyzed using optical microscopy and transmission electron microscopy. The as-received cone-shaped sample was cut into smaller pieces for these analyses. Detailed methods are described in the following sections.

2.2.1 Optical Microscopy and Sample Preparation

A preliminary analysis on the material’s microstructure evolution was first carried using optical microscopy. A batch of samples was prepared from the cone. Each sample measures
approximately 5mm x 5mm and 1.5mm in thickness. The samples were first annealed in a box furnace at different temperatures ranging from 200 °C to 700 °C for a constant annealing time of 40 minutes. After annealing, these samples were hot mounted for easy sample handling. The mounted samples were then grinded using abrasive papers starting with a grid of 120-, followed by 240-, 320-, 400-, 600-, and 800-. Finally, the samples were polished using 6 µm and 1 µm diamond spray. A copper sulphate based macro etchant was used to reveal the grain boundaries of the material.

2.2.2 Transmission Electron Microscopy

Based on the preliminary results, more detailed examinations were carried out using FEI Tecnai F20 Transmission Electron Microscopy (TEM). TEM samples were prepared from the bulk electroform. Similar to optical microscopy, samples measuring 5cm x 5cm were first cut out from the cone. In order for TEM examination, these samples were first thinned to approximately 0.1 mm (100 µm) by grinding using 120- grid abrasive papers. This process was achieved by attaching the sample to a hot-mounted block via double sided tape. Upon finishing grinding one side, the sample was soaked in acetone for a few hours to be separated from the double sided tape, followed by grinding of the opposite side. After the first initial thinning process, the sample was further grinded up to 800- grid abrasive paper on both sides. The final thickness of the sample was in the range of 80 to 100 µm. A TEM punch was used to produce disc-shaped samples having 3mm in diameter. Finally, they were electropolished in a 15% perchloric acid 85% ethonal electrolyte via double jet polishing technique. To analyze the microstructure at different annealing temperatures, the samples were first annealed in a conventional box furnace, followed by the preparations described above.

2.2.3 Grain Boundary Tracking via Semi-In-Situ Optimal Microscopy

Based on the optical micrographs obtained through preliminary analysis, Stage III faceted grains as described in Section 1.3.2 were indeed observed between 500 °C and 700 °C. To further study the mechanisms behind this process, a semi-in-situ method was designed to track the migrations of the faceted boundaries.
Based on a number of trials, an annealing temperature of 550 °C was chosen because it provided detectable grain growth within a moderate amount of time. A piece of sample was first grinded and polished. A micro-hardness machine was used to make several indents on the sample surface. It was then annealed in a tube furnace purged with argon gas. After 15 minutes, it was taken out of the furnace. Depending on the extent of oxidation, the sample was slightly polished for 5 to 10 seconds using 1 µm diamond suspension, followed by etching. The exact locations on the sample surface were recognized by the micro-hardness indents, and the microstructure changes were observed by optical microscopy. The sample was then put back to furnace for another 15 minutes. The same process applies after each annealing treatment.

2.2.4 In-Situ Transmission Electron Microscopy

In-situ hot-stage TEM was carried out to continuously observe the microstructure evolution. TEM samples were examined in a heated chamber, where constant monitoring of the microstructure was conducted. The temperature of the chamber, i.e. the specimen, was controlled manually. Hence the heating rate cannot be specified accurately. Two samples were prepared and observed using In-Situ TEM. The first sample, Hot-Stage 1 (HS1 for simplicity), was prepared and heated from the as-received state of the material. Observations on the sub-grain formation and growth of nanocrystalline grains were recorded. The second sample, Hot-Stage 2 (HS2), was first annealed into Stage III using conventional furnace, followed by In-Situ TEM observations, which were focused on the boundary mobility of the pre-formed faceted grains.

2.2.5 STEM-EDX

The chemical composition of the material was investigated using STEM-EDX. Pre-annealed samples having faceted boundaries were used. The chemical composition at the faceted grain boundaries, inside the large grown grains, and sub-micron matrix were analyzed.
2.3 Mechanical Testing

Upon obtaining the microstructure changes, the mechanical properties were expected to change accordingly. Hence the following mechanical tests were conducted. These include tensile testing, microhardness, Rockwell hardness, and fracture surface observation using SEM. A number of annealing conditions featuring particular microstructures were chosen.

2.3.1 Tensile Testing

Due to the thickness of the electroform, miniature tensile bars were able to be machined according to ASTM E 8/E 8M [41]. Detailed dimensions are shown in Figure 2.3. After obtaining the machined samples, they were annealed in a box furnace at various temperatures including 200 °C, 320 °C, 400 °C, 540 °C and 600 °C. Samples annealed at higher temperatures (400 °C, 540 °C, and 600 °C) showed slight bending and were hand-grinded to obtained flat surfaces. Tensile tests were carried using MTS 810 testing system under an applied strain rate of 0.010 mm/second. An extensometer was used to measure the percentage strain in the gauge.

*Figure 2.3 Miniature tensile specimens designed according to ASTM E 8/E 8M [41].*

G (gage length) = 12.5mm  
W (width) = 3mm  
T (thickness) = 1 mm  
R (radius of fillet) = 6  
L (overall length) = 50mm  
A (length of reduced section) = 16mm  
B (length of grip section) = 15mm  
C (width of grip) = 5 mm
2.3.2 Microhardness

Microhardness was used to find out the hardness of particular micro-features in the material under different annealing conditions. The microhardness values were obtained for samples annealed at the same temperatures as those for tensile testing, 200 °C, 320 °C, 400 °C, 540 °C and 600 °C. For samples annealed into Stage III (600 °C), hardness of both the matrix and large faceted grown grains were obtained.

2.3.3 Rockwell Hardness

After performing the tensile tests, a piece was taken from each fractured specimens to perform Rockwell hardness. The scale used on these specimens varies from HRC and HRB due to changing hardness upon annealing.

2.3.4 Fracture Surface Analysis using Scanning Electron Microscopy

The topography of the fracture surface of the fractured samples was investigated by Scanning Electron Microscopy (SEM). Comparisons were made between different annealing temperatures and possible fracture mechanisms were proposed.
3 Results

3.1 Investigation on Thermal Stability using DSC

Figure 3.1 shows the DSC curve obtained by heating the nickel specimen from room temperature to 600 °C at a heating rate of 10 °C/min. Two consecutive runs were performed on the same specimen, labelled as 1st run and 2nd run. An endothermic reaction occurred on both runs at 354°C, indicating a reversible transformation. This is known as the Curie temperature of nickel. An exothermic reaction which occurred only on the first run at 311°C indicates an irreversible reaction. Another irreversible reaction was observed during second run at 528 °C. By subtracting 1st run from 2nd run, all the irreversible reactions are obtained, shown by the line Different. Based on this line, an extremely broad exothermic reaction set in around 80 °C. Between 250 °C and 370 °C, a pronounced heat release was observed. The position of this peak is in close agreement with previous studies, 325°C [42] and 288°C [26]. In addition, a minor peak at 528 °C was detected. This minor peak has not been reported previously and is found to be the initiating temperature for Stage III faceted grain growth.

*Figure 3.1 DSC curve for nanocrystalline nickel obtained by heating from room temperature to 600 °C at a heating rate of 10 °C/min.*
3.2 Microstructure Evolution

3.2.1 Preliminary analysis using optical microscopy

The microstructure of as-received material was first analyzed using optical microscopy. The cross-section through the thickness of the electroform showed columnar structures adjacent to the inner and outer surfaces. Optical micrographs are shown in Figure 3.1. Since electroforming is a layer-by-layer deposition technique, the duel-microstructure observed could be a result of changing operation conditions during electroforming. Upon annealing at 200 °C, the duel structure disappeared. To avoid the inconsistency in the microstructure, all the samples used in the following analysis are made from the bulk or centre part of the electroform.

Figure 3.2 Optical micrograph showing duel microstructure through the thickness of the electroform.

The microstructure evolution upon annealing under different temperatures is shown in Figure 3.3. Only moderate changes can be seen between As-received sample and sample annealed up to 500 °C. However, the amount of changes cannot be easily quantified via optical microscopy. Between 500 °C and 540 °C, Stage III faceted grain growth is initiated. In conjunction with the DSC scan, this clearly shows that the minor peak observed at 528 °C is the starting point for faceted abnormal grain growth. It is interesting to note that the boundaries are faceted mainly during the growth process. While at 700 °C, Stage III is completed, and most boundaries are observed to be non-faceted.
3.2.2 TEM observation around major peak

Based on DSC scan, most of the microstructure changes occurred during the major heat release (Figure 3.1). As shown in Figure 3.3, little changes can be detected by optical microscopy. Therefore, further investigations were carried out using TEM. A number of annealing temperatures were selected around the heat release peak (Figure 3.4). These include 200°C (within the initial broad exothermic peak), 250°C (onset of the major peak), 320°C (maximum point of the major peak), and 370°C (end of the major peak).
Figure 3.4 Temperatures selected around the major heat release peak for detailed TEM observation.

The microstructure of the as-received sample is shown in Figure 3.5. It can be seen based on the dark field micrograph that the initial grain size of the as-received material is in the range of 20nm to 40nm. Upon annealing the samples at 200 °C and 250 °C for 40 minutes, only slight microstructure changes were found (Figure 3.6). The growth appears to be isolated and scattered in those sample annealed up to 250°C. It can be seen from Figure 3.6 (b) that some of the grains have grown to approximately 100nm. At 320°C, massive abnormal grain growth described as Stage I occurs and results a bimodal grain size distribution. The abnormally grown grains measure approximately 500nm, whereas the matrix grains are still in the nanometre range. By the end of the peak, 400°C, the entire nanocrystalline matrix has been consumed, and a relatively uniform grain size distribution was established. The grains are in the range of 200nm to 800nm. Further annealing results in uniform grain grown until reaching stage III which leads to faceted grain growth.
Figure 3.5 TEM micrographs showing the microstructure of as-received material.

Figure 3.6 TEM images showing samples annealed at (a) 200 °C, (b) 250 °C, (c) 320 °C, and (d) 400 °C.

(a) Annealed at 200 °C, 40 min
(b) Annealed at 250 °C
3.2.3 Stage III Semi-In-Situ Grain Boundary Tracking

Figure 3.7 shows the exact location on the sample surface annealed after 15, 30, and 45 minutes. The matrix appears to be dark, whereas the grown grains are white. It is shown that after each 15 minute intervals, more grains were observed and the existing grains have also grown moderately. This is indicated by the green circles. Interestingly, it was also observed that once a planar boundary is formed, it becomes relatively stable. This is indicated by the red circles.

Figure 3.8 shows a different location on the same samples annealed after 60, 75, and 90 minutes. Comparing to Figure 3.7, more grain growth than nucleation is observed. The red circles again indicate that the planar boundaries are very stable. The yellow circles show that grain growth occurs on the non-planar sides of the grains. As can be seen from Figure 3.8, the matrix adjacent to a growing grain appears to be dark prior to any growth (at 60 min). It then becomes somewhat gray (at 75 min). Finally, the gray area becomes part of the grown grain and completely white (at 90 min). In order to investigate the mechanisms, higher magnification micrographs are taken and shown in Figure 3.9.
Figure 3.7 The same location on the sample surface annealed after 15, 30, and 45 minutes at 550 °C. The black diamond shaped spots are etched microhardness indents. Green circles indicate nucleation and grain growth, while red circles indicate immobile planar boundaries.

Figure 3.8 The same location on the sample surface annealed after 60, 75, and 90 minutes at 550 °C.
3.2.4 In-Situ TEM on Grain Boundary Migration

The microstructures of the sample HS1 at various heating stages are shown in Figure 3.10. The sample was heated from its as-received state. The same location on the sample was observed and recorded. The red circles indicate the exact location of the sample. For tracking the overall changes in the microstructure and having direct comparisons, observations were made at relatively low magnifications.

*Figure 3.10 In-Situ TEM observation of microstructure changes with increasing temperature.*
It can be seen that little grain growth occurred during In-Situ TEM up till 500°C. Moderate changes were seen after raising the temperature above 500°C. More rapid grain growth was observed when the temperature was raised above 600°C. However observations were limited to temperatures below 630°C, because further increasing the temperature resulted in localized void formation.

Figure 3.11 shows the microstructure evolution of sample HS2 which contains pre-existing facets. The temperature was gradually raised to 600°C, and the sample was held at the temperature for 50 minutes. Apparent dislocation movement were found (Figure 3.10 a), but little microstructure changes occurred. When the temperature was further raised to 645°C, the faceted boundary seems to have become less planar. However, when the sample was cooled to room temperature, the boundary becomes fairly straight again

*Figure 3.11 In-Situ TEM observation of the planar boundary and its migration.*
Figure 3.12 shows the same location before and after the heating process. It can be seen that the planar boundary appears to have no changes. However, moderate grain growth in the adjacent matrix can still be detected.

*Figure 3.12 Microstructure on pre-annealed sample before and after In-Situ TEM examination. (a) Planar boundary observed before heating. (b) Planar boundary observed after heating at 600 °C for 50 minutes.*

![Microstructure](image)

(a) before heating  (b) after heating, cooled

3.2.5 STEM-EDX

The chemical composition at the planar interface was analyzed and shown in Figure 3.13. No significant amount of sulphur was detected. However minor traces of silicon and chlorine was found.

*Table 3.1 The chemical composition obtained using STEM-EDX at the locations shown in Figure 3.13.*

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Si (wt%)</th>
<th>S (wt%)</th>
<th>Cl (wt%)</th>
<th>Ni (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.93</td>
<td>0.30</td>
<td>1.00</td>
<td>97.78</td>
</tr>
<tr>
<td>2</td>
<td>0.22</td>
<td>0</td>
<td>0.23</td>
<td>99.55</td>
</tr>
<tr>
<td>3</td>
<td>0.57</td>
<td>0.21</td>
<td>1.27</td>
<td>97.95</td>
</tr>
</tbody>
</table>
3.3 Mechanical Testing

3.3.1 Tensile Testing

Tensile testing was conducted on samples with various annealing conditions. Figure 3.14 shows the fracture miniature tensile bars. It was found that the nanocrystalline material in its as-received state exhibits considerable ductility. After annealing at 200 °C for 40 minutes, the sample shows similar mechanical properties. Both samples are shown to have fractured along the gage length, as well as showing necking behaviour. However, the material becomes very brittle after annealing at temperature above 320 °C. The rest samples have fractured close to the grip, or even inside the grip.
Figure 3.14 Fractured miniature tensile bars at various annealing conditions after tensile testing.

(a) As-received  
(b) Annealed at 200 °C for 40 min.

(c) Annealed at 320 °C for 40 min.  
(d) Annealed at 400 °C for 40 min.

(e) Annealed at 540 °C for 40 min.  
(f) Annealed at 600 °C for 40 min.

Figure 3.15 shows the stress-strain curves obtained for as-received samples and samples annealed at 200 °C. The material shows considerable ductility, approximately 5% strain. The curves also demonstrate typical features including linear elastic deformation, uniform plastic deformation, Ultimate Tensile Stress (UTS), necking, and failure. Stress-strain curves were not obtained for material annealed above 320 °C due to the brittleness. Stress-strain curves were cannot be obtained for the rest of the samples.
Figure 3.15 Engineering stress-strain curves obtained for as-received samples and samples annealed at 200 °C for 40 minutes.

Even though the overall stress-strain curves for as-received samples and 200 °C annealed samples are very similar, differences can be observed in the elastic region of the stress-strain curves. Figure 3.16 shows a magnified portion on the elastic part. A slight increase in both elastic constant and conventional yield stress was observed after annealing.

Figure 3.16 Magnified portion on the elastic part of the stress-strain curves.
3.3.2 Microhardness

The following table shows the micro-hardness measurements obtained for the various microstructure features. Figure 3.17 shows the matching micrograph of the location of measurements. For the as-received, 200 °C, 320 °C, and 400 °C samples, faceted grain growth has not yet began, all the measurements in this case are called matrix. For the 540 °C sample, very few faceted grains were observed, therefore, only the matrix value was obtained. For 600 °C sample, the overall volume percentage of the faceted grains are considerably large, as shown in Figure 3.17 (f), both the matrix and faceted grain hardness values were obtained.

Table 3.2 Microhardness values obtained for samples annealed at various temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Matrix HV</th>
<th>Faceted Grain HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>472.5</td>
<td>N/A</td>
</tr>
<tr>
<td>200 °C</td>
<td>495.6</td>
<td>N/A</td>
</tr>
<tr>
<td>320 °C</td>
<td>289.9</td>
<td>N/A</td>
</tr>
<tr>
<td>400 °C</td>
<td>265.6</td>
<td>N/A</td>
</tr>
<tr>
<td>540 °C</td>
<td>220.4</td>
<td>Very few</td>
</tr>
<tr>
<td>600 °C</td>
<td>194.8</td>
<td>134.2</td>
</tr>
</tbody>
</table>

Figure 3.17 Micrographs showing the location for micro-hardness measurements at various annealing conditions.

(a) As-received      (b) 200 °C      (c) 320 °C      (d) 400 °C
(e) 540 °C      (f) 600 °C      (g) 600 °C Grain  (h) 600 °C matrix
A slight increase was seen after annealing at 200 °C. Above 200 °C, higher temperature results in lower microhardness values. For samples annealed at 600 °C, the harness value of the faceted grain is significantly lower than that of the matrix. A closer observation on the surface around the microhardness indent on the faceted grown grain shows slip bands (Figure 3.18). This shows that these faceted grains exhibit considerable ductility.

*Figure 3.18 The occurrence of slip bands after microhardness indentation, indicating considerable potential for plastic deformation for these abnormally grown faceted grains.*

3.3.3 Rockwell Hardness

The Rockwell hardness measurements are shown in the following table. Similar to the microhardness measurements, a slight increase in the harness value was found after annealing at 200 °C. Samples became significant softer and extremely brittle after annealing above 320 °C. Figure 3.19 shows the cracking behaviour in the sample annealed at 320 °C. This is fairly consistent with the results obtained from tensile testing.
Table 3.3 Rockwell hardness values for samples annealed at various temperatures.

<table>
<thead>
<tr>
<th>Condition</th>
<th>HRC</th>
<th>HRB</th>
<th>Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>44.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>200 °C</td>
<td>46.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>320 °C</td>
<td>31.9</td>
<td>97.5</td>
<td>YES</td>
</tr>
<tr>
<td>400 °C</td>
<td>-</td>
<td>67.4</td>
<td>YES</td>
</tr>
<tr>
<td>540 °C</td>
<td>-</td>
<td>59.1</td>
<td>YES</td>
</tr>
<tr>
<td>600 °C</td>
<td>-</td>
<td>61.3</td>
<td>YES</td>
</tr>
</tbody>
</table>

Figure 3.19 Hardness measurements using both HRC and HRB scales were performed on the sample annealed at 320 °C. Cracking occurs indicates the material is extremely brittle.

3.3.4 Fracture Surface Analysis

The fracture surfaces of the miniature tensile bars were analyzed using SEM and a transition from ductile to brittle upon annealing was clearly shown. Figure 3.20 shows relatively low magnifications of the fracture surface of as-received and 200 °C samples. Both micrographs demonstrate necking and typical cup-and-cone macro-fracture phenomenon. Upon annealing at 320 °C, the sample shows brittle fracture. Figure 3.21 indicates that a crack may have been initiated at a point, most likely a processing defect. The material then fails through crack propagation. The red circle shown in Figure 3.21 indicates the site of crack initiation whereas the red arrow shows the direction of crack propagation.
Figure 3.20 Fracture surfaces of as-received and 200 °C samples, showing typical cup-and-cone macro-fracture phenomenon.

Figure 3.21 Fracture surface of 320 °C sample, indicating crack initiation and propagation.
At 600 °C, the microstructure of the material is in Stage III and exhibits a large volume of faceted grains. Upon fracturing, these faceted grains can be clearly detected (Figure 3.2). The shapes of these grains indicate that the facets belong to the family of \{100\} planes, as shown by the red circle in Figure 3.2. The clean breaks at grain boundaries also suggest a brittle type intergranular fracture.

*Figure 3.22 Fracture surface of 600 °C sample, showing intergranular fracture.*

To further study the fracture mechanism, higher magnification micrographs were taken (Figure 3.23). Again as-received and 200 °C samples show similar morphology. The fracture surfaces are appeared to be dimple-dominated. This indicates a considerable amount of plastic deformation before during the facture process. A transition occurred from 200 to 320 °C. Based on conventional TEM analysis, Stage I abnormal grain growth occurs at 320 °C. From SEM images, the microstructure became coarser, which might also indicate grain growth. By further increasing the temperature to 400 °C, individual grains become visible. This further confirms intergranular. In addition, for 600 °C samples, secondary cracks can be detected, shown by the red circle.
Figure 3.23 Higher magnification observations showing a ductile to brittle transition with increasing the annealing temperatures.

Figure 3.24 shows detailed micro-features on the grain-matrix interface. At relatively low magnification, we can see apparent separation at grain-matrix interface. Higher magnification shows that the faceted grain boundaries are very rough and contains many indents. Each of the indents is a result from the matrix grains.
Figure 3.24 SEM micrographs showing detailed micro features on the matrix and faceted grains on the fracture surface of 600 °C sample.
4 Discussions

4.1 Microstructure evolution

One of the major objectives in this study is to find out the microstructure evolution of nanocrystalline nickel produce by a method different from electrodeposition, i.e. electroforming. It has been shown that indeed, a multi-stage growth process exists. However, clarifications should be made on the microstructure changes in Stage I and Stage III.

4.1.1 Stage I Abnormal grain growth and possible growth mechanisms

Previous studies have shown the observation of abnormal grain growth characterized by nanocrystalline matrix and sub-micron grown grains. Similar behaviour was observed in the present study. In addition, this stage can be further divided into two sub-stages: 1) scattered and isolated grain growth and 2) massive discontinuous grain growth (Figure 4.1). Before the occurrence of the major heat release peak (< 250 °C), very little grain growth was observed, whereas massive abnormal grain growth did not occur till the onset of the major heat release peak. The microstructure was considered to be relatively uniform before the major heat release peak. It was found to be consisted of bimodal grain size distribution only at the maximum point of the heat release peak (320 °C). This demonstrates that the maximum amount of grain growth is associated with the most heat release.

DSC has been a common technique to evaluate the process of recrystallization in conventionally deformed materials such as copper and aluminum [43-45]. A peak is often detected during the recrystallization process. However, grain growth after recrystallization often do not give rise to a heat release peak in the DSC scan. In the case of nanocrystalline material, the process of discontinuous sub-grain grown is very similar to recrystallization, as explained in section 1.3.2. Due to the high energy associated with grain boundaries and triple junctions in nanocrystalline materials, the heat release peak detected in DSC scan may have resulted from the massive elimination of grain boundaries during grain growth.
Figure 4.1 Stage I abnormal grain growth can be divided into two sub-stages according to the DSC scan. Scattered and isolated grain growth before the occurrence of the major heat release peak, and massive discontinuous grain growth that gives the heat release peak (between 250 °C to 370 °C).

As introduced in section 1.4.2, as the grain size decrease into the nanometre range, the volume fracture of the intercrystalline components increases dramatically. Based on dark field TEM micrographs, the starting grain size of the as-received material is estimated to be 20 nm. The volume fracture of the intercrystalline components would be approximately 15% according to Figure 4.2. Upon the completion of Stage I, the grain size becomes in range of sub-micron to micrometres. Based on TEM micrographs, the grain size upon annealing at 400 °C is much larger than 200nm. Hence the volume fracture of the intercrystalline components becomes less than 1.5%. Further increase in grain size, from 200 nm to 2 for example, the change in intercrystalline volume would be almost negligible. Therefore, only when the initial grain size is very small, energy released by grain growth would be considerable large and able to be detected by DSC scans.
Figure 4.2 Changes in the volume fraction of intercrystalline components is very large only in the nanometre region, whereas in the sub-micron or micrometre range, the changes are negligible.

As introduced in section 1.3.1, abnormal grain growth is often a result of anisotropic boundary migration. Materials produced through a deposition process are likely to have textures. For example, it has been found that copper produced by the same electroforming technique has strong <110> fibre texture [47, 48]. Upon annealing, the material starts to develop a new texture which is <111>. Electrodeposited nanocrystalline Ni was also found to have <111> texture [29]. Grain boundary mobility for closely oriented grains is found to be smaller than that of grains with larger misorientations. With this in mind, the initial stage of grain growth could be a result of rotation of closely orientation nanocrystalline grains, forming large sub-grains. This could be the mechanism behind scattered and isolated grain growth observed at low temperature annealing (T = 20 °C). However, it needs to be realized the extent of grain growth due to geometrical constrains. With the elimination of certain grain boundaries due to rotation and coalescence, the orientation between other grains might be changed. With increasing temperature (T = 320 °C), rapid boundary migration of certain oriented grains results in abnormal grain growth.
4.1.2 Faceting behaviour during Stage III

Similar faceting behaviour during Stage III grain growth was observed in the present study. The facets are believed to be the family of {111} planes based on two reasons:

1. The SEM observation of the fracture surface of the sample annealed at 600 °C, indicates cuboidal shaped grains.

2. EBSD study on the boundary orientation in nanocrystalline electrodeposited nickel indicates the family of {111} planes [32]

Faceting is also a type of abnormal grain growth. In summary, it may be a resulted from two distinct mechanisms: anisotropic boundary energy and anisotropic boundary migration [48].

Facets or planar interface is a very interesting phenomenon found in a number of scenarios. For example, the exact same faceted cuboid of β’-SnSb compound was found in a matrix of Sn-rich material during crystallization [48]. This facet interface however is a solid/liquid interface. Similar to a solid/vapour interface, i.e. free surface, it resumes a structure that minimizes interfacial energy. The surface free energy arrives from the broken bonds due to missing neighbouring atoms at the free surface. For fcc structured materials, the three closest-packed planes are (111), (200), and (220). The number of broken bonds as well as interfacial energy increases through this series. By annealing a single crystal in an inert atmosphere, the equilibrium shapes of fcc crystals often assume a form showing {100} and {111} facets. The above consideration involves purely interfacial energy. The faceting behaviour observed in the crystallization of β’-SnSb is a kinetic/diffusional process.

Figure 4.3 Cuboid faceted grains observed during the crystallization of SnSb [48].
Another scenario where similar {100} plane faceting was observed is during the recrystallization process of Ni-0.03wt%Si [50]. In this case, the system is a lot similar to the present study which is a solid/solid interface. The recrystallization process is stimulated by impurity particles. Based on EBSD analysis, these facets were indeed parallel to the family of {100} planes, and there is no systematic relationship between the faceted grain and the matrix. When the material is fully recrystallized, the facets have disappeared and the grains are equiaxed. The author suggests that this faceting behaviour is primarily resulted from boundary migration and not boundary energy.

*Figure 4.4 Faceted grain growth in a particle stimulated recrystallization of nickel silicon alloy [50].*

The faceting behaviour observed in the present study is very similar to that of the particle simulated recrystallization of Ni. The facets were observed during the growth process. After annealing at 700 °C, the grains are equiaxed and non-crystallographic. In addition, the semi-in-situ method shows that the facets are non-mobile. This further confirms that the faceting is mainly due to boundary mobility.

### 4.1.3 The absence of faceting behaviour and delayed grain growth during In-Situ TEM

During conventional annealing, major abnormal grain growth occurs at 320°C, and a uniform grain size of approximately 1 – 2 µm was obtained in samples annealed at 500°C. The growth process during In-Situ TEM seemed delayed as the microstructure obtained at 500°C is
significantly finer, still in the nanometre-range. In conventional annealing, Stage III is initiated between the annealing temperatures of 500 °C and 540 °C. During In-Situ TEM observation, faceted grain growth did not occur even after annealing the sample at 600 °C for over 30 minutes. However, it is important to point out that the microstructure evolution appears to be in step-growth fashion. The growth process is extremely fast and changes occur in the range of microseconds. This is similar to the observations made in previous studies [51]. However, unlike previous study where growth occurs mainly by the advancing of abnormal growth fronts, the growth was observed to be random and uniform in this study.

The difference between conventional annealing and In-Situ TEM annealing lies in the sample thickness. For conventional TEM observation, the sample having the initial thickness of 1.5 mm was first annealed in a box furnace and then prepared into thin TEM samples. On the other hand, samples for In-Situ TEM were first prepared into thin disc in its as-received state, followed by annealing. As introduced in section 1.2, most of the as-deposited material exhibit residual stress. By grinding the TEM sample to a thickness of less than 100 nm, this stress is likely to be removed during the thinning process. Massive abnormal grain growth was observed during conventional annealing at 320 °C, whereas normal grain growth was observed during In-Situ TEM at temperatures above 500 °C. This indicates that the driving force for abnormal grain growth might the residual stress produced during the deposition process.

4.2 Mechanical behaviour

As introduced in section 1.2.4, comparisons were made between a number of mechanical properties of conventional and nanocrystalline nickel. However, it has to be pointed out that most studies on the mechanical properties were carried out using electrodeposited nickel which was thin films. In the present study, the mechanical properties were obtained using miniature tensile bars designed according to the standards of tensile testing. Therefore, the mechanical properties revealed in the present study would be more realistic.
4.2.1 Mechanical properties of as-received material

Figure 4.5a shows a number of engineering stress-strain curves obtained for electrodeposited materials under different plating conditions [52]. By increasing the pH values, the grain size of the as-deposited material decreases from 300 nm to 40 nm. The thicknesses of the samples were approximately 30 µm. It can be seen that for the material produced with a pH value of 4.67, it started to plastically deform at a stress greater than 600 MPa. The overall plastic strain is approximately 0.9%, and the material does not show a UTS. According to the stress-strain curve obtained in the present study, the yield stress is approximately 600 MPa, similar that in the previous study. In addition, the material shows uniform plastic deformation, UTS, necking, and failure. The overall plastic strain is more than 5%.

Figure 4.5 Stress-strain curves obtain for (a) electrodeposited nanocrystalline nickel with a thickness of approximately 30 µm [52] and (b) electroformed nano-grained nickel with a thickness of 1 mm.

4.2.2 Increasing elastic constant and yield upon annealing at 200 °C

A slight increase in the elastic constant and the yield stress is observed after annealing the sample at 200 °C. The same behaviour was observed in nanocrystalline nickel produced by electrodeposition [53]. The samples tested were approximately 120 µm in thickness. Upon annealing at 150 °C, the yield stress increased from 839 MPa to 920 MPa. The fracture surface
also showed similar morphology (Figure 4.6). For conventional pure metals, annealing always results in a reduction in the material’s strength. This is due to the removing of dislocations inside the grains. For nanocrystalline materials, dislocation sources are mainly at the grain boundaries instead of inside the grains. It has been suggested that annealing results in removing of these dislocations. As a result, available dislocation sources are depleted after annealing and the material is strengthened [53]. In addition, recalled that most materials produced through deposition technique exhibit residual stress or internal stress (section 1.2.1). Such stress maybe also released by annealing at low temperatures, very much like recovery. The small amount of isolated and scatter grain growth observed by TEM might be initiated at locations with relatively high stress and internal energy.

Figure 4.6 Fracture surface of (a) as-received electrodeposited nanocrystalline nickel, (b) 150 °C annealed, and (c) 300 °C annealed [53].

4.2.3 Brittleness introduced by annealing

Upon annealing the samples above 320 °C, the material becomes very brittle. Such brittleness was observed in a number of studies [52, 53]. Based on microhardness testing, faceted grains are very ductile indicated by the occurrence of slip bands after indentation. However, results from Rockwell hardness and tensile shows extreme brittleness. SEM micrographs show clear intergranular fracture. This indicates the weakening of grain boundaries after annealing. The reason behind this is not very clear. However it is believed that such weakening is a result of impurity segregation at grain boundaries. In the previous investigations, considerable amount of sulphur was detected. In the present study however, the amount of sulphur is very small, less
than 0.5%. Other than sulphur, minor traces of other elements including Silicon and Chlorine were detected.
5 Conclusion

In the present study, electroformed nano-grained nickel was investigated for its microstructure evolution and changes in mechanical properties upon annealing. A number of techniques including DSC, optical microscopy, TEM, semi-in-situ optical microscopy, and hot-stage in-situ TEM were used to analyze grain growth and mechanisms behind it. The main findings are summarized in the following points:

1. Although the material was processed with a method different from electrodeposition, a multi-stage growth process was indeed observed.

2. In addition, a new stage was found at low temperature annealing (< 250 °C), during which scattered and isolated abnormal grain growth was observed. Major abnormal grain growth described by Stage I in previous studies did not occur until the appearance of the major heat release peak at 320 °C. This indicates that the energy release was a result of massive grain growth and grain boundary eliminations.

3. An endothermic reaction was detected at 528 °C, at which Stage III appears whereby large faceted grains start forming. This minor peak has not been reported previously. Interestingly, the peak is endothermic and appeared only during the second run. This also suggests that the faceted grain growth is a continuous process.

4. Semi-in-situ optical observations showed that the faceted grain boundaries are very stable once formed, while grain growth occurred mainly on the non-faceted boundary fronts. It was also found that the growth occurred by the formation of sub-grains adjacent to the grown grain. These sub-grains were then merged with or “eaten” by the grown large grain.

5. Finally the hot-stage in-situ TEM showed delayed grain growth and very uniform grain growth. This indicates that the abnormal grain growth might be driven by the growth lattice strains. Such driving force for abnormal grain growth might have been removed during the process of TEM sample preparation as the material has become very thin.

6. In previous studies, the faceted grain boundaries were observed to migrate in a planar fashion and with high migration rates. In addition, a considerable amount of sulphur was
detected at these grain boundaries. It has been suggested that wetting of sulphur over these facet interface has caused such growth behaviour.

The mechanical behaviour of nano-grained nickel upon annealing at various temperatures were investigated by tensile testing, microhardness and Rockwell hardness. The fracture surface obtained through tensile testing was observed using SEM. The electroformed material in the present study is significantly thicker compared to electrod Deposited materials used in previous studies. Therefore, mechanical properties obtained through tensile testing were reflected more realistically.

7. After annealing at 200 °C, a slight increase was observed in the elastic constant, yield stress, and hardness of the material. This behaviour is opposite to conventional materials, and could be a result of removal of residual stresses in the as-electroformed material. A general trend of decreasing hardness with increasing annealing temperature was found at temperatures greater than 200 °C.

8. The material became very brittle after annealing at temperatures higher than 320 °C. This was demonstrated in tensile tests, Rockwell hardness tests, and SEM observation on fracture surfaces. The major factors detected on the fracture surface reveal the brittleness is caused by intergranular fracture.

9. It has been suggested by previous studies that this brittleness might be caused by sulphur segregation along grain boundaries. However very little sulphur (< 0.5 wt %) was found at faceted grain boundaries through STEM-EDX. Minor traces of silicon and chlorine was also found which could have caused embrittlement in the material. This might indicate the intrinsic low strength of the grain boundaries in the material.
6 Future Works

Up to this point, a number of problems still remain unsolved and can be further studied. These include the following:

1. The migration of the faceted grain boundaries during Stage III grain growth is very slow. This is totally opposite of the observations made before. Further investigation on the stability of faceted (planar) grain boundaries may be required.

2. If the faceted boundaries are indeed non-mobile, detailed investigation on the reasons behind it may be carried out. Alternatively methods may be used to detect the chemical composition of the material and impurity segregation at the faceted grain boundaries.

3. Determining the mechanisms that cause embrittlement in the material upon annealing at 320 °C.

4. The stability of the material upon deformation and cyclic deformation. Microstructure evolution or changes may be obtained through mechanical activation.
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Appendices

Appendix 1 DSC scans for obtained at heating rates of 10 °C/min and 20 °C/min.
Appendix 2 Optical micrographs showing the thickness cross-section of the electroform. The circumference cross-section shows the surface that is parallel to the circumference of the cone, whereas the longitudinal shows the vertical cross-section as demonstrated by the figure below.
Columnar structure adjacent to surface

Transition from surface to centre

Microstructure in the centre

Centre
Appendix 3 Optical Micrographs showing preliminary analysis on the microstructure evolution

Annealed at 300 °C

Annealed at 400 °C

Annealed at 500 °C

Annealed at 300 °C

Annealed at 400 °C

Annealed at 500 °C
Annealed at 300 °C

Annealed at 400 °C

Annealed at 500 °C
Annealed at 300 °C

Annealed at 400 °C

Annealed at 500 °C

Annealed at 500 °C
Appendix 4 TEM micrographs showing the microstructure of as-received sample and samples annealed 200 °C, 320 °C, 370 °C, and 400 °C.

As-received
As-received
200 °C
200 °C
$250 \, ^{\circ}C$
$320 \, ^\circ C$
320 °C
$370 \, ^\circ C$
370 °C
$400 \, ^\circ C$
400 °C
Appendix 5 Semi-in-situ tracking of faceted grain boundaries using optical microscopy. Annealing temperature is 550 °C

15 min.  

30 min.  

45 min.  

60 min.  

75 min.  

90 min.
Annealed for 30 min.

Annealed for 45 min.

Annealed for 60 min.
Annealed for 30 min.

Annealed for 45 min.

Annealed for 60 min.
Appendix 6 Hot-stage in-situ TEM micrographs

337 °C

345 °C

354 °C

362 °C
491 °C

520 °C

526 °C

525 °C - < 1 min.