STRUCTURE AND PROPERTIES OF ELECTRODEPOSITED NANOCRYSTALLINE NI AND Ni-FE ALLOY CONTINUOUS FOILS

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Department of Materials Science and Engineering
University of Toronto

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2013

ABSTRACT

This research work presents the first comprehensive study on nanocrystalline materials produced in bulk quantities using a novel continuous electrodeposition process. A series of nanocrystalline Ni and Ni-Fe alloy continuous foils were produced and an intensive investigation into their structure and various properties was carried out. High-resolution transmission electron microscopy (HR-TEM) revealed the presence of local strain at high and low angle, and twin boundaries. The cause for these local strains was explained based on the interpretation of non-equilibrium grain boundary structures that result when conditions of compatibility are not satisfied. HR-TEM also revealed the presence of twin faults of the growth type, or “growth faults”, which increased in density with the addition of Fe. This observation was found to be consistent with a corresponding increase in the growth fault probabilities determined quantitatively using X-ray diffraction (XRD) pattern analysis.

Hardness and Young’s modulus were measured by nanoindentation. Hardness followed the regular Hall-Petch behaviour down to a grain size of 20 nm after which an
inverse trend was observed. Young’s modulus was slightly reduced at grain sizes less than 20 nm and found to be affected by texture. Microstrain based on XRD line broadening was measured for these materials and found to increase primarily with a decrease in grain size or an increase in intercrystal defect density (i.e., grain boundaries and triple junctions). This microstrain is associated with the local strains observed at grain boundaries in the HR-TEM image analysis. A contribution to microstrain from the presence of growth faults in the nanocrystalline Ni-Fe alloys was also noted. The macrostresses for these materials were determined from strain measurements using a two-dimensional XRD technique. At grain sizes less than 20 nm, there was a sharp increase in compressive macrostresses which was also owed to the corresponding increase in intercrystal defects or interfaces in the solid.
ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to Professor Uwe Erb. His mentorship through learning, dialog, and challenge over the course of this research was exceptional. I’d like to especially thank Dr. Gino Palumbo, a distinguished individual in this field of scientific research and in the industry, who with no reservation opened the door and introduced me to the world of materials science and engineering. It was an honour to have Professor Emeritus Karl T. Aust’s involvement in this work since its inception. His inspiring support and encouragement over the course of my studies is truly appreciated. The guidance and support of my supervisory committee members, Professors Zhirui Wang, Doug D. Perovic, Nazir P. Kherani, and Glenn D. Hibbard are gratefully acknowledged. I would like to also acknowledge the past and present members of the Nanomaterials Research Group for the many insightful discussions and technical assistance, in particular, Dr. Yijian Zhou and Dr. Gordana Avramovic-Cingara. The technical expertise and assistance of Sal Boccia is also very much appreciated. Many thanks are owed to my co-workers at Integran Technologies, Inc. including: Francisco (Paco) Gonzalez, Jon McCrea, Iain Brooks, Peter Lin, Nandakumar Nagarajan, Andy Robertson, Dave Limoges, and Konstantinos (Gus) Panagiotopoulos. I would also like to thank my family and friends for their enduring support over the course of this long journey. Finally, I am indebted to my wife, Luciana, and our daughter, Ilaria. Their lasting patience over these trying years was instrumental in making this dream of mine a reality.
For my parents, Tonino & Joan.
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LIST OF SYMBOLS

\begin{align*}
A & \quad \text{Contact area} \\
A_{\text{RX}} & \quad \text{Radiocrystallographic anisotropy factor} \\
a & \quad \text{Lattice parameter; atoms} \\
a_0 & \quad \text{Equilibrium interatomic spacing value} \\
a_{hkl} & \quad \text{Lattice parameter of respective (hkl)} \\
B_{\text{inst}} & \quad \text{Full-width at half-maximum (FWHM) due to the instrument} \\
B_m & \quad \text{Experimentally measured full-width at half-maximum (FWHM)} \\
B_{\text{size}} & \quad \text{Full-width at half-maximum due to grain size} \\
B_{\text{strain}} & \quad \text{Full-width at half-maximum due to microstrain} \\
c_{ij} & \quad \text{Elastic stiffnesses} \\
C.G. & \quad \text{Center of gravity} \\
d & \quad \text{Grain size; interplanar spacing} \\
d_0 & \quad \text{Interplanar spacing of an unstrained lattice} \\
d_f & \quad \text{Final grain size} \\
d_{hkl} & \quad \text{Interplanar spacing for respective hkl} \\
d_i & \quad \text{Initial grain size} \\
E & \quad \text{Young’s modulus} \\
E_0 & \quad \text{Published Young’s modulus for polycrystalline materials} \\
E_g & \quad \text{Young’s modulus of the grain interior}
\end{align*}
\( E_{gb} \) Young’s modulus of the grain boundary

\( E_i \) Young’s modulus for the indenter

\( E_r \) Reduced Young’s modulus

\( E_{ij} \) Young’s modulus of triple junction

\( E_m \) Measured Young’s modulus

\( E_{VRH} \) Young’s modulus (Voigt-Reuss-Hill average)

\( e \) Free electrons

\( e^{-2M} \) Temperature factor

\( F \) Structure factor; bond force

\( F_a \) Attractive bond-force

\( F_r \) Repulsive bond-force

\( F_t \) Total bond-force

\( f \) Atomic scattering factor; interface stress

\( f_g \) Grain interior volume fraction

\( f_{gb} \) Grain boundary volume fraction

\( f_{ic} \) Total intercrystal volume fraction

\( f_{ij} \) Triple junction volume fraction

\( G \) Internal (free) energy; shear modulus

\( G_R \) Shear modulus (Reuss bound)

\( G_V \) Shear modulus (Voigt bound)
\( G_{VRH} \)  Shear modulus (Voigt-Reuss-Hill average)

\( H \)  Enthalpy (stored energy); hardness

\( h \)  Contact height provided by the depth-load data

\( h_c \)  Contact depth

\( h_f \)  Constant height determined by least squares fitting procedure

\( h_{\text{max}} \)  Peak (maximum) displacement

\( hkl \)  Miller indices

\( I \)  Relative intensity

\( I_{hkl} \)  Orientation index for respective \( hkl \)

\( i \)  Intensity of diffraction line

\( i_{hkl} \)  Intensity of diffraction line for respective \( hkl \)

\( K \)  Bulk modulus

\( K_R \)  Bulk modulus (Reuss bound)

\( K_V \)  Bulk modulus (Voigt bound)

\( K_{VRH} \)  Bulk modulus (Voigt-Reuss-Hill average)

\( L \)  Camera length

\( l_i \)  Direction cosines

\( m \)  Constant determined by a least squares fitting procedure

\( N \)  Plant normal direction

\( n \)  Order of reflection

\( P \)  Point on a given \( \{hkl\} \) diffraction ring
P'  Point on a given \{hkl\} diffraction ring from corresponding diffraction vector

P  Load

P_0  Constant load determined by least squares fitting procedure

P_{\text{max}}  Peak (maximum) load

p  Multiplicity factor

p_{ij}  Stress coefficients

p_{ph}  Pseudo-hydrostatic stress coefficient

R  Radius of diffraction ring

S  Measured stiffness, entropy

s_{ij}  Elastic compliances

T  Absolute temperature

T_c  Curie temperature

T_p  Peak temperature

U  Bond-energy

U_a  Attractive bond-energy

U_r  Repulsive bond-energy

U_t  Total energy

V  Valency of an atom

x  Atom fraction of the solute; two-body separation
Greek Symbols

\( \alpha \)  
bcc (body-centered cubic) crystal

\( \beta \)  
Growth fault probability

\( \gamma \)  
Angle; fcc (face-centered cubic) crystal

\( \gamma_{gb} \)  
Grain boundary energy

\( \overline{\gamma}_{gb} \)  
Average grain boundary energy

\( \gamma_{sv} \)  
Free surface energy

\( \Delta \)  
Grain boundary thickness

\( \Delta \rho \)  
Increment in electrical resistivity

\( \Delta C.G. \)  
Displacement of the center of gravity

\( \Delta d \)  
Change in interplanar spacing

\( \Delta f_{ic} \)  
Change in intercrystal volume fraction

\( \Delta G \)  
Change in internal (free) energy resulting from cold work

\( \Delta H \)  
Change in enthalpy (stored energy)

\( \Delta H_{ic} \)  
Excess interfacial enthalpy

\( \Delta H_{total} \)  
Change in total enthalpy (stored energy)

\( \Delta P \)  
Power difference

\( \Delta S \)  
Change in entropy increase due to cold work

\( \Delta V \)  
Difference in valency of the solute and solvent atoms

\( \epsilon \)  
Microstrain due to \( \Delta d / d \); depth potential well

\( \epsilon_{ij} \)  
Strain components

\( \epsilon_n \)  
Strain in the plane normal direction
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta )</td>
<td>Anisotropy factor</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Diffraction angle</td>
</tr>
<tr>
<td>( \theta_0 )</td>
<td>Diffraction angle corresponding to an unstrained lattice</td>
</tr>
<tr>
<td>( \theta_{hkl} )</td>
<td>Angle for the ((hkl)) diffraction peak</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Poisson ratio</td>
</tr>
<tr>
<td>( \nu_i )</td>
<td>Poisson ratio for the indenter</td>
</tr>
<tr>
<td>( \pi )</td>
<td>Pi (mathematical)</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Internal stress; pair separation</td>
</tr>
<tr>
<td>( \sigma_{ij} )</td>
<td>Internal stress components</td>
</tr>
<tr>
<td>( \sigma_{ph} )</td>
<td>Pseudo-hydrostatic stress component</td>
</tr>
<tr>
<td>( \phi )</td>
<td>Angle of measurement</td>
</tr>
<tr>
<td>( \chi )</td>
<td>Angle of measurement</td>
</tr>
<tr>
<td>( \psi )</td>
<td>Angle of measurement</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Angle of measurement</td>
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</tbody>
</table>
## LIST OF ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>2D-XRD</td>
<td>Two-dimensional X-ray diffraction</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>bcc</td>
<td>Body-centered cubic</td>
</tr>
<tr>
<td>BF</td>
<td>Bright-field</td>
</tr>
<tr>
<td>DF</td>
<td>Dark-field</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transform</td>
</tr>
<tr>
<td>FPA</td>
<td>Fundamental parameter approach</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width at half-maximum</td>
</tr>
<tr>
<td>GADDS</td>
<td>General area detector diffraction system</td>
</tr>
<tr>
<td>GFP</td>
<td>Growth fault probability</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal close-packed</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IFFT</td>
<td>Inverse fast Fourier transform</td>
</tr>
<tr>
<td>MDSC</td>
<td>Modulated differential scanning calorimetry</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SAD</td>
<td>Selected area diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking fault energy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>VHN</td>
<td>Vickers hardness number</td>
</tr>
<tr>
<td>VRH</td>
<td>Voigt-Reuss-Hill</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
CHAPTER 1
Introduction

1.1. Background and Motivation for Study

Nanocrystalline materials are of great interest since they can have enhanced, diminished, or strikingly similar characteristics when compared to their conventional polycrystalline counterparts. When the grain size is reduced sufficiently below 100 nm, certain structurally sensitive characteristics are greatly enhanced, e.g., yield strength, hardness, and wear resistance, while electrical conductivity is diminished [Erb et al. (2007)]. Hardness, in particular, obeys the Hall-Petch relationship down to about 20 nm, however a unique phenomenon occurs at grain sizes less than 20 nm where a deviation from the expected behaviour is observed. This deviation is due primarily to a change in deformation mechanisms [Chokshi et al. (1989), Palumbo et al. (1990), Wang et al. (1997)]. On the other hand, structurally insensitive characteristics tend to remain similar over a wide grain size range, e.g., Young’s modulus, magnetic saturation, heat capacity, and thermal expansion [Erb et al. (2007)]. The Young’s modulus of nanocrystalline materials produced by compaction of inert gas condensed precursor powders was initially reported to have significant reductions (>50%), e.g., Nieman et al. (1991). However, this synthesis technique is known to produce materials with a substantial amount of porosity that was eventually considered to be an artifact causing the observed reductions in Young’s modulus [Krstic et al. (1993), Zugic et al. (1997)]. Thus, it is extremely important that the synthesis method be taken into consideration when studies are performed and conclusions are made. The electrodeposition technique is an example of a process which is known to produce negligible amounts of porosity, e.g., nanocrystalline Ni [Van Petegem et al. (2003)] and Ni-2.5wt.%P [Zhou et al. (1997)].
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(2009)]. As a result, only small deviations are observed in the Young’s modulus for electrodeposited materials [Zhou et al. (2003a), Zhou et al. (2003b), Zhou et al. (2009)].

In general, electrodeposited nanocrystalline materials are of significant commercial importance [Palumbo et al. (2003), McCrea et al. (2011)]. In particular, the nanocrystalline Ni-Fe alloys have many interesting properties. For example, at approximately 20 wt.%Fe, an alloy commonly known as permalloy possesses unique soft magnetic properties including a high magnetic permeability and a low coercivity. However, certain microstructural defects may affect these properties. In conventional polycrystalline Ni-Fe alloys, plastic deformation introduces internal stresses which can bring about negative effects on certain magnetic properties. Electrodeposited nanocrystalline materials have similar magnetic saturation when compared to their polycrystalline counterparts [Aus et al. (1992), Aus (1999)], but other properties such as coercivity are affected by grain size [Herzer (1995)]. Aus (1999) reported a decreasing coercivity trend with increasing Fe in electrodeposited nanocrystalline Ni-Fe alloys which is similar to that reported for their large grain polycrystalline counterparts [Marsh (1938), Bozorth (1978)]. However, the coercivity values for the nanocrystalline Ni-Fe alloys were noticeably higher, even when no plastic deformation had been imposed on the material. A limited understanding for this observation provokes the need for more study on this subject and related matters, including the influences of processing, microstructure, and internal stresses.

In many respects, electrodeposited nanocrystalline Ni and Ni-Fe alloys have been studied quite extensively [Erb et al. (2007)]. All of these studies have been based on
materials that have been produced as individual coupons in a batch-wise manner using a standard electroplating set-up, namely with a stationary cathode. A novel technique for producing continuous electrodeposited nanocrystalline metal and metal matrix composite foils for use in various applications has the advantage of being able to yield bulk quantities of material with practically unlimited length [Palumbo et al. (2005)]. This also proves to be a commercially viable method and serves to fulfill demand in an economical and efficient manner. Due to the nature of the continuous deposition process, i.e., a rotating circular cathode which is also referred to as a “drum”, therein lies various questions around the effects of this method on the structure and properties of the materials produced. Therefore, studies are necessary on materials produced using this technique.

In general, there are still some characteristics and properties of these materials which require an advanced understanding. Microstructural studies on electrodeposited nanocrystalline materials have often been limited to the X-ray diffraction (XRD) and conventional transmission electron microscopy (TEM) methods. Only a few studies have used high-resolution transmission electron microscopy (HR-TEM) with a narrow scope to examine the microstructure of electrodeposited nanocrystalline materials. For example, Mehta et al. (1995) reported the presence of low angle grain boundaries and twin boundaries in electrodeposited nanocrystalline Ni and Ni-1.2wt.%P. However, the grain boundary characteristics were not studied in great detail. Mehta et al. (1995) also investigated the presence of lattice defects and noted that electrodeposited nanocrystalline Ni and Ni-1.2wt.%P had very few dislocations and thus, the dislocation density in these materials is considered to be very low. The presence of other lattice defects in these materials, for
example, stacking faults, still remains to be analyzed. Since the addition of Fe to Ni in the fcc phase is known to decrease the stacking fault energy [Charnock and Nutting (1967)], stacking faults are likely to be present. Although the presence of stacking faults has been reported in electrodeposited nanocrystalline Ni and Ni-Fe alloys [Yang et al. (2009), Wu et al. (2006), Ebrahimi and Li (2003)], an in-depth analysis on both a qualitative and quantitative basis is still necessary. In general, additional information on grain boundary characteristics and lattice defects can lead to a better understanding of their possible effects on various material properties and behaviour.

The indentation behaviour of these electrodeposited nanocrystalline materials, e.g., hardness and Young’s modulus, has been studied in some detail. The hardness of nanocrystalline Ni was studied by El-Sherik et al. (1992) who observed a noticeable deviation from the regular Hall-Petch relationship. Nanocrystalline Ni-Fe alloys were also studied by Cheung et al. (1995) who showed a similar deviation from the regular Hall-Petch relationship but also noted that these changes were not due to any solid solution strengthening effect. Rather, the deviation from the Hall-Petch relationship is considered to be a result of a change in the dominant deformation mechanism [e.g., Chokshi et al. (1989)]. In the case of Young’s modulus, only electrodeposited nanocrystalline Ni-2.5wt.%P has been studied systematically with grain size [Zhou et al. (2003a), Zhou et al. (2003b)]. There remains the opportunity to also systematically study the Young’s modulus of electrodeposited nanocrystalline Ni and Ni-Fe alloys. In addition to the effect of grain size, alloying may also be taken into consideration along with other potentially influential factors such as anisotropy. Additionally, the potential effects of internal stresses on the properties of
these nanocrystalline materials should also be considered. For example, it has been suggested by Cammarata and Eby (1991) that the strains which result from decreasing grain size and the corresponding effect of interface stresses can produce higher order elastic effects. That is, very fine grained materials may have slightly reduced Young’s moduli if internal stresses are present.

Electrodeposition processes typically produce materials that have some degree of internal stress [Schlesinger and Paunovic (2000)]. These internal stresses may be analyzed on both a microscopic and a macroscopic scale. For example, there are several studies which consider the effect of grain size on microstrain (or microstress) for electrodeposited Ni [Mishra et al. (2004), Wang (1997)] and Ni-Fe alloys [Li and Ebrahimi (2003)]. Generally speaking, microstrain results from atomic scale imperfections, e.g., dislocations, vacancies, grain boundaries, voids, inclusions [Macherauch and Kloos (1987)], which induce XRD line broadening or a detectable non-uniform strain [Cullity and Stock (2001)]. For nanocrystalline materials, various studies have shown that microstrain clearly increases with decreasing grain size, especially at less than 20 nm [e.g., Li and Ebrahimi (2003), Qin and Szpunar (2005)]. The nature of this microstrain has been related to observable local strains at grain boundaries using HR-TEM, e.g., for nanocrystalline Pd produced the inert gas condensation technique [Wunderlich et al. (1990)]. A systematic study over a broad grain size range to determine microstrain from XRD line broadening combined with an investigation on the grain boundary characteristics of electrodeposited nanocrystalline materials has yet to be carried out. In addition to this, an investigation on the presence of
lattice defects, such as stacking faults, may also reveal a contribution to microstrain induced XRD line broadening.

Macroscopic stresses (macrostresses) are manifested over large distances or many grains. These macrostresses cause shifting of the characteristic XRD lines [Macherauch and Kloos (1987)], or a detectable uniform strain [Cullity and Stock (2001)]. There are only a few studies which provide some insight into a microstructural relationship with macrostress. For example, in an investigation on electrodeposited nanocrystalline Ni-Fe, Czerwinski (1996) established a relationship between grain size and macrostress in Fe-Ni alloy deposits (15wt.%Ni): a decrease in grain size is accompanied by a rise in macrostresses. The technique used in this study was the “bent-strip” method [Kouymdjiev (1985)] which is inexpensive and thus, quite popular in practice. However, this method has often produced results which are inconsistent from study to study. On the other hand, XRD methods are rarely used in practice, yet they offer the advantage of being substantially more accurate and consistent. El-Sherik et al. (2005) used an XRD method to measure the macrostress in electrodeposited nanocrystalline Ni (10 nm) and compared it with a large grain electrodeposited Ni (5000 nm) to find that the nanocrystalline electrodeposit had a macrostress which was about six times greater. A systematic study with grain size that covers a broad range using an XRD technique can provide a more accurate and consistent means to experimentally decipher a structure-macrostress relationship.

1.2. Research Objectives

The research objectives of this study are based on the current opportunities for the
contribution of knowledge in this field. The synthesis technique employed in this study to produce the nanocrystalline Ni and Ni-Fe alloys was electrodeposition of foils in a continuous process. Using these materials, an intensive investigation into certain characteristics and properties was carried out. The main research objectives were:

1. To synthesize a series of nanocrystalline Ni and Ni-Fe alloy foils spanning a broad grain size range using a novel continuous electrodeposition technique [Palumbo et al. (2005)].

2. To characterize the series of nanocrystalline Ni and Ni-Fe alloys using X-ray diffraction (XRD), conventional and high-resolution transmission electron microscopy (HR-TEM), and thermal analysis. In particular, an attempt was made to divulge as much microstructural information as possible using HR-TEM for the purpose of assessing possible relationships with the behaviour of these materials.

3. To determine the hardness and Young’s modulus of these materials using the nanoindentation technique. In particular, Young’s modulus was studied extensively for any effect related to grain size and other possible influencing factors, such as alloying with Fe and anisotropy.

4. To determine the microstrain in these materials and evaluate the relationship with grain size. Additionally, to determine if there are other possible influencing factors, including lattice defects such as stacking faults which can arise from alloying with Fe.
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5. To systematically determine the macrostresses from strain measurements using a two-dimensional (2D) XRD technique as a function of grain size and investigate the origins of these macrostresses in electrodeposited nanocrystalline materials.
1.3. References


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CHAPTER 2
Literature Review

2.1. Electrodeposited Nanocrystalline Metals and Alloys

2.1.1. Synthesis

There have been many reports describing electrodeposits with ultra-fine structure [Safranek (1986), Schlesinger and Paunovic (2000)]. However, no systematic studies were published before the late 1980’s on the synthesis of nanocrystalline materials using the electrodeposition technique. This was the motivation for McMahon and Erb (1989) to carry out such investigations on electrodeposited nanocrystalline Ni-P alloys which eventually led to the identification of a process (Fig. 2.1) by Erb and El-Sherik (1994) and Erb et al. (1995) to electrodeposit a wide range of nanostructured metals and alloys with control over the grain size for the purpose of optimizing material properties.

Figure 2.1. Electrochemical processing of nanocrystalline metals and alloys: (1) plating cell, (2) electrolyte, (3) anode, (4) ammeter, (5) power source, (6) cathode, (7) transistered switch, (8) wave generator, (9) oscilloscope, and (10) constant temperature bath [Erb et al. (1995)].
In this process, deposit growth conditions are controlled to favour massive nucleation regardless of coating thickness. These deposits show no cross-sectional structure transition from fine-grained-equiaxed to coarse-grained columnar structure with strong grain shape anisotropy, as in the case of conventional electrodeposits [Erb et al. (2007)]. In conventional electroplating, the deposit shows considerable gradients (through the thickness) in grain shape and size with most final grain sizes being larger than 1 μm (Fig. 2.2a). If the plating parameters are chosen such that massive crystal nucleation dominates over the crystal growth competition at any given stage in the plating process, a nanocrystalline structure over the entire thickness can be obtained (Fig. 2.2b).

Figure 2.2. Cross-sectional structure of (a) conventional and (b) nanocrystalline electrodeposits [Erb et al. (2007)].

2.1.2. Structure of Fully Dense Nanocrystals

Gleiter (1989) first expressed the basic ideas surrounding the structure of nanomaterials where he recognized that large volume fractions of grain boundaries exist in materials with very small grain sizes. In particular, for grain sizes less than 20 nm, the grain
boundary component can reach large volume fraction values. Fig. 2.3 shows a schematic diagram of the atomic structure of a two-dimensional nanocrystalline material.

Figure 2.3. Schematic diagram of a two-dimensional structure of nanocrystalline materials [Gleiter (1989)].

The boundary core regions (open circles in Fig. 2.3) are characterized by a reduced atomic density and interatomic spacings deviating from the ones of a perfect lattice (black circles). Using a three-dimensional treatment involving tetrakaidecahedral grains (Fig. 2.4a), Palumbo et al. (1990) presented a detailed calculation showing the variation of the total intercrystal volume fraction, $f_{ic}$, consisting of grain boundaries, $f_{gb}$, and triple junctions, $f_{tj}$, as a function of grain size, $d$ (Fig. 2.4b). The volume fractions were calculated by using a grain boundary thickness, $\Delta$, of 1 nm,

$$f_{ic} = 1 - \left[ \frac{(d - \Delta)}{d} \right]^3$$  \hspace{1cm} (2-1)

$$f_{gb} = \frac{3\Delta(d - \Delta)^2}{d^3}$$  \hspace{1cm} (2-2)

$$f_{tj} = f_{ic} - f_{gb}$$  \hspace{1cm} (2-3)
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The intercrystal volume fraction \( f_{ic} \) increases from a value of 0.3% at 1000 nm to more than 50% at grain sizes less than 5 nm. The triple junction volume fraction \( f_{tj} \) displays a stronger grain size dependence when compared to the grain boundary volume fraction \( f_{gb} \).

In the range of 100 nm to 2 nm, the triple junction volume fraction increases by three orders of magnitude, while the grain boundary volume fraction increases by a little over one order of magnitude.

![Tetrakaidecahedral grains](image1.png)

![Effect of grain size on volume fractions](image2.png)

Figure 2.4. (a) Tetrakaidecahedral grains, (b) effect of grain size on calculated volume fractions of intercrystal regions, grain boundaries and triple junctions, assuming a grain boundary thickness of 1 nm [Palumbo et al. (1990)].

2.1.3. Properties

2.1.3.1. Hardness

Nanocrystalline Ni produced by electrodeposition was first studied systematically by El-Sherik et al. (1992). They found that grain refinement of electroplated Ni (<100 nm) resulted in unique and improved properties when compared to conventional polycrystalline
Ni. For example, the hardness of the electrodeposited Ni ranges from about 150 VHN for deposits with \( \sim 100 \mu m \) grain size to about 650 VHN at 10 nm [El-Sherik et al. (1992)]. At grain sizes less than 30 nm, a noticeable deviation from the regular Hall-Petch relationship was observed (dashed line in Fig. 2.5). This deviation was considered to be an effect of increasing grain boundary and triple junction volume fractions similar to that described by McMahon and Erb (1989) in their study of nanocrystalline Ni-P alloys, and consequently, differences in deformation mechanisms.

![Figure 2.5](image)

**Figure 2.5.** Hardness as a function of \( d^{-1/2} \) for as-prepared nanocrystalline Ni electrodeposits [El-Sherik et al. (1992)].

Cheung et al. (1995) developed an electroplating bath which could be used to produce nanocrystalline Ni-Fe alloys (0-28 wt.%Fe) in bulk form. Using X-ray diffraction, it was found that deposits in the range of Fe concentration studied preserved the face-centered cubic (fcc) structure. The grain size was measured using the Scherrer XRD line broadening
technique [Cullity and Stock (2001)] and found to decrease with increasing Fe concentration (Fig. 2.6). Grimmett et al. (1993) in an earlier study and Li and Ebrahimi (2003) in a later study found similar correlations.

Figure 2.6. Effect of Fe concentration on the grain size of electrodeposited nanocrystalline Ni-Fe alloys [Cheung et al. (1995)].

The Vickers microhardness was measured as a function of Fe concentration and compared to conventional polycrystalline materials [Cheung et al. (1995)] as shown in Fig. 2.7. The hardness of conventional polycrystalline Ni is reported to be 85 VHN and as the Fe concentration increases the hardness essentially remains constant up to 51 wt.%Fe. The hardness of the nanocrystalline counterpart, on the other hand, increases from 490 VHN to 625 VHN at 17 wt.%Fe and then decreases to about 580 VHN at 28 wt.%Fe.
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Figure 2.7. Microhardness of electrodeposited nanocrystalline and conventional polycrystalline Ni-Fe alloys as a function of Fe concentration [Cheung et al. (1995)].

Figure 2.8. Hall-Petch plot for electrodeposited nanocrystalline Ni-Fe alloys showing transition from regular to inverse Hall-Petch behaviour [Cheung et al. (1995)].
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The observed variation in microhardness cannot be explained by solid-solution strengthening and therefore the grain size was considered using a Hall-Petch plot [Cheung et al. (1995)], as shown in Fig. 2.8. Initially, decreasing the grain size increased the microhardness to a peak value of 625 VHN (average grain size, 14 nm) and then decreased with further decrease in grain size leading to an inverse Hall-Petch behavior similar to that observed in other nanocrystalline materials produced by electrodeposition [McMahon and Erb (1989), El-Sherik et al. (1992)]. Similar results were found in a later study by Li and Ebrahimi (2003).

2.1.3.2. Young’s Modulus

The earliest studies on the influence of grain size on the Young’s modulus produced inconsistent and often conflicting results. Significant reductions (>50%) of Young’s modulus were observed in nanocrystalline materials produced by compaction of inert gas condensed precursor powders, e.g., Nieman et al. (1991). However, this synthesis technique is conducive to producing materials with a substantial amount of porosity [Krstic et al. (1993), Zugic et al. (1997)]. The effect of porosity is illustrated in Fig. 2.9 which shows a plot of the normalized Young’s modulus, $E_m / E_0$, where $E_m$ is the measured Young’s modulus value and $E_0$ is the published value for the polycrystalline counterpart, as a function of grain size [Zhou et al. (2003b)]. Two regions are defined in Fig. 2.9: Region I (materials with negligible porosity) and Region II (materials which contain considerable porosity).

Shen et al. (1995) measured the Young’s modulus using nanoindentation over a large grain size range of fully dense nanocrystalline Fe produced by mechanical milling/alloying
Figure 2.9. Compilation of normalized Young’s modulus $E / E_0$, where $E$ is the measured Young’s modulus value and $E_0$ is the published value for the polycrystalline counterpart, as a function of grain size [Zhou et al. (2003b)].

and showed that the Young’s modulus values between 80 and 20 nm are practically the same as for polycrystalline material. Only smaller grain sizes (< 20 nm) revealed some reductions up to about 6%. Shen et al. (1995) also suggested that the effect of the intercrystal defects can be estimated by using a simple rule of mixtures taking into consideration three main components: grain boundary ($E_{gb}$), triple junction ($E_t$), and grain interior ($E_g$). The volume fraction is dependent on the grain size, $d$, grain boundary thickness, $\Delta$, and grain shape based on Eq. 2-1, 2-2, and 2-3 [Palumbo et al. (1990)]. Zhou et al. (2003a,b) studied fully dense nanocrystalline Ni-P alloys produced by electrodeposition with decreasing grain size from about 30 to 4 nm and in the same manner as Shen et al. (1995), they considered the effect of increasing intercrystal volume fraction with decreasing grain size due to grain
boundaries and triple junctions. Below 20 nm, a continuous but very gradual decrease in the Young’s modulus was observed down to about 86% of the value for polycrystalline Ni at a grain size of 4 nm (see Fig. 2.10). This reduction was explained in terms of the sharp increase in grain boundary and triple junction volume fractions. Using the composite model suggested by Shen et al. (1995) and Young’s modulus values for materials with different grain sizes, calculations by Zhou et al. (2003a) showed that $E_g = 204$ GPa, $E_{gb} = 184$ GPa and $E_{tj} = 143$ GPa. The reduced Young’s modulus values for the grain boundaries ($E_{gb}$) and triple junctions ($E_{tj}$) may be attributed to the increase in free volume in the interfacial region (see Fig. 2.3). Assuming the same interatomic force and bonding curves in the interfacial region as in a perfect crystal lattice, the increase in interatomic spacing would result in a lower Young’s modulus. This hypothesis was further studied by Zhou et al. (2009) by
positron annihilation spectroscopy. The measurements showed that there are indeed excess free volumes in the grain boundaries and triple junctions which are smaller than a vacancy in a perfect lattice.

Another important factor that is known to influence Young’s modulus is the preferred crystallographic orientation, or texture. The Young’s modulus of conventional electroplated Ni has been measured by several authors [e.g., Mazza et al. (1996), Sharpe et al. (1997), Cho et al. (2003)], however a rather large range of values were obtained (160 to 247 GPa). Fritz et al. (2003) also measured the Young’s modulus using different measuring techniques including the laser-acoustic method, instrumented microindentation, and resonance frequency of laterally and vertically swinging cantilevers. They also found a large range of Young’s modulus values and on closer examination the variability was attributed to the texture of the electrodeposited Ni. The lower values corresponded to (100) textured electrodeposits while a higher value corresponded to a nearly isotropic Ni or weak (110) textures. Torrents et al. (2010) studied the effect of annealing on the Young’s modulus of nanocrystalline Ni. As-received electrodeposited nanocrystalline Ni samples were annealed at a series of different temperatures ranging from 323 to 693 K. After annealing, the samples were rapidly cooled in air and then characterized. In this particular case, an increasing Young’s modulus with increasing anneal temperature was attributed to the preferred orientation along the [200] direction that was observed in the as-received samples which continuously diminished with increasing temperature. Auerswald and Fecht (2010) produced a series of nanocrystalline Ni-W samples using different inhibitors to evaluate their effectiveness at minimizing internal stress. The Young’s modulus for each of the samples was also measured using
nanoindentation. The highest values were consistent with the sample that had a predominant (111) texture.

2.1.4. Release of Stored Energy

Due to the high concentration of interfacial defects in nanocrystalline materials, there is strong driving force for grain growth which makes the structure unstable at elevated temperatures. Therefore, the thermal stability of nanocrystalline materials is a matter of importance since it may impose a limit on the number of possible applications. Reviews on the thermal stability of nanocrystalline electrodeposits are given by Hibbard et al. (2002), Aust et al. (2003) and Aust et al. (2004). Thermal stability is often studied using anisothermal annealing methods, such as differential scanning calorimetry (DSC) or modulated differential scanning calorimetry (MDSC). These methods allow for a thorough study of the release of stored energy in the material. The release of stored energy corresponds to the area under the anisothermal anneal curve which is developed during the analysis.

In conventional polycrystalline metals energy is normally stored after they are cold worked. Most of the cold work is expended in the form of heat; however, during the cold working process a fraction of the work is stored as strain energy which corresponds to lattice defects created during the deformation process. When cold worked metals are annealed they normally go through a transformation process in three stages: 1. recovery, 2. recrystallization, and 3. grain growth. During the recovery process some of the stored energy is relieved by dislocation reconfiguration. The result is some reduction in dislocation density and/or
dislocation rearrangements and an overall lower stored or strain energy. Even when this is complete, the grains are still in a relatively high strain energy state. The next stage – recrystallization – results in the formation of a new set of strain-free and, usually, equiaxed grains. The driving force to achieve this new structure is simply the difference in internal energy between the strained and unstrained material. It is also at this point that the mechanical properties of the metal are restored to the pre-cold worked state. Finally, if left at elevated temperatures, the strain-free grains will grow during the process of grain growth. The driving force for grain growth is the reduction of the total grain boundary energy of the system.

When compared to an unstrained metal, the internal (free) energy of a strained metal, is approximately equal to the stored energy. Cold work increases the entropy of a metal, however it is small when compared to the increase in internal energy and thus, the $-T\Delta S$ term is negligible. Therefore,

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (2-4)

becomes,

$$\Delta G \approx \Delta H$$  \hspace{1cm} (2-5)

where, $\Delta G$ is the free energy resulting from the cold work, $\Delta H$ is the enthalpy, or stored energy, $S$ is the entropy increase due to the cold work, and $T$ is the absolute temperature [e.g., Reed-Hill and Abbaschian (1994)]. An example of one of the earlier studies on the release of stored energy in a cold worked polycrystalline metal was that of Clarebrough et al. (1955), who subjected cold worked Ni to an anisothermal heat treatment at 6°C/min (see Fig. 2.11). They defined three distinct heat release regions:
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$A(a')$ – disappearance of vacancies into the dislocations forming sub-grain boundaries; no change in hardness, slight decrease in electrical resistivity.

$A(a') + B$ – movement of dislocations from within grains into the boundary regions, mutual annihilation of dislocations of opposite sign (dislocation annihilation), and rearrangement of the dislocations into configurations of lower energy (dislocation polygonization); no change in hardness, slight decrease in electrical resistivity.

$C$ – recrystallization; rapid decrease in hardness and electrical resistivity.

---

Figure 2.11. Power difference ($\Delta P$), increment in electrical resistivity ($\Delta \rho$), and hardness (VHN) for specimens of polycrystalline Ni deformed in torsion and heated at 6°/min [Clarebrough et al. (1955)].

When nanocrystalline Ni is anisothermally annealed it exhibits heat releases that are not necessarily due to the same types of heat release events when compared to cold worked conventional polycrystalline Ni. A typical nanocrystalline Ni anisothermal anneal curve is
shown in Fig. 2.12 [Klement et al. (1995a)]. The maximum heat release in the anisothermal anneal curve is referred to as the peak temperature, \( T_p \), and can be used as a relative measure of the thermal stability.

![Anisothermal anneal curve (DSC) of a 10 nm electrodeposited Ni sample at a heating rate of 10 °C/min](image)

Figure 2.12. Anisothermal anneal curve (DSC) of a 10 nm electrodeposited Ni sample at a heating rate of 10 °C/min [Klement et al. (1995a)].

The \( \Delta H \) (area under the curve) can be used to determine the interfacial enthalpy if the grain sizes and shapes of the initial nanostructure and the final structure after grain growth are known. The \( \Delta H \) for the total heat release in Fig. 2.12 was found to be about 18 J/g which is in good agreement with measurements of other materials such as nanocrystalline Pd where a 16 J/g heat release was found [Rupp and Birringer (1987)]. Klement et al. (1995a) and Klement et al. (1995b) described the three distinct exothermic reactions shown in Fig. 2.12 in the following manner:

1. “nucleation” and abnormal grain growth induced by sub-grain coalescence (80-289°C)
(2) normal grain growth process (289-370°C)

(3) growth towards equilibrium (370-500°C)

In the first stage, the formation of the first grown grains may be explained by a combination of a relaxation and the subgrain coalescence model known from primary recrystallization [Hu (1963), Li (1962)]. Further to this, Rupp and Birringer (1987) suggested that a relaxation of the nanocrystalline microstructure takes place at a sufficiently high temperature. This relaxation leads to positions of “lower energy” for the grain boundaries creating the first grown grains “accidentally” by removing low angle grain boundaries. These three events are considered to be the major contributors to the observed heat releases, however there may be other factors involved such as the influence of impurities. In particular, S and C tend to be present in significant quantities in electrodeposited Ni. Klement et al. (1995a) investigated the influence of S and concluded that there is likely a significant enrichment of S in the grain boundaries which may hinder the formation of larger grains with boundaries in equilibrium positions and diminishes the third exothermic stage of the anisothermal anneal curve. Unfortunately, they were not able to determine the influence of C which is also present in nanocrystalline Ni. Similar DSC curves for annealed nanocrystalline Ni were later presented by Wang et al. (1997) and Hibbard et al. (2002).

2.2. **Internal Stress**

2.2.1. Overview

In conventional metals, internal stresses may be introduced by various means. These stresses are normally present when regions of the material are inhomogeneously elastically or plastically deformed in a permanent manner such that strain incompatibilities occur. Internal
stresses are self-equilibrating, so the resultant force produced must be zero. Macherauch and Kloos (1987) classify these stresses into three categories using the term “homogeneous” to describe the condition “constant in magnitude and direction”:

I. Nearly homogeneous across large areas (several grains) of a material and are equilibrated within the whole body.

II. Nearly homogeneous across microscopic areas (one grain or parts of a grain) of a material and are equilibrated across a sufficient number of grains.

III. Inhomogeneous across submicroscopic areas of a material (several atomic distances within a grain) and are equilibrated across small parts of a grain.

Type I stresses are called “macrostresses” but are commonly known as either “residual” or simply “internal” stresses. On the other hand, Type II and III stresses are commonly referred to as “microstresses”. Note that in the case of Type III stresses, the corresponding strain values are typically reported which are referred to as “microstrain”.

There are many processes which generate internal stresses including mechanical, thermal, and chemical treatments or any combination of these. Table 2.1 lists the main sources and sub-sources of Type I stresses. In all cases, the resulting internal stress depends heavily on the geometrical conditions and on the parameters of the treatments and processes applied. Type I stresses are usually observed after the material has been exposed to elastic-plastic loading resulting in a homogeneous lattice strain. Type I stress varies over large
Table 2.1. Main-sources and sub-sources of Type I stresses [Macherauch and Kloos (1987)].

<table>
<thead>
<tr>
<th>Main-sources of the first kind of stresses</th>
<th>Sub-sources of the first kind of stresses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic-plastic loading</td>
<td>Bending, Torsion, Tension, Compression</td>
</tr>
<tr>
<td>Machining</td>
<td>Grinding, Turning, Milling, Planing, Drilling</td>
</tr>
<tr>
<td>Joining</td>
<td>Welding, Soldering, Brazing, Adhering</td>
</tr>
<tr>
<td>Founding</td>
<td>-</td>
</tr>
<tr>
<td>Forming</td>
<td>Rolling, Drawing, Forging, Pressing, Spinning, Shot Peening</td>
</tr>
<tr>
<td>Heat-Treating</td>
<td>Quenching, Transformation, Hardening, Case Hardening, Nitriding</td>
</tr>
<tr>
<td>Coating</td>
<td>Depositing, Cladding, Spraying, Electroplating, Plating, Galvanizing</td>
</tr>
</tbody>
</table>

Figure 2.13. Different sources of Type III stresses or “inhomogeneous microstresses” [Macherauch and Kloos (1987)].
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distances and causes shifting of the characteristic XRD lines [Macherauch and Kloos (1987)].
On the other hand, Type II stresses vary over the grain scale and can also cause XRD line
shifts. These Type II stresses may also be referred to intergranular stresses which are always
present in polycrystalline materials and are a result of the varying elastic and thermal
properties between differently oriented grains which form grain boundaries [Withers and
Bhadeshia (2001)]. Finally, Type III stresses result from a number of imperfections in the
materials on an atomic scale, for example, dislocations, vacancies, grain boundaries, voids,
inclusions, etc, resulting in an inhomogeneous lattice strain [Macherauch and Kloos (1987)].
Fig. 2.13 schematically displays typical examples based on a simple cubic grain structure.

Each of the types of stresses mentioned can affect XRD lines. A homogeneous stress
typically results in a uniform strain while an inhomogeneous stress results in a non-uniform
strain. When the material is uniformly strained the interplanar spacing changes from their
stress-free value to some new value. This uniform strain effectively causes a shift of the
diffraction lines to new $2\theta$ positions (see Fig. 2.14b). On the other hand, the non-uniform
strain varies from one grain to another or from one part of a grain to another part on a
microscopic scale. In this case, the lattice planes usually become distorted in such a way that
the spacing of any particular $(hkl)$ set varies from one grain to another. This non-uniform
microstrain causes a broadening of the diffraction lines (see Fig. 2.14c). Usually, both
uniform and non-uniform strains are superimposed [Cullity and Stock (2001)].

There are a variety of methods available for measuring the internal stresses in
materials that are deposited (e.g., vapour deposited, electrodeposited, etc.) using various
Figure 2.14. Effect of uniform and non-uniform strains (left side of the figure) on diffraction peak position and width (right side of the figure). (a) Shows the unstrained sample, (b) shows uniform strain, and (c) shows non-uniform strain within the volume samples by the X-ray beam [Cullity and Stock (2001)].

synthesis techniques, e.g., the curvature or “bent strip” method and X-ray diffraction. A comparison of these two stress measurement methods for thin films has often led to significant differences [Noyan et al. (1995)]. The X-ray diffraction method involves determining the strain in the material via a change in lattice parameter whereas the curvature technique measures the deflection of a substrate having a deposit resulting from the distribution of forces of the deposit and substrate around the neutral plane. The nature of this interaction with the substrate may be classified as being either extrinsic or intrinsic. Extrinsic stresses are often related to thermal stresses that result from the incompatibility of the two materials coefficient of thermal expansion [D’Heurle and Harper (1989)]. Extrinsic stresses may also arise from the lattice mismatch at the interface between the two materials [Buckel
(1970)]. On the other hand, intrinsic stresses result from the growth process of the depositing material on the substrate [Klokholm and Berry (1968), D’Heurle and Harper (1989)].

2.2.2. Electrodeposited Metals and Alloys

Internal stresses in electrodeposited metals can also be referred to as “intrinsic stresses” since they are not directly caused by applied loads. Internal stresses cause long range bending of metal strips which are electroplated on one side and therefore may be quite uniform over large distance. These stresses are the type which most electroplaters understand as “internal stress” [Schlesinger and Paunovic (2000)]. The first investigation on this subject was recorded by Gore (1858) and almost 20 years later, Mills (1877) and others made the first attempt to measure the stresses in electrodeposits. Internal stresses can cause distortions, cracking of the deposit, loss of adhesion to the substrate, increased corrosion, etc [Schlesinger and Paunovic (2000)]. High internal stresses can also deteriorate fatigue properties of, for example, Ni deposited onto steel. High internal stresses in electrodeposited permalloy cause increased coercivity values when compared to thermally prepared permalloy [Safranek (1986)]. In general, there is considerable practical and commercial importance of understanding internal stresses in electrodeposited metals.

It is a well-known fact that certain sulfur-containing organic compounds cause a reduction in internal stress when present in the plating solution in rather small amounts [Kushner (1958), Weil (1971a), Safranek (1986), Armanev and Sotirova-Chakarova (1993a), Dini (1993)]. Armanev and Sotirova-Chakarova [1993a] indicated that the deposition of Ni in the presence of saccharin (C_7H_5NO_3S) may cause structural changes
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which are considered to be due to the adsorption and inclusion of S in the crystal lattice of Ni and along the grain boundaries. It is generally accepted that saccharin decreases grain size owing to the restriction of lateral crystal growth during the deposition process. El-Sherik and Erb (1995) observed a decrease in grain size as a function of saccharin concentration in the production of nanocrystalline Ni. Armyanov and Sotirova-Chakarova [1993a] also noted that plating in the presence of saccharin impedes hydrogenation while other additives, for example, 1,4-butynediol can promote hydrogenation of the coatings [Armyanov and Sotirova (1988)]. In fact, it was found that the addition of saccharin to the bath decreases by one-fifth the content of hydrogen occluded in the Ni deposit [Mukasa and Maeda (1980)].

There is general agreement that increasing Fe concentration in Ni electrodeposits results in an increased internal stresses and therefore, Fe acts as a “stress-intensifier” [Kushner (1958), Weil (1971a), Nakamura et al. (1985), Safranek (1986), Sotirova-Chakarova and Armyanov (1990), Armyanov and Sotirova-Chakarova (1993b), Dini (1993), Grimmett et al. (1993), Hadian and Gabe (1999)]. To manage the increase in stress for applications requiring a significant amount of Fe, saccharin has also been widely used as a “stress-reducer” in Ni-Fe alloy deposits [Safranek (1986), Toledo (1970), Uehara (1963), Wolf (1963), Maeda and Mukasa (1967)]. In a study by Perakh [1975] using a constant concentration of saccharin, there was an observed increasing internal stress with increasing Fe content. Similarly, Sotirova-Chakarova and Armyanov [1990] used a constant concentration of saccharin and found that when the amount of Fe increased from 0 to 28 wt.%, the tensile internal stresses increased. They also noted a decrease in grain size with
increasing Fe and suggested that this may be the reason for the observed increase in internal stresses.

2.2.3. Theories on the Origins of Internal Stresses

There are numerous experimental results on the effects of such factors as current density, acidity, temperature, and bath composition on internal stresses. For example, Kushner (1958), Weil (1971a) and Safranek (1986) described the effect of these variables on Ni electrodeposits. Most reports in the literature indicate that there is a rise in the internal stress with increasing current density. A sharp rise in internal stress in the range of pH values 4 to 6 is also observed. Increasing temperature decreases the internal stress. Increasing Fe concentration in the Ni deposit is generally known to increase the internal stress while it is also a well known fact that the addition of certain sulfur-containing organic substances to the electrolyte causes an internal stress reduction [Weil (1971a)]. In the past, the effects of processing variables have often been used to explain the observed internal stresses. However, this traditional approach does not provide a fundamental understanding of internal stresses by taking into consideration the effect of processing variables on the microstructure of the electrodeposited material.

Since the time studies on internal stresses appeared in the open literature, there have been a number of theories presented to explain experimental results. Buckel (1970) pointed out that aside from thermal stresses, there may be up to six other mechanisms including: incorporation of atoms (e.g. residual gases or chemical reactants), lattice mismatch between the substrate and the deposit, variation of the interatomic spacing with crystal size,
recrystallization processes, voids and dislocations, and phase transformations. Weil (1971b), in his review article for electrodeposited materials provided an overview of the major theories which were broken down into five categories: hydrogen effects, changes in foreign substances, lattice defects, crystallite-joining (or coalescence), and excess energy.

While no grain size measurements were made, Kushner (1958) introduced the concept that grain boundaries are essentially high energy regions or active centers where initially depositing metal atoms likely gains its first foothold with the parent metal lattice. Thus, it appears to be obvious that grain size as such must have some effect on internal stresses. Kushner (1958) also studied in some detail the effect of hydrogen and determined that it cannot be the main cause of internal stresses and that microstructural features, such as grain size, may play a more influential role. Other studies have also considered the effect of grain boundaries as an origin of internal stresses. Feigenbaum and Weil (1979) studied structure-internal stress relationships in the early stages of Ni electrodeposition and found that as the thickness increases, the “coalescence” internal stress decreases. They also identified the influence of sulfur-containing organic additives as affecting “coalescence” by influencing the size and shape of the joining crystallites and the surface energies, which are the driving forces for the process.

Coalescence mechanisms based on the effect of grain boundaries are the most developed [e.g. Doljack and Hoffman (1972), Hoffman (1976), and Nix and Clemens (1999)] Coalescence mechanisms have been used to explain the origins of internal stresses in electrodeposited metals [e.g., Feigenbaum and Weil (1979), Czerwinski (1996a), Lin et al.
The coalescence mechanism has also been applied to metals produced by other means, such as sputtering [Mitra et al. (2001), Shamsutdinov et al. (2007)]. Realizing that there has been no success in making quantitative predictions, Doljack and Hoffman (1972) made one of the first attempts to relate the observed internal stresses with the grain size in vapor-deposited polycrystalline Ni thin films on polished silicon substrates. In their study, they considered the final grain size, the surface free energy, the average grain boundary energy and the elastic constants to calculate an internal stress value. A model was proposed whereby a grain separation potential is introduced and a value for the grain boundary relaxation distance $\Delta$ is computed from this potential for each grain diameter, $d$. The internal stress, $\sigma$, is obtained by inserting the values of $\Delta$ and $d$ in the expression,

$$\sigma = \frac{E \Delta}{(1-\nu) d}$$  \hspace{1cm} (2-6)

where, $E$ and $\nu$ are the usual elastic constants of the deposited material. Taking this concept into consideration, Kushner (1973) in his experiments with electrodeposited Ni, described the magnitude of the stress as being dependent on the grain size. That is, the smaller the grain size, the higher the number of grains per unit area and thus, the higher the measured internal stress.

Hoffman (1976) in a later publication emphasized the importance of grain boundaries and their contribution to internal stresses. A grain boundary model was developed which considered the decrease in energy when a grain boundary is formed from two growing isolated surfaces. Using this concept a grain boundary potential model was introduced for Ni,

$$2\gamma_{sv} - \gamma_{gb} \approx \frac{5}{3}\gamma_{sv}$$  \hspace{1cm} (2-7)
where, \( \gamma_{sv} \) is the free surface energy and \( \bar{\gamma}_{gb} \) is the average grain boundary energy per unit area. Thus, when two isolated crystal blocks grow together to form a grain boundary, the energy of the system is lowered by an amount equal to approximately \( \frac{5}{3} \gamma_{sv} \). Since there is constraint due to the adhesion with the substrate, the surface free energy decrease becomes a strain energy increase in the adjoining crystals.

This mechanism was further explored and it was generally agreed upon that internal stresses are associated with the formation of grain boundaries [Abermann and Koch (1985), Nix and Clemens (1999), Sheldon et al. (2001), Freund and Chason (2001)]. Fig. 2.15 describes the before and after effect of crystal coalescence. The process of crystal coalescence leads to an internal stress. The concepts presented by Nix and Clemens (1999) were further refined by Freund and Chason (2001) which resulted in a model that is based on

![Figure 2.15. Polycrystalline thin film before and after the point of crystallite coalescence [Nix and Clemens (1999)].](image)

the theory of contact of elastic solids with cohesion. The model was developed based on one-dimensional, two-dimensional, and three-dimensional states of deformation of coalescing islands. The latter case was found to provide estimates of film stress generally consistent with observations.

2.2.4. Internal Stress Measurements in Nanocrystalline Materials

Various measurements of internal stresses in a number of different nanocrystalline materials have been made, for example, nanocrystalline metals [Sanders et al. (1995), Mitra et al. (2001), El-Sherik et al. (2005), Shamsutdinov et al. (2007), Chung et al. (2011)] and nanocrystalline metal alloys [Czerwinski (1996a,b), Czerwinski (1998), Li and Ebrahimi (2003), Lin et al. (2005), Lee et al. (2005), Auerswald and Fecht (2010), Pathak et al. (2011)]. However, there are only a few which provide some insight into a structure-stress relationship. For example, in a structure-stress investigation of electrodeposited nanocrystalline Ni-Fe, Czerwinski (1996a) established a relationship between grain size and internal stress in Fe-Ni alloy deposits (15wt.%Ni): a decrease in grain size is accompanied by a rise in internal stresses. In this study, internal stresses were measured using the curvature or “bent strip” method and grain sizes determined by imaging thin foils with a TEM. The results showed that the coalescence theory was applicable for grains with sizes less than 100 nm and a deposit thickness less than 500 nm. However, for thicker deposits the coalescence contribution diminished. Given this observation, it was suggested that for thicker layers, other factors might have an influence on the stress generation. Hydrogen was considered, but ruled out since post-deposition stress evolution was small (approximately 4.5%). Czerwinski (1996a) specifically emphasized that to date there is no clear explanation of the stress
changes during electrodeposition and that all hypotheses should be related to the deposit microstructure. In a more recent example of a structure-internal stress relationship study, Shamsutdinov et al. (2007) produced magnetron sputtered nanocrystalline Fe thin films of varying grain size on Si wafers and measured the curvature to determine the internal stress. The internal stress was also found to increase with decreasing grain size.

In many of these studies, the internal stress in electrodeposited materials has been measured using the curvature or “bent strip” method which often leads to conflicting results. On the other hand, XRD methods are rarely used since the method is not as cost effective and practical as the curvature or “bent strip” method. However, XRD methods have the advantage of isolating the intrinsic stresses in the material rather than combining both intrinsic and extrinsic stresses as is in the case of the curvature or “bent strip” method. Furthermore, the ability to isolate the intrinsic stresses can allow for a better correlation to the structure of the material. For example, El-Sherik et al. (2005) used an XRD method to measure the internal stresses in nanocrystalline Ni electrodeposits (10 nm) and microcrystalline Ni electrodeposits (5000 nm). It was found that nanocrystalline Ni electrodeposits had about six times the compressive internal stress of microcrystalline Ni. This study further supports the effect of grain size on internal stress values and the need for obtaining an advanced understanding of this phenomenon.

2.2.5. Microstrain in Nanocrystalline Materials

Microstrain in conventional polycrystalline metals and alloys is normally caused by high dislocation densities resulting from deformation processes. However, the microstrain in
nanocrystalline materials has generally been reported to increase with decreasing grain size, e.g., Eckert et al. (1992), Weissmuller et al. (1995), Eastman et al. (1995), Sanders et al. (1995), Sun et al. (1996), Malow and Koch (1997), Zhao et al. (2001), Li and Ebrahimi (2003), Mishra et al. (2004), Derlet et al. (2005), Qin and Szpunar (2005), and Biju et al. (2008), even when no external loads have been applied. In as-prepared nanocrystalline inert gas condensed [Weissmuller et al. (1995)] and electrodeposited [Mehta et al. (1995)] materials, dislocation densities are typically very low and thus, are not considered to be a major contributor to the observed microstrain. Nanocrystalline materials typically have a high volume fraction of intercrystal defects (grain boundaries and triple junctions) which can become quite significant at the smallest grain sizes [Palumbo et al. (1990)]. For example, at a grain size of 10 nm, about 24% of the volume consists of grain boundaries and 3% of triple junctions (Eq. 2-1, 2-2, 2-3). Local strains in nanocrystalline materials have often been reported to appear near grain boundaries. Using high-resolution transmission electron microscopy (HR-TEM) inert gas condensed nanocrystalline Pd with grain sizes less than 10 nm exhibited distorted lattice planes near grain boundaries [Wunderlich et al. (1990)]. Similar observations were made for materials synthesized by other means, e.g., crystallization of amorphous precursors, mechanical alloying, and severe plastic deformation [Ping et al. (1995), Li et al. (2000), Valiev et al. (2000)].

The use of X-ray line profile analysis for the characterization of nanocrystalline materials has been shown to be a powerful tool, especially when combined with transmission electron microscopy [Ungar (2007)]. Considering the earlier HR-TEM observations of distorted lattice planes near grain boundaries [Wunderlich et al. (1990), Ping et al. (1995), Li
et al. (2000), Valiev et al. (2000)], Qin and Szpunar (2005) developed a quantitative model to describe the dependence of microstrain induced XRD line broadening on grain size. The model is based on the assumption that excess volume in the grain boundaries produces a stress field that causes the lattice strain. Stukowski et al. (2009), employed molecular dynamics simulations to investigate the atomistic origin of microstrain in nanocrystalline materials. In their study, it was concluded that microstrain induced XRD line broadening is generated by long range displacement fields that spread throughout the grains. In general, the presence of a significant volume fraction of intercrystal defects associated with relatively small grain sizes in nanocrystalline materials is considered to be the dominant factor in controlling the microstrain and thus, the basis upon which most theoretical models are constructed. Often, there is good agreement between theoretical and experimental values; however, there are also noticeable variations that could be related to other possible sources which can also contribute to microstrain induced XRD line broadening in nanocrystalline materials [Li and Ebrahimi (2003), Qin and Szpunar (2005), Qin et al. (2008)].

Wagner (1957) established that both twin and deformation stacking faults can be detected from the XRD patterns of fcc metals and alloys. On the (111) planes of fcc metals and alloys, twin stacking faults ($ABCACBA$, also referred to as growth stacking faults [Wagner (1957)]) cause an asymmetric line broadening and a negligible peak shift [Paterson (1952)], whereas deformation stacking faults ($ABCACABC$, also referred to as intrinsic stacking faults [Wagner (1957)]) cause a symmetric line broadening and a small peak shift [Paterson (1952)]. An illustration of these types of stacking faults is given in Fig. 2.16. As in the case of dislocations, deformation stacking faults in nanomaterials are considered to be
present in negligible quantities when prepared by non-mechanical methods and have not experienced any deformation thereafter. However, twin stacking faults have been shown to be present in conventional electrodeposited fcc metals and alloys, e.g., Ag, Cu, Ni and Ni-Fe [Hinton et al. (1963), Hofer et al. (1965), Suoninen (1967), Nakahara (1981), Anderson et al. (1973)], even when no deformation has taken place. In particular, electrodeposited Ni has been shown to possess twin stacking faults of the growth type and not of the deformation induced type [Nakahara (1981)]. From this point onward, we refer to such twin stacking faults of the growth type as “growth faults”. The presence of these growth faults and their contribution to microstrain induced XRD line broadening in these materials produced using electrodeposition processes should be considered.

![Figure 2.16. Types of stacking faults: (a) normal fcc sequence, (b) deformation or intrinsic stacking fault, (c) extrinsic stacking fault, and (d) twin or growth stacking fault [Wagner (1957)].](image-url)
2.3. References


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CHAPTER 3
Experimental Methods

3.1. Introduction

This chapter provides an overview of the experimental methods used during the course of this research. These methods were chosen based on their ability to provide the information necessary to meet the objectives of this study. The synthesis method used to produce the nanocrystalline Ni and Ni-Fe alloys is described. In addition, a brief description of the methods used for materials characterization, testing and analysis is given along with the specific details.

3.2. Synthesis of Continuous Nanocrystalline Ni and Ni-Fe Foils

3.2.1. Drum Plater

There are a number of methods available to synthesize nanocrystalline materials including sputtering, laser ablation, inert gas condensation, high energy ball-milling, sol-gel deposition, and electrodeposition. As described in Chapter 2, electrodeposition allows for the ability to produce a large number of fully dense metals and metal alloys at high production rates and low capital investment in practically a single step process. One particular process is described by Palumbo et al. (2005), where a “drum plater” is used to produce foils in a continuous manner. Fig. 3.1 schematically shows a cross-sectional view of the drum plating apparatus. The drum, which is made of Ti (30 cm in diameter and 30 cm in length), acts as the cathode while the anode consisted of a Ti mesh basket filled with Vale-Inco Ni R-Rounds. The tank also contains a pump and filter system to remove fine
particulate from the electrolyte that may produce defects by being co-deposited with the metal. An additional pump system is used to provide adequate agitation to the cathode in order to prevent mass transfer limiting effects during the electrodeposition process. A heater and temperature controller are also used to maintain the electrolyte temperature to within the prescribed working range. The power supply is equipped to deliver direct or pulsed current and is normally set to within the working ranges known to produce a nanostructured electrodeposit [El-Sherik and Erb (1995), Erb and El-Sherik (1994), Erb et al. (1995)]. When the power source supplies a constant current, the foil thickness may be controlled by adjusting the drum rotation speed.
3.2.2. Electrodeposited Nanocrystalline Ni

Simple mechanisms used to describe the cathodic reactions during Ni plating (i.e., 
Ni^{2+} + 2e^{-} \rightarrow \text{Ni}) do not take into consideration the existence of the NiOH\(^{+}\) ion that is usually present in considerable concentrations at the cathode due to pH change at the interface during the codeposition of H [Piatti et al. (1969)]. A detailed cathodic reaction mechanism for the electrodeposition of Ni has been proposed in several studies, e.g., Matulis and Slizys (1964) and Piatti et al. (1969), to have the following sequence,

\[
\begin{align*}
\text{Ni}^{2+} + \text{H}_2\text{O} & \leftrightarrow \text{NiOH}^{+} + \text{H}^{+} \quad (3-1) \\
\text{NiOH}^{2+} + \text{e}^{-} & \rightarrow (\text{NiOH})_{\text{ads}} \quad (3-2) \\
(\text{NiOH})_{\text{ads}} + \text{H}^{+} + \text{e}^{-} & \leftrightarrow \text{Ni} + \text{H}_2\text{O} \quad (3-3)
\end{align*}
\]

where, the subscript ads refers to the NiOH\(^{+}\) ion in the adsorbed state. In the study by Piatti et al. (1969), it was concluded that Ni deposition depends strongly on the pH of the solution.

The electrodeposited nanocrystalline Ni foils were synthesized using the electrodeposition technique described in El-Sherik and Erb (1995), Erb and El-Sherik (1994), and Erb et al. (1995). A Watt’s type electrolyte was used for the production of the Ni samples consisting of primarily nickel sulfate (NiSO\(_4\)·6H\(_2\)O), nickel chloride (NiCl\(_2\)·6H\(_2\)O), boric acid (H\(_3\)BO\(_3\)), and proprietary additives supplied by Integran Technologies, Inc. (Mississauga, Canada). The proprietary additives consisted of a grain refiner/stress reducer (Nanovate™ A24) and a wetting agent (Nanovate™ B16). The proprietary additives were mixtures of organic compounds. The nanocrystalline Ni samples were produced in the first electrolyte by varying the concentration of Nanovate™ A24 (0, 0.1, 1.0, 2.0 and 10 g/L). Nanovate™ B16 (held constant at 5 mL/L) prevents the development of pits in the deposit.
caused by gas bubbles forming on the cathode surface by lowering the surface tension of the solution. With a lowered surface tension any gas bubbles that are formed on the surface may easily detach from the cathode surface. All other chemical constituents in the electrolyte were also held constant. The pH for both solutions was kept within a range of 2.3-2.6 and the temperature at 58-62°C. The samples were plated to a thickness of 50 μm by adjusting the drum rotation speed to obtain a continuous foil that was collected on a spool.

3.2.3. Electrodeposited Nanocrystalline Ni-Fe

The cathodic reaction mechanism for the electrodeposition of Ni-Fe is referred to as “anomalous”, meaning the less noble Fe deposits preferentially under most plating conditions [Brenner (1963), Dahms and Croll (1965)]. There have been numerous studies directed towards understanding the deposition mechanism, e.g., Romankiw (1987), Nichol and Philip (1976), Andricacos et al. (1989), Hessami and Tobias (1989), Matlosz (1993), Yin et al. (1995), Yin (1997), Nakano et al. (2004). Most recently, Nakano et al. (2004) proposed a mechanism for the anomalous behaviour of the Ni-Fe electrodeposition process from sulfate solution at low pH by taking into the consideration the preferential adsorption of the FeOH⁺ ion due to the smaller dissociation constant of the FeOH⁺ compared with the NiOH⁺ during the multi-step cathodic reaction process. Nakano et al. (2004) provide a reaction mechanism for the Ni-Fe electrodeposition based on the assumption that the deposition of the Ni and Fe is preceded by the formation of metal hydroxide ions,

\[
M^{2+} + OH^- \leftrightarrow MOH^+ \quad (3-4)
\]

\[
MOH^+ + e^- \rightarrow (MOH)_{ads} \quad (3-5)
\]

\[
(MOH)_{ads} + e^- \leftrightarrow M + OH^- \quad (3-6)
\]
where, M is the metal (Ni or Fe). Since the dissociation constant of the FeOH$^+$ ion is much lower than the NiOH$^+$ ion, it is likely that during this series of cathodic reactions the concentration of the FeOH$^+$ ion is much higher at the interface allowing for Fe to be preferentially deposited.

The electrodeposited nanocrystalline Ni-Fe foils were synthesized using the same electrodeposition technique as that of the Ni foils [El-Sherik and Erb (1995), Erb and El-Sherik (1994), Erb et al. (1995)]. A modified Watt’s type electrolyte was also used for the production of the Ni-Fe foils consisting of primarily nickel sulfate (NiSO$_4$·6H$_2$O), nickel chloride (NiCl$_2$·6H$_2$O), ferrous sulfate (FeSO$_4$·5H$_2$O), boric acid (H$_3$BO$_3$), and proprietary additives supplied by Integran Technologies, Inc. (Mississauga, Canada). The same proprietary additives used to produce the nanocrystalline Ni foils were used in this electrolyte, i.e., Nanovate™ A24 and Nanovate™ B16. In addition to these, the electrolyte was formulated to also include a proprietary complexing agent (Nanovate™ C77). A complexing agent is commonly used in Ni-Fe alloy electroplating where its primary function is to form a ligand with Fe to prevent the precipitation of ferric compounds in the electrolyte [Brenner (1963)].

The nanocrystalline Ni-Fe samples with different Fe concentration were produced by varying the concentration of FeSO$_4$·5H$_2$O (4, 7, 9, and 13 g/L) in the electrolyte while the Nanovate™ A24 concentration was held constant at 2 g/L. All other chemical constituents in the electrolyte other than those mentioned were also held constant. The pH for the solution was kept within a range of 2.3-2.6 and the temperature at 58-62°C. The samples were plated
to a thickness of 50 μm by adjusting the drum rotation speed to obtain a continuous foil that was collected on a spool.

3.3. Compositional Analysis

3.3.1. Energy Dispersive X-Ray Spectroscopy (EDS)

Energy dispersive X-ray spectroscopy (EDS) is an analytic technique commonly used for the elemental analysis or chemical characterization of various types of materials. The EDS technique detects X-rays emitted from the sample while it is being bombarded by an electron beam that is supplied by a scanning electron microscope (SEM). For the purposes of this study, the technique was used to analyze the Fe concentration in the Ni-Fe alloy deposits. The equipment employed was a JEOL JXA 840A Scanning Electron Microscope (SEM) equipped with an energy dispersive X-Ray spectrometer (EDS). The SEM was operated at 20 kV to develop an image at approximately 500 X magnification which is adequate for an accurate EDS measurement. The calibration of the EDS was checked using a standard sample prior to carrying out the analysis on the samples. A minimum of five readings were taken at different locations to determine the average elemental composition for each of the samples in wt.%.

3.3.2. LECO Carbon/Sulfur Analyzer

S and C are the two main impurities known to be present in electrodeposited nanocrystalline Ni and Ni-Fe by virtue of the process outlined in El-Sherik and Erb (1995), Erb and El-Sherik (1994), Erb et al. (1995). S, in particular, is known to affect various properties including impact strength [Dini et al. (1975)] and corrosion [Marcus and Talah
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These impurities can be introduced from the various organic additives used in the electrolyte, such as the proprietary additives Nanovate™ A24, B16 and C77.

The majority of metals and their alloys will combust in oxygen when heated to a high enough temperature. The S in the sample is oxidized to sulfur dioxide (SO₂) and the C to carbon dioxide (CO₂). These gases can be then be measured by infrared (IR) detectors to quantify the amount of S and C in the sample. Complete systems for this type of analysis are made, for example, by LECO (St. Joseph, MI, USA). In this study, S and C were analyzed using a LECO Carbon/Sulfur analyzer (model No. CS-244-784-000). Prior to analysis, the starting weight in a crucible is recorded and then the “accelerator” is added. In this analysis, W was used as the “accelerator”. Samples of approximately 0.5 g were analyzed in duplicate to determine the S and C concentrations in wt.%.

3.4. Microstructural Characterization

3.4.1. Scanning Electron Microscopy (SEM)

A Hitachi S-4500 field emission scanning electron microscope (SEM) operated at 15 kV was employed to image the surface of the samples produced in this study. An analysis of the surface quality and morphological characteristics was performed to assess the effectiveness of the electrodeposition technique and the overall quality of the samples that were prepared.
3.4.2. Transmission Electron Microscopy

3.4.2.1. Conventional

In this study, a Hitachi H-800 Transmission Electron Microscope (TEM) operated at 200 kV was used to produce bright-field (BF) and dark-field (DF) images as well as selected area diffraction patterns. The dark-field (DF) images were used specifically to determine the grain size of the sample by counting at least 200 grain diameters and determining the equivalent-circle diameters. Selected area diffraction (SAD) patterns were indexed using the following equation:

\[ \lambda \cdot L = Rd \]  

(3-7)

where, \( L \) is the cameral length, \( d \) the interplanar spacing, \( \lambda \) the electron wavelength at 200 kV acceleration voltage and \( R \) is the radius of the diffraction ring.

3.4.2.2. High-Resolution

A Titan II FEI 80-300 high-resolution transmission electron microscope (HR-TEM) operated at 200 kV was used for defect analysis in several electrodeposits. A series of at least twenty images were examined to determine grain boundary characteristics and to identify any lattice defects. These features were analyzed by generating Fast Fourier Transform (FFT) patterns and inverse FFT (IFFT) images using the image processing software by Gatan – Digital Micrograph™ v.3.11.0.

3.2.2.4. Sample Preparation

All TEM samples were prepared from the 50 µm foils produced using the electrodeposition technique described earlier. 3 mm discs were stamped out of the 50 µm
foils using a Gatan sample punch. A Struers Tenupol-3 jet polishing system was used to thin the foils. The jet polishing solution employed was a mixture of 90-80% methanol and 10-20% perchloric acid (by volume). During the jet polishing process, the solution was kept at a temperature between -40 and -50°C using liquid nitrogen. The general jet polishing parameter working ranges are listed in Table 3.1.

Table 3.1. Parameter working ranges for jet polishing using the Struers Tenupol-3.

<table>
<thead>
<tr>
<th>Control Variables</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage</td>
<td>10 – 30 V</td>
</tr>
<tr>
<td>Amperage</td>
<td>0.3 – 0.7 A</td>
</tr>
<tr>
<td>Fluid Flow Rate</td>
<td>3 – 6</td>
</tr>
<tr>
<td>Polishing Time</td>
<td>Maximum</td>
</tr>
<tr>
<td>Light Sensor</td>
<td>Maximum</td>
</tr>
</tbody>
</table>

3.4.3. X-Ray Diffraction (XRD)

X-ray diffraction (XRD) was used extensively as a tool to characterize the microstructure of all materials produced in the current study. Various methods were applied to determine lattice parameters, interplanar spacing, crystallographic texture, grain size, microstrain and growth fault probabilities in these materials.

In this study, diffraction patterns were generated primarily using an automated Siemens/Brucker D5000 diffractometer. The system is equipped with a high power line focus Cu-Kα (λ = 0.1542 nm) source operating at 50 kV/35mA. A solid-state Si/Li Kevex detector was used for removal of Kβ lines. The diffraction patterns were collected on a θ/2θ Bragg-Brentano reflection geometry with fixed slits. A step scan mode was used for data
acquisition with step size of 0.02° (2θ) and counting time of 2.5 s per step. The 2θ range used was 30 to 130°. Data processing was carried out with Bruker AXS software Eva™ v.8.0. Additional diffraction patterns were produced using a Rigaku MiniFlex equipped with a Co-Kα (λ = 0.1790 nm) source operated at 40kV/15mA and a step size of 0.02° 2θ per minute over a range of 40 to 120°. Data processing was carried out with MDI Jade 5.0.26 (SP1) software. The 50 µm foil samples were cut into 2 cm x 2 cm squares which is approximately the sample holder size.

3.4.3.1. Basic Equations

The Bragg law for constructive interference in XRD is given by the following equation,

\[ n\lambda = 2d_{hkl} \sin \theta \]  

where, \( d_{hkl} \) is the interplanar spacing and \( \theta \) is the diffraction angle, \( \lambda \) is the X-ray wavelength, and \( n \) is the order of reflection which may be any integer (1, 2, 3, …). The interplanar spacing, \( d_{hkl} \), is a function of the Miller indices (\( h, k, \) and \( l \)) as well as the lattice parameters. In the case of crystal structures having cubic symmetry,

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]  

where, \( a \) is the lattice parameter (unit cell edge length).

3.4.3.2. Texture

The degree of preferred orientation may be determined by comparing relative intensities of particular types of planes in the material with those in a random structure. In
the case of a fibre texture, the orientation index can be obtained from the conventional X-ray diffractometer with $\theta$-2$\theta$ geometrical arrangement. The degree of preferred orientation can be quantitatively described in terms of the orientation index, $I_{hkl}$. The orientation index, $I_{hkl}$, which is defined as the fractional intensity of a particular set of planes to its fractional intensity in the same material with a random structure [Willson and Rogers (1964)],

$$I_{hkl} = \left( \frac{i_{hkl}}{\sum i} \right)_{e} = \left( \frac{i_{hkl}}{\sum i} \right)_{r}$$

(3-10)

where, $i_{hkl}$ is the intensity of a diffraction line, $\sum i$ is the sum of the intensity of all the diffraction lines (i.e., $hkl = 111, 200, 222, 311$, etc for fcc materials), and the subscripts $e$ and $r$ are for the electrodeposit and the random structure, respectively. If the orientation index for a line is equal to 1, then the structure is random. If the orientation index does not equal 1, then a texture exists.

3.4.3.3. Line Broadening

Line broadening in XRD for polycrystalline materials is commonly from a contribution of grain size, microstrain, and instrumental effects [Cullity and Stock (2001)]. These contributions can be effectively separated by considering the lines to be broadened according to either a Lorentzian or Gaussian shape. For Lorentzian shaped lines,

$$B_{m} = B_{size} + B_{strain} + B_{inst}$$

(3-11)

and for Gaussian shaped lines,

$$B_{m}^{2} = B_{size}^{2} + B_{strain}^{2} + B_{inst}^{2}$$

(3-12)
where, $B_m$ is the experimentally measured full-width at half-maximum (FWHM), $B_{size}$ is the FWHM due to grain size, $B_{strain}$ is the FWHM due to microstrain, and $B_{inst}$ is the FWHM due to the instrument. The $B_{inst}$ may be determined by various methods including performing XRD using identical conditions on either a well annealed (large grain size) or powder sample of the same substance.

3.4.3.4. Grain Size

Another use for the diffraction pattern is the estimation of crystal size [Cullity and Stock (2001)]. When the size of the crystals is less than about 100 nm there is sufficient diffraction line broadening to allow for the determination of the crystal size using the Scherrer formula,

$$B_{size} = \frac{0.9\lambda}{d \cos \theta}$$  \hspace{1cm} (3-13)

where, $B_{size}$ = FWHM of the broadened diffraction line on the $2\theta$ scale in radians and $d$ = the diameter of the crystals, or grain size. In this study, the grain size of each of the samples was determined by analyzing the (111) and the (200) lines of XRD patterns generated using the Rigaku MiniFlex (Co-K$_\alpha$) diffractometer. The software used to analyze the grain size provides an accurate estimation of grain size by taking into account the instrumental line broadening. The instrumental line broadening was determined by generating an XRD pattern of a polycrystalline nickel powder and measuring the FWHM for each of the resulting lines.
3.4.3.5. Microstrain

In addition to line broadening due to small crystals, non-uniform microstrain and stacking faults also cause X-ray diffraction lines to broaden [Cullity and Stock (2001)]. Microstrain analysis was performed on the (XRD) patterns generated using the Siemens/Bruker D5000 (Cu-K$_\alpha$) diffractometer for each of the deposits produced. In this case, line broadening due to the instrument is accounted for by using the fundamental parameters approach (FPA). The full-width at half-maximum (FWHM) of multiple broadened XRD lines were determined by employing the double-Voigt method [Balzar (1999)] using the Bruker AXS profile fitting software Topas™ v.2.1. This method separates the effects of line broadening due to grain size and microstrain while maximizing accuracy by considering both Gauss and Cauchy distribution functions. The line broadening due to microstrain is calculated based on the relationship obtained by differentiating Bragg’s law with respect to the interplanar spacing, $d$, to yield the relation [Wilson (1962)],

$$ B_{\text{strain}} = 4\varepsilon \tan\theta $$  \hspace{1cm} (3-14)

where, $B_{\text{strain}}$ is the line broadening (FWHM) due to microstrain, $\varepsilon = \Delta d / d$ is the measured microstrain which represents the variation in interplanar spacing, and $\theta$ is one half of the line’s $2\theta$ peak value in radians.

3.4.3.6. Growth Fault Probabilities

Growth fault probabilities, $\beta$, were determined using the XRD patterns and employing the method described by Cohen and Wagner (1962). The method analyzes the peak asymmetry by determining the displacement of the center of gravity of a peak from the peak maximum which is then used to calculate the probability, $\beta$, of finding growth faults,
\[ \Delta C.G.(2\theta)_{111} = +11\beta \tan \theta_{111} \]  (3-15)
\[ \Delta C.G.(2\theta)_{200} = +14.6\beta \tan \theta_{200} \]  (3-16)

where, \( \Delta C.G. \) is the displacement of the center of gravity for the (111) and (200) peaks in degrees, and \( \theta_{111} \) and \( \theta_{200} \) are one half of the 2\( \theta \) values for the (111) and (200) peaks in degrees, respectively. Combining (3-15) and (3-16) we arrive at,

\[ \Delta C.G.(2\theta)_{111} - C.G.(2\theta)_{200} = (11\tan \theta_{111} + 14.6 \tan \theta_{200})\beta \]  (3-17)

and by rearranging Eq. 3-17, the growth fault probability can be determined,

\[ \beta = \frac{\Delta C.G.(2\theta)_{111} - \Delta C.G.(2\theta)_{200}}{(11\tan \theta_{111} + 14.6 \tan \theta_{200})} \]  (3-18)

The XRD patterns generated were employed for this analysis to determine the growth fault probabilities for each of the samples produced in this study. \( \Delta C.G. \) was determined using a non-linear least squares fitting program.

3.5. Thermal Analysis

Differential scanning calorimetry (DSC) is a technique that measures the temperature and heat flow associated with transitions in materials as a function of time and temperature. It provides qualitative and quantitative information about the chemical and physical changes that involve endothermic or exothermic processes. In the case of nanocrystalline materials, the total enthalpy or total heat release (\( \Delta H_{total} \)) corresponding to grain growth in the form of an exothermic event allows for determination of the peak temperature, \( T_p \), which can be used as a relative measure of the thermal stability.
In this study, a TA Instruments Q20 conventional DSC was used to measure the heat flow from the samples produced in this study. 3 mm discs were stamped out of the 50 μm foils using a Gatan sample punch. In order to obtain a sufficient heat flow signal, about 7-12 mg of sample was required. Several 3mm discs were stacked on top of each other and sealed in hermetic Al containers. The temperature range was approximately 50 to 500°C. All samples were subjected to a heating rate of 5°C/min. The exothermic event corresponding to grain growth was integrated using TA Universal Analysis 2000 Version 4.7A software to determine the total heat release ($\Delta H_{\text{total}}$) and peak temperature, $T_p$.

3.6. Nanoindentation

There have been many advances in the development of a nanoindentation technique for determining the mechanical properties of materials on the submicron level [Pethica et al. (1983), Oliver et al. (1986), Doerner and Nix (1986)]. The technique is based on developing load-displacement data that is eventually analyzed allowing for the determination of mechanical properties such as the hardness, $H$, and Young’s modulus, $E$. The technique was further refined by Oliver and Pharr (1992), Fischer-Cripps (2002), Klinger and Rabkin (2003), and Oliver and Pharr (2004) which eventually lead to the development of an ASTM standard (E2546-07 “Standard Practice for Instrumented Indentation Testing”) that was released after the initiation of the work in this thesis.

The method employed in this thesis is the same described by Oliver and Pharr (1992) and is based on the Berkovich indenter (three-sided pyramid). Fig. 3.2 presents a cross-
Figure 3.2. Schematic representation of a section through an indentation identifying the parameters used in the analysis [Oliver and Pharr (1992)].

Figure 3.3. A schematic representation of load versus indenter displacement data. $P_{\text{max}}$ is the peak indentation load; $h_{\text{max}}$ is the indenter displacement at peak load; $h_{f}$ is the final depth of contact impression after unloading; and $S$ is the initial unloading stiffness [Oliver and Pharr (1992)].
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section of an indentation that identifies the parameters used in the analysis and Fig. 3.3 shows a schematic of a load versus indenter displacement data. According to Oliver and Pharr (1992), the relationship used to describe the unloading data for the stiffness measurement is,

\[ P = P_0(h - h_f)^m \]  

(3-19)

where, \( P \) is the load and \( h \) is the contact height provided by the depth-load data, and \( P_0, m, \) and \( h_f \) are all constants determined by a least squares fitting procedure. At peak load, the load and displacement are \( P_{\text{max}} \) and \( h_{\text{max}} \). Given \( P_{\text{max}}, h_{\text{max}} \) can be calculated using Eq. 3-19.

The measured stiffness, \( S \), at \( h_{\text{max}} \) may be calculated as follows,

\[ S = \frac{dP}{dh} = mP_0(h_{\text{max}} - h_f)^{m-1} \]  

(3-20)

The contact depth, \( h_c \), is calculated using,

\[ h_c = h_{\text{max}} - \frac{3P_{\text{max}}}{4S} \]  

(3-21)

Finally, the contact area, \( A(h_c) = 24.5h_c^2 \), is calculated and values for the hardness, \( H \), and reduced Young’s modulus, \( E_r \), are determined,

\[ H = \frac{P_{\text{max}}}{A} \]  

(3-22)

\[ E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \]  

(3-23)

The Young’s modulus, \( E_m \), may be calculated using the following equation,

\[ \frac{1}{E_r} = \frac{1-\nu^2}{E_m} + \frac{1-\nu_i^2}{E_i} \]  

(3-24)
Where, \( \nu \) is the Poisson’s ratio of the specimen and \( E_i \) and \( \nu_i \) are the Young’s modulus and Poisson’s ratio for the indenter.

In this study, the hardness and Young’s modulus were determined using a SHIMADZU Dynamic Ultra-Micro Hardness Tester with a Berkovich (three sided pyramid) nanoindenter. Measurements were made by using cyclic loading (four cycles per load) in order for the last unloading curve to be almost purely elastic, allowing for a reliable Young’s modulus determination. At the beginning of each set of measurements, the mechanical drift of the equipment was minimized by a stabilization process whereby loading was carried out at 100 mN for approximately 1.3 hrs. To assure reliability, the equipment was regularly calibrated using a series of standard relatively isotropic samples, including fused quartz, W, and Al, representing a wide range of Young’s modulus values. The samples were prepared by mounting on their cross-section, mechanically grinding and polishing to a mirror finish. Each sample was measured under five different loads (150, 130, 110, 90 and 70 mN) with four trials per load. The loading rate was 13.3 mN/s for all loads. The last elastic unloading curves were analyzed to determine hardness and Young’s modulus using the procedure outlined by Oliver and Pharr (1992).

3.7. Macrostress

The effects of strain on diffraction lines are described as either uniform or non-uniform [Cullity and Stock (2001)]. If the grain is under uniform tension, the \( d \)-spacing is larger than \( d_0 \), and the corresponding diffraction line shifts to lower angles as shown in Fig. 3.4 for the normal (N) direction.
Figure 3.4. Schematic of the strain measurement based on the Bragg law. N is the plane normal direction and when there is a strain the $d$-spacing is not in equilibrium and thus there is a strain, $\varepsilon_n$, in the plane normal direction [He (2009)].

In the case where the grain is under uniform compression the $d$-spacing is smaller and diffraction line shift is to the left. This line shift is the basis of the X-ray method for the determination of macrostress [James and Cohen (1980)]. There are two main XRD methods for determining internal stress: conventional and two-dimensional (2D). In both cases, the Bragg law is the basis of the stress analysis and is used to detect changes in the $d$-spacing of a variety of grains in different orientations along the sample plane.

The conventional method is carried out with an X-ray diffractometer equipped with a point detector. In the case of a 2D X-ray diffractometer, an area detector is used. When using an area detector parts of the diffracted rings become visible as opposed to simply lines on the diffractometer plane in the conventional method. 2D X-ray diffraction has the advantage of including a larger number of crystallites which provides better accuracy and
Figure 3.5. An illustration of the difference between conventional and 2D X-ray diffraction [He (2009)].

Figure 3.6. An illustration of the diffraction cone due to stresses [He (2009)].
sampling statistics (see Fig. 3.5). This method to determine macrostress has been well developed by He (2009). In 2D X-ray diffraction, an unstressed sample will produce a regular cone having the same $2\theta$ at all $\gamma$ angles. In a stressed sample, the cone is not regular but distorted and thus the $2\theta$ value becomes a function of $\gamma$ and the sample orientation ($\omega, \psi, \phi$). The strain may then be related to the degree of cone distortion via the Bragg law. Referring to Fig. 3.6, consider a point on a given \{hkl\} diffraction ring, P, such that the corresponding diffraction vector points to $P'$. The strain can then be measured based on the true strain definition [He (2009)],

$$
\varepsilon_{(hkl)}^{(\gamma,\omega,\psi,\phi)} = \ln \frac{d}{d_0} = \ln \frac{\sin \theta_0}{\sin \theta} = \ln \frac{\lambda}{2d_0 \sin \theta}
$$

(3-25)

Given the stress tensor is comprised of the stress components from a volume element (see Fig. 3.7), an expression can be derived to relate this to the strain measured from the cone distortion [He (2009)],

$$
p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{22}\sigma_{22} + p_{13}\sigma_{13} + p_{23}\sigma_{23} + p_{33}\sigma_{33} = \ln \left( \frac{\sin \theta_0}{\sin \theta} \right)
$$

(3-26)

where, $p_{ij}$ are stress coefficients that include the Young’s modulus, Poisson’s ratio, and X-ray elastic constants for the material being analyzed. A complete derivation of this equation can be found in He (2009). In most stress determinations, and especially in the case of electrodeposited metals, the thickness of the material is relatively low and thus, the average stress in the normal direction is taken to be zero. Furthermore, when the stress is biaxial, $\sigma_{33} = \sigma_{13} = \sigma_{23} = 0$. In order to accommodate for the fact that a precise $d_0$ value is not
Figure 3.7. (a) Stress components on a volume element [He (2009)], and (b) the stress tensor.

available, a directionless “faulty stress” is introduced into the equation and is termed a “pseudo-hydrostatic stress” [He (2009)], however, it does not have a physical meaning. Accounting for the biaxial stress and introducing the “pseudo-hydrostatic stress”, Eq. 3-26 is reduced to,

\[
p_{11}\sigma_{11} + p_{12}\sigma_{12} + p_{22}\sigma_{22} + p_{ph}\sigma_{ph} = \ln\left(\frac{\sin\theta_0}{\sin\theta}\right)
\]

(3-27)

where, \( p_{ph} \) and \( \sigma_{ph} \) are the “pseudo-hydrostatic” stress coefficient and the “pseudo-hydrostatic” stress, respectively. It should also be noted that in the analysis it is recommended to take into account the anisotropic nature of these materials, i.e., considering the fact that stresses determined from diffracting crystallographic planes may have different values. As such, a radiocrystallographic anisotropy factor, \( A_{RX} \), is introduced into the analysis and used to calculate the X-ray elastic constants for the plane on which the
measurement takes place. For face-centered cubic Ni-based materials, $A_{rx} = 1.52$ [He (2009)].

In this study, macrostress determinations were carried out using an XRD system configuration consisting of a Bruker SMART 6000 CCD detector, a Bruker D8 3-circle fixed-$\chi$ (or $\psi$) goniometer, a Rigaku Ru200 rotating anode Cu-K$_\alpha$ ($\lambda = 0.1542$ nm) X-ray generator, and a Goebel cross-coupled parallel-focusing mirror. The diffractometer was operated at 45kV/30mA to generate the Cu-K$_\alpha$ radiation with a monochromator. Each sample was measured at a fixed $\omega$ and $\psi$ angle of 165.0° and 35.2°, respectively. The $\phi$ angle range was 135 to 240° and the step size was 15°. The $2\theta$ values were integrated along a $\gamma$ range of 63.3 to 117.2° with a step size of 0.01°. The software used in the analysis was provided by Bruker Advanced X-Ray Solutions (1999) for their General Area Detector Diffraction System (GADDS) V.4.1.29. For the analysis, the (311) ring occurring in the $2\theta$ range of 90.5 to 95.5° was chosen in order to maximize spatial resolution.
3.8. References


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CHAPTER 4
Materials Synthesis and Characterization

4.1. Introduction

Ni naturally occurs in the $\gamma$ (fcc) phase. When alloyed with Fe, it can either occur in the $\gamma$ (fcc) phase or the $\alpha$ (bcc) phase. There are many interesting properties associated with Ni-Fe alloys. For example, at approximately 20wt.%Fe in the $\gamma$ (fcc) phase an alloy commonly known as permalloy is a material with unique soft magnetic properties, including a high magnetic permeability. At approximately 64wt.%Fe also in the $\gamma$ (fcc) phase a commercial alloy commonly known as Invar has a uniquely low coefficient of thermal expansion. Given the importance of these materials in commercial applications, the Ni-Fe family of alloys has been a subject of interest for many years.

Figure 4.1. Fe-Ni binary alloy phase diagram [Scott (1992)].
One of the first proposals for the Ni-Fe phase diagram was made as early as 1904 [Osmond and Cartaud (1904)]. The most recent version can now be found in handbooks, e.g., Scott (1992). Fig. 4.1 presents the equilibrium phase diagram for Ni-Fe. When produced using conventional metallurgical processing methods, the resulting alloys will normally have structures that agree with the phase diagram. Electrodeposited alloys, on the other hand, do not entirely follow the conventional phase diagram partly because of the relatively low temperatures at which the materials are synthesized. Fig. 4.2 shows the phases commonly seen in electrodeposited Ni-Fe alloys as a function of Fe concentration [Fukumuro et al. (2004)].

![Figure 4.2](image-url)  

For example, according to the Ni-Fe equilibrium phase diagram (Fig. 4.1), compositions in the neighbourhood of Ni-(10-28)wt.%Fe show the presence of the ordered FeNi₃ structure in the γ(fcc) phase. The phase diagram holds true for this particular subset of Ni-Fe alloys when produced using conventional metallurgical processing methods. However, electrodeposited Ni-Fe alloys in the same compositional range may not entirely exhibit the ordered FeNi₃ structure which, again, could be due to the relatively low temperatures at which the synthesis process is operated at. As a result, the Ni-Fe alloys produced by electrochemical synthesis techniques typically have non-equilibrium structures.
Chapter 4 – Materials Synthesis and Characterization

The determination of the crystal structure of Ni-Fe alloys by, for example, X-ray diffraction, is somewhat ineffective since the respective atomic scattering factors of Ni and Fe are similar. That is, the structure factor values for superlattice reflections in the unit cell with an ordered FeNi$_3$ structure are so small that any scattering of X-rays are practically undetectable. Electron diffraction is also ineffective, since the scattering characteristics of the electrons by Ni and Fe are also very similar. Other methods, such as Mössbauer spectroscopy, can be used to study the short range order; however, the interpretation of the data is often challenging and is likely to lead to significant uncertainties [Cranshaw (1987)].

The existence of an ordered structure in electrodeposited Ni-Fe alloys has been suggested indirectly in the study of the thermal properties of nanocrystalline Ni-Fe alloys by Turi (1997). Turi (1997) noted significantly increased total enthalpy releases upon grain growth when compared to nanocrystalline Ni samples with similar grain sizes. The additional release of energy was owed to the formation of the ordered FeNi$_3$ structure from the initial disordered structured obtained from the electrodeposition synthesis technique.

In this chapter, the results from the synthesis method used to produce the nanocrystalline Ni and Ni-Fe alloy foils along with a series of microstructural characterizations is presented. The microstructural characterization is grouped into four main categories: (1) scanning electron microscopy, (2) transmission electron microscopy, (3) X-ray diffraction, and (4) thermal analysis. The main objective is to divulge as much information as possible in order to explain the macroscopic behaviour of these materials to be discussed in later chapters, including, the hardness, Young’s modulus and internal stresses.
4.2. Synthesis of Nanocrystalline Ni and Ni-Fe Alloys

A summary of the materials produced for this study, using the method described in Chapter 3 (Section 3.2), is given in Table 4.1. It includes the compositional analysis determined using EDS for Fe and the LECO analyzer for quantification of S and C.

Table 4.1. Summary of materials produced for this study with deposit Fe, S, and C concentrations.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>FeSO₄·5H₂O (g/L)</th>
<th>Nanovate™ A24 (g/L)</th>
<th>Fe (wt.% )</th>
<th>S (wt.% )</th>
<th>C (wt.% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0021</td>
<td>0.0185</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0.0335</td>
<td>0.0332</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
<td>0.0242</td>
<td>0.0174</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>1.0</td>
<td>0</td>
<td>0.0349</td>
<td>0.0214</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>0.0419</td>
<td>0.0196</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>2.0</td>
<td>7.3</td>
<td>0.0324</td>
<td>0.0269</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>2.0</td>
<td>16</td>
<td>0.0331</td>
<td>0.0496</td>
</tr>
<tr>
<td>8</td>
<td>9</td>
<td>2.0</td>
<td>23</td>
<td>0.0372</td>
<td>0.0239</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>2.0</td>
<td>32</td>
<td>0.0281</td>
<td>0.0470</td>
</tr>
</tbody>
</table>

Synthesis of the Ni samples was carried out by varying the concentration of Nanovate™ A24 in the electroplating solution. As a result, there is a clear trend in the relationship between the Nanovate™ A24 concentration in the solution and the bulk S concentration in the deposit. Note that even when there is no Nanovate™ A24 in the electrolyte, i.e. for sample no. 1, there is still a measureable quantity of S. The source of the S in this case is likely the SO₄²⁻ ions which are present in the electrolyte and/or the proprietary wetting agent (Nanovate™ B16) which is a mixture of organic species that may contain S. Fig. 4.3 presents a plot of the S concentration in the deposit vs. the Nanovate™ A24 concentration in the electrolyte. Initially, there is a sharp increasing S concentration
trend with increasing Nanovate™ A24 concentration that eventually plateaus. The C concentration in the deposit for samples 1, 2, 3, 4 and 5 do not display any notable trend.

![Graph showing sulfur concentration vs. Nanovate™ A24 concentration](image)

Figure 4.3. S concentration in the nanocrystalline Ni deposit vs. the Nanovate™ A24 concentration in the electrolyte used to produce nanocrystalline Ni samples no. 1-5.

The nanocrystalline Ni-Fe samples were produced by holding the Nanovate™ A24 concentration constant at 2 g/L and varying the concentration of FeSO₄·5H₂O in the electrolyte. Fig. 4.4 presents a plot of the Fe concentration in the deposit vs. the FeSO₄·5H₂O concentration in the electrolyte. Similar to the findings of Cheung et al. (1995) and Li and Ebrahimi (2003), effectively increasing the Fe metal content in the electrolyte increases the Fe concentration in the deposit. In this particular case, the relationship between the Fe concentration in the deposit and the FeSO₄·5H₂O in the electrolyte is approximately linear. The S in the deposit for the nanocrystalline Ni-Fe samples remains relatively constant.
Figure 4.4. Plot of Fe concentration in the deposit vs. FeSO$_4$·5H$_2$O in the electrolyte used to produce nanocrystalline Ni-Fe samples no. 2, 6, 7, 8 and 9.

over the entire Fe concentration range (Table 4.1). This is not surprising since the Nanovate™ A24 concentration was held at a constant value of 2 g/L. On the other hand, the C concentration is somewhat variable and does not seem to have any trend. In the case of all samples produced, it should be noted that there are multiple sources of C, including the proprietary grain refiner/stress reducer (Nanovate™ A24), the proprietary wetting agent (Nanovate™ B16), and specific to the Ni-Fe electrolyte, the proprietary complexing agent (Nanovate™ C77). It is likely that the variability of the C concentration is a result of the varying “free” complexing agent concentration. The “free” complexing agent concentration is considered to be the concentration of complexing agent which has not formed a ligand with Fe$^{3+}$ (ferric) ions. The concentration of Fe$^{3+}$ ions can depend on a number of factors including the O$_2$ concentration in the electrolyte. The consequence of high O$_2$ concentrations
in the electrolyte is an increased concentration of Fe$^{3+}$ ions due to the oxidation of the Fe$^{2+}$ ion. Thus, it is likely that the variability of the C in the deposit for the nanocrystalline Ni-Fe alloys is dependent on the effective concentration of organic species in the electrolyte.

4.3. Deposit Quality and Morphology

SEM images of various samples were taken to evaluate their surface quality and morphology. Images of the “free” anode facing surface were taken. Shown in Fig. 4.5-4.7 are examples of the surfaces observed at 60,000 X magnification. Additional images of these and the other samples may be found in Appendix A. Sample no. 1 (Ni), shown in Fig. 4.5, displays evidence of faceting which is indicative of relatively large grain sizes. The rest of the samples (Fig. 4.6-4.7) displayed generally smooth surfaces with no evidence of faceting indicating that the grain sizes are relatively small. All samples were without any signs of pores or microcracks. Some surface contamination (dark patchy areas) is visible in the images, which becomes more prominent with increasing Fe concentration.

In previous studies, electrodeposited nanocrystalline Ni [El-Sherik and Erb (1995)] were found to have a cauliflower-like morphology that was affected by the saccharin concentration in the electrolyte. As cauliflower-like features were not observed in the current images, differences in processing parameters, e.g., the current density at which the electrodeposition process was operated is likely to be one of several influencing factors and therefore, should be taken into consideration. High current densities tend to induce the formation of nodules while low current densities tend to promote leveling or smoothing of the surface. In addition to this, past studies [e.g., El-Sherik and Erb (1995)] used a stationary
Figure 4.5. SEM image (60,000X) of sample no. 1 (Ni) showing faceting.

Figure 4.6. SEM image (60,000X) of sample no. 5 (Ni).

Figure 4.7. SEM image (60,000X) of sample no. 9 (Ni-32wt.%Fe).
flat Ti cathode in a confined space to produce samples whereas in the present case, a rotating Ti curved (drum) surface was employed. Sample size may also be a factor, where in this case, foils were substantially larger compared to the coupon samples produced by El-Sherik and Erb (1995).

In the case of the Ni-Fe samples, there is some consistency with previous studies, e.g., Cheung et al. (1995), Czerwinski (1998) and Ebrahimi and Li (2003), whereby the surface was in fact generally smooth. Similar to the current study, Cheung et al. (1995) observed no signs of microcracking. However, in the case of Czerwinski (1998) and Ebrahimi and Li (2003) significant microcracking was observed. The presence of microcracking was owed to the internal stresses in the electrodeposits which are high enough to exceed the fracture strength of the material [Czerwinski (1996), Czerwinski (1998), Czerwinski and Kedzierksi (1997)]. The microcracking observed by Czerwinski (1998) and Ebrahimi and Li (2003) was owed to the absence of organic additives in the electrolyte which behave as stress reducers. In the present study and that of Cheung et al. (1995) a stress reducer was employed in part to prevent the onset of microcracking.

4.4. Transmission Electron Microscopy (TEM)

4.4.1. Conventional

TEM bright-field (DF), dark-field (DF) images, and selected area diffraction (SAD) patterns are presented in Fig. 4.8 for sample no. 5 (Ni, 23 nm) and Fig. 4.9 for sample no. 7 (Ni-16wt.%Fe, 12 nm). The images for the remaining samples can be found in
Figure 4.8. TEM images of sample no. 5 (Ni, 23 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure 4.9. TEM images of sample no. 7 (Ni-16wt.%Fe, 12 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Appendix B. All diffraction patterns display characteristics of an fcc structured material. For samples no. 2-9, the dark field images were used to determine the average grain sizes by determining at least 200 equivalent-circle diameters for each material. The grain sizes that are presented in Table 4.2 have error values corresponding to one standard deviation and are rounded to the nearest whole number.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe (wt.%)</th>
<th>Grain Size (nm)</th>
<th>$f_{ic}$</th>
<th>$f_{gb}$</th>
<th>$f_{tj}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>~255*</td>
<td>0.012</td>
<td>0.012</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>81±51</td>
<td>0.037</td>
<td>0.036</td>
<td>0.000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>44±30</td>
<td>0.067</td>
<td>0.065</td>
<td>0.002</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>37±21</td>
<td>0.079</td>
<td>0.077</td>
<td>0.002</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>23±11</td>
<td>0.125</td>
<td>0.119</td>
<td>0.006</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>32±18</td>
<td>0.091</td>
<td>0.088</td>
<td>0.003</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>12±7</td>
<td>0.230</td>
<td>0.210</td>
<td>0.020</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>10±5</td>
<td>0.271</td>
<td>0.243</td>
<td>0.028</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>10±5</td>
<td>0.276</td>
<td>0.247</td>
<td>0.029</td>
</tr>
</tbody>
</table>

* Extrapolated from the Hall-Petch relationship (Chapter 5, Table 5.1, Fig. 5.3)

The grain size for sample no. 1 (*) was extrapolated from the Hall-Petch relationship that will be discussed in Chapter 5. Included in Table 4.2 are the respective total intercrystal volume fraction, $f_{ic}$, grain boundary volume fraction, $f_{gb}$, and triple junction volume fraction, $f_{tj}$, for the purpose of illustrating the significance in the presence of these defects with progressively decreasing grain size. Volume fractions were calculated by using a grain boundary thickness, $\Delta$, of 1 nm using Eq. 2-1, 2-2, and 2-3 [Palumbo et al. (1990)]. The intercrystal volume fraction increases rapidly at grain sizes less than 20 nm. As an example,
at a grain size of 10 nm, approximately 27% of the material consists of intercrystal defects which represent a significant fraction of the total volume.

Figure 4.10. Cumulative volume fraction vs. grain size for the nanocrystalline Ni and Ni-Fe samples produced for this study. The sample no.’s are labeled at the top of each distribution curve.

The grain size distributions shown for grain sizes less than 20 nm tend to display log-normal characteristics. On the other hand, at grain sizes greater than 20 nm, a broad distribution is typically evident. In order to further illustrate the distribution of grain sizes within a given sample a cumulative volume fraction vs. grain size plot is presented in Fig. 4.10. The use of this analysis for illustrating grain size distribution is important since it provides a more realistic interpretation of volume fractions of grains with a given grain size present in the material in comparison the grain size distributions presented in Fig. 4.8 and 4.9. That is, when converted to volume fraction, the distribution of size of grains which make-up of the material becomes more evident [Soong (2009)]. In this case, it can be seen
that samples no. 7-9 have a relatively narrow grain volume fraction distribution, however, as the average grain size increases greater than 20 nm a progressively broader grain volume fraction distribution is observed for samples no. 2-5.

During the synthesis of the samples, changes were made to the chemical constituents in the electrolyte that can have a considerable effect on the microstructure of the resulting materials (see Table 4.2). The nanocrystalline Ni samples (no. 1-5) were produced by gradually increasing the Nanovate™ A24 concentration in the electrolyte. In addition to the increase of S concentration in the deposit, gradually increasing the Nanovate™ A24

![Figure 4.11. Plot of grain size vs. Nanovate™ A24 concentration in the electrolyte used to produce the nanocrystalline Ni samples no. 1-5.](image-url)
concentration in the electrolyte was also found to cause a substantial decrease in grain size which is similar to the findings of El-Sherik and Erb (1995). Fig. 4.11 presents a plot of resulting grain size vs. Nanovate™ A24 concentration in the electrolyte. In the case of the Ni-Fe samples (samples no. 2, 6-9), the Nanovate™ A24 concentration was held constant at 2 g/L, however, as the FeSO₄·5H₂O concentration was increased there was a corresponding grain refinement effect. This result is consistent with those of Cheung et al. (1995) and Li and Ebrahimi (2003) who also found that with an effectively increasing Fe/Ni ion ratio in the electrolyte, there is a decrease in grain size along with an increase in the Fe concentration in the deposit. Fig. 4.12 describes this effect by plotting the grain size vs. the Fe concentration in the deposit. With small additions of Fe (<15wt.% in Ni, the grain size is dramatically decreased. Additions greater than 15wt.% have a lesser effect on decreasing the grain size.
4.4.2. High-Resolution*

A defects analysis was carried out on the series of HR-TEM images. Samples no. 5, 7, and 9 were used for this purpose and examples of HR-TEM images are shown in Fig. 4.13, 4.14, and 4.15, respectively. In general, the HR-TEM images for all three materials revealed small grains (<100nm) with lattice resolution. The grain sizes obtained using conventional TEM image analysis corresponded well with observations using HR-TEM. There are no observable signs of coarse porosity which is consistent with previous studies on materials synthesized using the electrodeposition technique [e.g., Van Petegem et al. (2003), Haasz et al. (1995), Zhou et al. (2009)]. Further analysis would be required to confirm the presence of low porosity using a more appropriate technique such as positron annihilation.

Figure 4.13. HR-TEM image of sample no. 5 (Ni, 23 nm).

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Figure 4.14. HR-TEM image of sample no. 7 (Ni-16wt.%Fe, 12 nm).

Figure 4.15. HR-TEM image of sample no. 9 (Ni-32wt%Fe, 10 nm).
spectroscopy [e.g., Van Petegem et al. (2003), Zhou et al. (2009)]. However, it should be noted that electrodeposited nanocrystalline metals produced in a similar manner as the samples in the current study are typically about 99-100% dense [Van Petegem et al. (2003)], and may possess excess free volumes at the grain boundaries with sizes smaller than a vacancy in a perfect lattice [Zhou et al. (2009)].

There was also no evidence of co-deposited second phases in these materials. This is consistent with the SAD patterns produced using conventional TEM (e.g., Fig. 4.8c and 4.9c) which show no signs of the presence of second phases. The absence of second phases is also demonstrated in the XRD patterns that are presented later (e.g., Fig. 4.26 and Fig. 4.27). In order to assess the presence of edge dislocations, numerous grains having an [011] zone axis were examined from the series of HR-TEM images. Very few edge dislocations were observed which is consistent with earlier findings on electrodeposited nanocrystalline Ni, Ni-P, and Ni-Fe alloys [Mehta et al. (1995), Giallonardo et al. (2012)]. Wu et al. (2007) also examined HR-TEM images of as-received nanocrystalline Ni samples produced using the electrodeposition technique and very few dislocations were observed. Note that there is considerable strain contrast at some of the grain boundaries as will be discussed in later parts of this section.

Triple junctions, high and low angle grain boundaries, and twin boundaries were examined in detail. Fig. 4.16 shows a well defined triple junction from sample no. 5 (Ni, 23 nm). The zone axes for grains, A, B, and C, are [001], [112] and, [011], respectively. Since
Figure 4.16. HR-TEM image of a triple junction in sample no. 5 (Ni, 23 nm). To the right of the image are the FFT patterns for grains A, B, and C corresponding to zone axes [001], [112], and [011], respectively.

Figure 4.17. HR-TEM image of the boundary between grains A and B from Fig. 4.16. The respective zone axes for grains A and B are [001] and [112].
the zone axes are quite different, the grain boundaries are considered to be high angle boundaries. Another section of the grain boundary between grains A and B away from the triple junction is shown in Fig. 4.17. In this figure, there is some noticeable contrast at the grain boundary which may be a result of the presence of accommodation strains similar to what has been observed in other studies [e.g., Valiev et al. (2000)].

Shown in Fig. 4.18 is an image of a low angle grain boundary. The FFT patterns (Fig. 4.19) show that grains A and B have the same [011] zone axis and are slightly rotated with respect to each other. As a result, the grain boundary may be described as a tilt boundary. Since the zone axes are the same, the FFT was used to determine the misorientation angle which is about 13°. This tilt boundary also displays accommodation

![HR-TEM image of a low angle grain boundary from sample no. 7 (Ni-16wt.%Fe, 12 nm) having a 13° angle of misorientation with grain A and B both having a [011] zone axis.](image)
Figure 4.19. FFT of grain A and grain B from Fig. 4.18 both having a [011] zone axis and showing a slight rotation with respect to each other.

Figure 4.20. IFFT image of Fig. 4.18 showing the accommodation of dislocations (marked by the arrows) at the low angle grain boundary.
strain which could have developed during the crystal joining process. In a closer examination of the boundary by producing an IFFT image (Fig. 4.20), dislocations, which are characteristic of a low angle tilt boundary, are identified (marked by the arrows). That is, when the misorientation angle is low enough between the two grains which form the tilt boundary, an array of edge dislocations can be accommodated. The dislocation positions are also consistent with the darker contrast areas at the fringe of grain B suggesting that there is an emanating strain field.

Shown in Fig. 4.21 is an example of two twin boundaries from sample no. 5 (Ni, 23 nm) within a grain having a [011] zone axis. The FFT pattern (inset) of the twins displays streaking between the spots in the [111] direction and as a result, the twinning planes are

![Figure 4.21. HR-TEM image of two twin boundaries from sample no. 5 (Ni, 23 nm). Inset is the indexed FFT pattern and the zone axis is [011].](image-url)
Figure 4.22. IFFT of Fig. 4.21 showing dislocations (marked by the arrows) at the twin boundary necessary to compensate for the misalignment of the lattices.

(111). In a closer examination of the IFFT image (Fig. 4.22), the twin boundary formed between A and B shows both coherent and incoherent characteristics while the twin boundary formed between B and C is generally coherent. Coherency is evident when there is alignment between the lattices or, as seen in the IFFT image (Fig. 4.22), continuity of the planes through the twin boundary. Incoherent regions in the twin boundary formed between A and B are evident due to the presence of dislocations (marked by the arrows). It is generally accepted that a dislocation array is required to compensate for the misalignment between lattices of the parent and the twin [Reed-Hill and Abbaschian (1994)].

It should be noted that not all grain boundaries were found to possess local strains which is consistent with Ebrahimi and Li (2003) who identified an unstrained low angle grain
boundary in an electrodeposited nanocrystalline Ni-21wt.%Fe alloy. However, based on the observations made in the current study, the occurrence of strained grain boundaries is rather significant. The appearance of these local strains at grain boundaries is consistent with previous studies on nanocrystalline materials synthesized by other means, e.g., inert gas condensation followed by in-situ compacting, crystallization of amorphous precursors, mechanical alloying, and severe plastic deformation [Wunderlich et al. (1990), Ping et al. (1995), Li et al. (2000), Valiev et al. (2000)].

The nature of these local strains at grain boundaries can be explained based on the interpretation of a non-equilibrium grain boundary that results when the conditions of compatibility based on misorientation parameters are not satisfied. Such grain boundaries have long-range elastic fields since local elastic deformation is necessary for joining of the crystals [Valiev et al. (1986)]. Notwithstanding the synthesis technique used to produce nanocrystalline materials, there is a commonality amongst the various studies to suggest that the local strains at grain boundaries are intrinsic. This implies that the local strains at grain boundaries can play a crucial role in contributing to microstrain induced XRD line broadening often seen in nanocrystalline materials, which increases as grain size is decreased [Qin and Szpunar (2005)]. As a result, it is conceivable that with decreasing grain size there is also a tendency for an increase in the occurrence of local strains at grain boundaries.

When a comparison was made between the series of images that were analyzed (e.g., Fig. 4.13-4.15), it was evident that with increasing Fe concentration in the deposit, there is
Figure 4.23. HR-TEM image and indexed FFT pattern (inset) of the faulted regions in the grain interior of sample no. 5 (Ni, 23 nm) having a [011] zone axis.

Figure 4.24. HR-TEM image and indexed FFT pattern (inset) of the faulted regions in the grain interior of sample no. 7 (Ni-16wt.%Fe, 12 nm) having a [011] zone axis.
also an increase in the density of lattice defects. A closer examination of these features in the grain interiors was carried out on the series of images for each of the samples. As shown in the example images (Fig. 4.23-4.25), faulted regions are evident. Fig. 4.23 displays evidence of faulted regions in sample no. 5 (Ni, 23 nm) observed with a [011] zone axis and a corresponding FFT pattern showing streaking in the [111] direction. Fig. 4.24 also shows evidence of faulted regions in sample no. 7 (Ni-16wt.%Fe, 12 nm) observed with a [011] zone axis and a corresponding FFT pattern showing streaking in the [111] direction. Sample no. 9 (Ni-32wt.%Fe, 10 nm) revealed a higher density of faulted regions, also observed with a [011] zone axis and a corresponding FFT pattern showing signs of streaking (Fig. 4.25) in the [111] direction.
The streaking in the [111] direction, i.e., normal to the (111) planes, is characteristic for the presence of twinning [Williams and Carter (2009)]. This confirms that the defects are indeed twin stacking faults of the growth type, or “growth faults”, which are not caused by deformation processes. This is also consistent with previous studies which have noted the presence of faulted regions for both electrodeposited nanocrystalline Ni [Nakahara (1981), Yang et al. (2009), Wu et al. (2006)] and Ni-Fe alloys [Ebrahimi and Li (2003)]. In particular, it is consistent with the study of Nakahara (1981) on electrodeposited Ni who identified these faulted regions to have twinning characteristics. According to Nakahara (1981) these growth faults develop during the electrodeposition process. The normal stacking sequence on the (111) planes can change when a successive layer accidentally initiates with atoms binding to the wrong sites during the growth process. That is, if the stacking sequence for a growth fault is $ABCACBA$, then during the growth process the $C$ layer atoms have mistakenly occupied the $B$ sites resulting in the faulted sequence. Furthermore, the addition of soluble alloying elements in fcc metals is known to decrease the stacking fault energy [Murr (1975)], including fcc Ni alloys [Nie et al. (1995)]. The addition of Fe to conventional polycrystalline Ni decreases the stacking fault energy almost linearly down to a minimum value at around 65wt.% Fe after which there is an increasing trend corresponding with a transition to the bcc structure [Charnock and Nutting (1967)]. In the present case, it is likely that there is an increased occurrence of changes in the stacking sequence on the (111) planes during the electrodeposition process for those samples with higher Fe concentration resulting in the observed increased density of these growth faults.
4.5. **X-Ray Diffraction**

The line positions and intensities were calculated for polycrystalline Ni with random crystallographic texture according to the *Bragg law* and the following X-ray diffraction intensity expression [Cullity and Stock (2001)],

\[
I = |F|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M}
\]  \hspace{1cm} (4-1)

where, \(I\) is the relative integrated intensity (arbitrary units), \(F\) is the structure factor, \(p\) is the multiplicity factor, \(\theta\) is the Bragg angle, and \(e^{-2M}\) is the temperature factor. For fcc materials \(F = 4f\) for \(hkl\) unmixed Miller indices and \(F = 0\) for \(hkl\) mixed Miller indices. All values for \(f\) and \(p\) were taken from tables presented in the book by Cullity and Stock (2001). Table 4.3 lists the details of the calculations where \(f\) is the atomic scattering factor, \(\lambda\) is the wavelength of the X-ray (0.1542 nm for Cu-K\(\alpha\) radiation), and \(hkl\) are the corresponding line positions.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>(h^2 + k^2 + l^2)</th>
<th>(\sin \theta)</th>
<th>(\theta)</th>
<th>(2\theta)</th>
<th>(\sin(\theta/\lambda))</th>
<th>(f)</th>
<th>(F^2)</th>
<th>(p)</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>3</td>
<td>0.379</td>
<td>22.3</td>
<td>44.5</td>
<td>0.246</td>
<td>19.09</td>
<td>5830</td>
<td>8</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>4</td>
<td>0.438</td>
<td>26.0</td>
<td>51.9</td>
<td>0.284</td>
<td>17.95</td>
<td>5155</td>
<td>6</td>
<td>46.1</td>
</tr>
<tr>
<td>220</td>
<td>8</td>
<td>0.619</td>
<td>38.2</td>
<td>76.5</td>
<td>0.401</td>
<td>14.89</td>
<td>3547</td>
<td>12</td>
<td>26.1</td>
</tr>
<tr>
<td>311</td>
<td>11</td>
<td>0.725</td>
<td>46.5</td>
<td>93.0</td>
<td>0.471</td>
<td>13.38</td>
<td>2866</td>
<td>24</td>
<td>31.8</td>
</tr>
<tr>
<td>222</td>
<td>12</td>
<td>0.758</td>
<td>49.3</td>
<td>98.6</td>
<td>0.492</td>
<td>12.97</td>
<td>2691</td>
<td>8</td>
<td>9.7</td>
</tr>
<tr>
<td>400</td>
<td>16</td>
<td>0.875</td>
<td>61.1</td>
<td>122.1</td>
<td>0.568</td>
<td>11.60</td>
<td>2154</td>
<td>6</td>
<td>7.0</td>
</tr>
</tbody>
</table>
XRD patterns were generated using the method described in Chapter 3. Each pattern possesses characteristic fcc lines: (111), (200), (220), (311), (222) and (400) which are in order of increasing $2\theta$ value. Examples of XRD patterns for samples no. 5 (Ni, 23 nm) and 7 (Ni-16wt.%Fe) are shown in Fig. 4.26 and 4.27, respectively. The XRD patterns for the remaining samples can be found in Appendix C. Note that the (220) line was generally very weak for all samples except for sample no. 3 (Ni, 44 nm).

![XRD pattern for sample no. 5 (Ni, 23 nm).](image1)

Figure 4.26. XRD pattern (Cu-K$_\alpha$) for sample no. 5 (Ni, 23 nm).

![XRD pattern for sample no. 7 (Ni-16wt.%Fe, 12 nm).](image2)

Figure 4.27. XRD pattern (Cu-K$_\alpha$) for sample no. 7 (Ni-16wt.%Fe, 12 nm).
4.5.1. Lattice Parameter

The lattice parameter for each of the samples was determined using the interplanar spacing values derived from the (111) and (200) lines. The results are summarized in Table 4.4. For the Ni samples, the lines remain at relatively consistent $2\theta$ positions. In the case of the Ni-Fe alloys, there is a general tendency for the lines to shift gradually to lower $2\theta$ positions with increasing Fe indicating that the lattice parameter is being affected by alloying. The lattice parameter values derived from the (111) lines are plotted in Fig. 4.28 as a function of Fe concentration along with those determined in other studies on materials produced using electrodeposition and conventional metallurgical processing methods.

In general, the results are similar to those obtained from studies that used electrodeposition [Jartych et al. (1992), Grimmett et al. (1993), Leith et al. (1993), Li and

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe (wt%)</th>
<th>$2\theta_{111}$ ($^\circ$)</th>
<th>$d_{111}$ (nm)</th>
<th>$a_{111}$ (nm)</th>
<th>$2\theta_{200}$ ($^\circ$)</th>
<th>$d_{200}$ (nm)</th>
<th>$a_{200}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>44.52</td>
<td>0.2035</td>
<td>0.3525</td>
<td>51.88</td>
<td>0.1763</td>
<td>0.3525</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>44.54</td>
<td>0.2034</td>
<td>0.3524</td>
<td>51.88</td>
<td>0.1763</td>
<td>0.3525</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>44.52</td>
<td>0.2035</td>
<td>0.3525</td>
<td>51.92</td>
<td>0.1761</td>
<td>0.3523</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>44.52</td>
<td>0.2035</td>
<td>0.3525</td>
<td>51.86</td>
<td>0.1763</td>
<td>0.3526</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>44.54</td>
<td>0.2035</td>
<td>0.3524</td>
<td>51.82</td>
<td>0.1764</td>
<td>0.3529</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>44.40</td>
<td>0.2041</td>
<td>0.3534</td>
<td>51.74</td>
<td>0.1767</td>
<td>0.3534</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>44.30</td>
<td>0.2045</td>
<td>0.3542</td>
<td>51.58</td>
<td>0.1772</td>
<td>0.3544</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>44.20</td>
<td>0.2049</td>
<td>0.3550</td>
<td>51.44</td>
<td>0.1777</td>
<td>0.3553</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>44.06</td>
<td>0.2056</td>
<td>0.3560</td>
<td>51.20</td>
<td>0.1781</td>
<td>0.3562</td>
</tr>
</tbody>
</table>
Figure 4.28. Plot of lattice parameter vs. Fe concentration in the deposit.

Ebrahimi (2003), Fukumuro et al. (2004), and Wei (2006)]. The lattice parameter in all cases tends to increase linearly with the addition of Fe. In addition to this, the current results also agree well with metallurgically processed Ni-Fe alloys [Jette and Foote (1936), Owen et al. (1937), Bradley et al. (1937)]. The expected linear dependence of the lattice parameter on composition is commonly known as Vegard’s law. As a solute is introduced into a solution, there is a corresponding increase or decrease in lattice parameter based on a rule of mixture,

\[
a_{\text{solution}} = (1 - x)a_{\text{solute}} + xa_{\text{solvent}}
\]  

(4-2)

where, \( a \) is the lattice parameter of the solution, solvent, and solute, respectively, and \( x \) is the atom fraction of the solute. In order to calculate the lattice parameter of the solution, the lattice parameters of the solvent and solute must be given. The samples produced in this study all possess characteristics of the fcc structure. Thus, the lattice parameter for the
solvent is taken as 0.3517 nm for fcc Ni [Jette and Foote (1936), Bradley et al. (1937), Owen et al. (1937)] and for the solute 0.3639 nm for fcc-Fe at the allotropic-transformation temperature (912°C) [Basinski et al. (1955)]. Vegard’s law values are also plotted in Fig. 4.28. In general, there is good agreement with Vegard’s law over the Fe concentration range.

4.5.2. Texture

The orientation index, $I_{hkl}$, is a measure of the relative intensity of each of the characteristic lines as compared to a randomly oriented nickel powder standard [Willson and Rogers (1964)]. The fractional intensities of the first four lines corresponding to the principal crystallographic directions for the samples were divided by the corresponding fractional intensities of the standard (Table 4.3) to obtain the orientation index for each diffraction line. The orientation indices were calculated using the method of Willson and Rogers (1964) described in Chapter 3 (Eq. 3-10) employing the XRD patterns generated for each of the samples. Table 4.5 presents the orientation indices for the four principal crystallographic directions.

The materials used in this study typically have dominant (111) and (200) peaks that are similar to previous X-ray diffraction patterns presented for Ni and Ni-Fe alloy electrodeposits [El-Sherik and Erb (1995), Cheung et al. (1995)]. The only exception is sample no. 3 whose (220) and (311) peaks are relatively significant in intensity. Electrodeposited nanocrystalline materials are known to have fibre textures [McMahon and Erb (1989), Czerwinski et al. (1997)]. In this particular case, it may be said that samples no. 1, 2, 4, 6, 7, 8 and 9 have a strong (200) fibre texture. Sample no. 3 has a weak (200) fibre
texture and is closest to the random orientation relative to the other samples based on the orientation indices for the (220) and (311) peaks. Sample no. 5 has a weak (111)(200) double-fibre texture.

Table 4.5. Orientation indices for the four principal crystallographic directions of the nanocrystalline Ni and Ni-Fe samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe (wt.%)</th>
<th>$I_{111}$</th>
<th>$I_{200}$</th>
<th>$I_{220}$</th>
<th>$I_{311}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.08</td>
<td>4.30</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0.33</td>
<td>3.65</td>
<td>0.05</td>
<td>0.13</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>1.03</td>
<td>1.57</td>
<td>0.58</td>
<td>0.47</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.73</td>
<td>2.73</td>
<td>0.06</td>
<td>0.19</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>1.32</td>
<td>1.28</td>
<td>0.09</td>
<td>0.39</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>0.53</td>
<td>3.21</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>0.85</td>
<td>2.46</td>
<td>0.09</td>
<td>0.17</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>0.80</td>
<td>2.56</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>0.87</td>
<td>2.39</td>
<td>0.10</td>
<td>0.20</td>
</tr>
</tbody>
</table>

4.5.3. Grain Size

The grain size was estimated by using the Scherrer formula (Eq. 3-13) and the FWHM of the (111) and (200) broadened lines. The results are summarized in Table 4.6. Immediately, it can be seen that the grain size estimations resulting from the (111) broadened lines are consistently greater than those resulting from the (200) broadened line. Since XRD is an indirect method, grain sizes determined by imaging techniques, such as TEM, are often considered to be more reliable. A plot of XRD grain size vs. the TEM grain size is presented in Fig. 4.29 to assess the grain size difference for the two methods.
Table 4.6. Summary of grain size estimations using the Scherrer formula for the (111) and (200) broadened lines.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>[Fe] (wt.%)</th>
<th>XRD Grain Size (nm)</th>
<th>TEM Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(111)</td>
<td>(200)</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>43</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>23</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>19</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>19</td>
<td>13</td>
</tr>
<tr>
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<td>16</td>
<td>16</td>
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<td>8</td>
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<td>14</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>12</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 4.29. Plot of XRD grain size estimations vs. TEM grain size determinations. The reference (dashed) line represents a 1:1 agreement between the two methods.
The dashed line in Fig. 4.29 represents the agreement between the two methods. As seen in Fig. 4.29, the agreement between the XRD and TEM grain size estimations is good for those samples with grain sizes less than 20 nm. In fact, for these samples the TEM grain sizes are bound by the (111) and (200) estimations. According to the earlier analysis, the grain size distribution for these samples (no. 7-9) is log-normal and the grain volume distribution is relatively narrow. When TEM grain sizes are greater than 20 nm, the XRD grain size estimations tend to be considerably lower.

The use of XRD analysis to predict the grain size of materials with a broad grain size distribution that includes coarse grains (i.e., greater than 100-300 nm) is typically inaccurate. This results from the fact that the coarse grains do not affect line broadening [Klug and Alexander (1974)] leading to the inability of XRD analysis to determine accurately the grain size of such materials [He et al. (2004)]. For the current study, evidence of broader grain size distributions are typically observed at average grain sizes greater than 20 nm which results in the underestimations. It is at this transition point where the XRD grain size begins to significantly disagree with the grain sizes determined via TEM image analysis. Thus, XRD grain size estimations are more accurate when the average grain size is less than 20 nm, and the grain size distributions are much narrower.

It should be noted that grain size estimations from XRD line width measurements (e.g., using Eq. 3-13) typically give volume-weighted “column lengths”. In order to reconcile this, the XRD volume-weighted “column length” must be compensated to yield an average grain diameter. Although TEM is normally used to verify the accuracy of
estimations provided by XRD methods, it should also be recognized that this analysis can produce notable uncertainty when considering the fact that the number of grains that can be analyzed is normally small in comparison with the rest of the sample. In addition to this, TEM image analysis is carried out based on the assumption that grains are approximately equiaxed [Krill and Birringer (1998)].

4.5.4. Growth Faults

4.5.4.1. Probabilities*

The results of the HR-TEM analysis earlier identified the presence of lattice defects which are considered to be growth faults since no external loads were applied on the samples. Based on this, a further analysis was carried out to quantify the growth fault probabilities in the series of electrodeposited nanocrystalline Ni and Ni-Fe alloys. Quantification of growth faults was performed by analyzing (111) and (200) peak asymmetries from the XRD patterns of each sample to determine their respective growth fault probabilities using Eq. 3-18 [Cohen and Wagner (1962)]. Note that the stacking fault probability is often considered to be inversely proportional to the stacking fault energy at constant dislocation density [Charnock and Nutting (1967)]. Table 4.7 presents the respective growth fault probabilities for each of the samples.

The growth fault probabilities for the nanocrystalline Ni samples were found to be relatively low. In other words, the relatively high stacking fault energy for pure Ni (120-130

Table 4.7. Growth fault probabilities for the series of nanocrystalline Ni and Ni-Fe alloys.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe (wt.%</th>
<th>Grain Size (nm)</th>
<th>Growth Fault Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>~255</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>81±51</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>44±30</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>37±21</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>23±11</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>32±18</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>12±7</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>10±5</td>
<td>1.0</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>10±5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Figure 4.30. Plot of growth fault probability vs. Fe concentration in the deposit showing an increasing trend with increasing Fe. The dashed line is a (linear) best fit for the current data.
mJ/m² [Carter and Holmes (1977)]) is consistent with the relatively low growth fault probabilities determined for the pure nanocrystalline Ni samples. This is also consistent with the low occurrence of growth faults observed in the HR-TEM image analysis. In the case of the nanocrystalline Ni-Fe samples, the growth fault probabilities significantly increased with increasing Fe. Fig. 4.30 shows a plot of the growth fault probabilities versus Fe concentration. This increasing trend with Fe is similar to that of Sambongi (1965) who noticed that the addition of Fe to conventional polycrystalline Ni increased the deformation stacking fault probability which reached a maximum near 50 wt.% Fe. More recently, Ni and Zhang (2012) demonstrated the effects of Fe concentration on the mechanical behaviour of nanocrystalline Ni-Fe alloys and noted an increasing compound (deformation and growth) fault probability with increasing Fe after rolling.

As mentioned earlier, the addition of soluble alloying elements in fcc metals is known to decrease the stacking fault energy [Murr (1975)], including Ni alloys [Nie et al. (1995)]. In the case of fcc Ni-Fe alloys, the addition of Fe to conventional polycrystalline Ni decreases the stacking fault energy almost linearly down to a minimum value at around 65wt.%Fe. For example, at 10, 20 and 30wt.%Fe, the stacking fault energies are approximately 103, 89 and 73 mJ/m², respectively [Charnock and Nutting (1967)]. Similarly, as seen in Fig. 4.30, the growth fault probabilities increase more or less in a linear manner with increasing Fe concentration in the deposit. This observation provides evidence to support the earlier HR-TEM image analysis which showed an increased presence of growth faults with increasing Fe concentration.
4.5.4.2. Electron Structure

The electron structure of alloys has often been recognized as having a controlling influence on the physical properties of solid solutions [Hume-Rothery and Raynor (1983)]. The controlling factor is referred to as the electron concentration which is typically expressed as the free-electron-to-atom ratio, $e/a$. The $e/a$ ratio can be calculated in the following manner,

$$
e/a = 1 + x \Delta V$$

where, $x$ is the atomic fraction solute content, and $\Delta V = V_{solute} - V_{solvent}$ is the difference in valency of the solute and solvent atoms, respectively. The theory assumes that an alloy forms a crystal structure which accommodates the valence electrons with the lowest free energy. Several studies have shown that the there is a clear decreasing trend for stacking fault energy with an increase in the $e/a$ ratio [Howie (1961), Thornton et al. (1962), Murr (1975)]. Wang (2004) employed this theory to describe the dependency of the $e/a$ ratio on the stacking fault energy of various Cu alloys as it relates to cyclic deformation response and the transition of wavy-slip mode to planar-slip mode. When the stacking fault energies for polycrystalline Cu-Al, Cu-Zn and Cu-Mn fcc alloys are plotted as a function of the $e/a$ ratio, there is a clear decreasing trend down to a minimum value. In other words, as the $e/a$ ratio increases, the slope of the curve decreases. In fact, the slope goes to zero or the trend effectively reaches a minimum stacking fault energy value.

A similar analysis for the current study was carried out to examine the dependency of the stacking fault energy on the $e/a$ ratio. Using the stacking fault energy values of
Charnock and Nutting (1967) for the entire range of Ni-Fe alloys a plot vs. the respective $e/a$ ratio may be constructed (see Fig. 4.31). In order to apply the electron theory the two atoms used to form the alloy must have differing valences. The valency for Ni is taken to be 2. In the case of Fe, there are two valences: 2 and 3. Thus, to calculate $e/a$ ratios, the valency for Fe is assumed to be 3.

Increasing $e/a$ ratio for the Ni-Fe alloys is synonymous with increasing Fe in the alloy. The stacking fault energy for the Ni-Fe alloys decreases linearly and reaches a minimum value at approximately 65wt.%Fe which corresponds to an $e/a$ ratio of approximately 1.66. The stacking fault energy then begins to increase in a linear manner with further additions of Fe or increasing $e/a$ ratio. Note that near the minimum, the alloy
is transitioning from the fcc phase to the bcc phase with increasing Fe and the reason for the change in slope is, in fact, this phase transformation. Also plotted in Fig. 4.31 are the growth fault probabilities determined for the series of nanocrystalline Ni and Ni-Fe alloys produced in the current study. As previously described, the growth fault probabilities for the nanocrystalline Ni-Fe alloys as a function of Fe concentration behave in a similar manner as that of the stacking fault energies of their polycrystalline counterparts. That is, the growth fault probabilities and the stacking fault energies of both the nanocrystalline and polycrystalline alloys have an approximate linear dependence with Fe concentration. Similarly, they both also have a linear dependence with respect to the $e/a$ ratio. Since there is a defined relationship between the stacking fault energy or growth fault probability and the $e/a$ ratio, it follows that the electron theory applies to the Ni-Fe alloys. This emphasizes the importance of the $e/a$ ratio in controlling their various physical and other properties. Thus, it can be said that the growth fault probability or stacking fault energy for the Ni-Fe alloys also depend on the $e/a$ ratio instead of simply the nature and concentration of the solute [Tiwari and Ramanujan (2001)].

4.6. Thermal Analysis

4.6.1. Total Enthalpy (Stored Energy)

The main defects found in fully dense, single phase nanocrystalline materials are intercrystal defects. For example, at a grain size of about 10 nm, approximately 27% of the volume consists of grain boundaries and triple junctions (see Fig. 2.4b). In conventional deformed polycrystalline materials, the release of stored energy during annealing is often a result of recovery, recrystallization, and grain growth. The recovery process is accompanied
by a reduction in dislocation density while the recrystallization process forms new strain-free grains. Finally, at sufficiently high temperatures grain growth will occur. In nanocrystalline materials, the release of energy is often based on the assumption that the presence of dislocations and other lattice defects is negligible. Thus, the energy released in these materials is almost exclusively the result of grain growth or decreasing the number of intercrystal defects in the system.

This energy release can be measured via calorimetric techniques and used to characterize the material’s total enthalpy, $\Delta H_{\text{total}}$, or stored energy due to intercrystal defects by integrating anisothermal heat release curves. In this study, differential scanning calorimetry (DSC) was used to produce anisothermal anneal curves for all nine samples. Only those anisothermal anneal curves which produced significant heat releases were analyzed, i.e., samples no. 4-9. Examples of the anisothermal anneal curves are given in Fig. 4.32 for sample no. 4 (Ni, 37 nm) and Fig. 4.33 for sample no. 9 (Ni-32wt.%Fe, 10 nm). Table 4.8 summarizes the total enthalpy, $\Delta H_{\text{total}}$, the peak temperature, $T_p$, and Curie temperature, $T_c$, values for all of the specimens along with the respective grain sizes determined using TEM image analysis.

With the exception of samples no. 1-3 the anisothermal anneal curves experienced a minimal amount of exothermic heat release prior to the main heat release corresponding to grain growth. This initial heat release is considered to be due to subgrain coalescence leading to the onset of the abnormal grain growth stage in the annealing process [Klement et
Figure 4.32. Anisothermal anneal (DSC) curve for sample no. 4 (Ni, 37 nm).

Figure 4.33. Anisothermal anneal (DSC) curve for sample no. 9 (Ni-32wt.%Fe, 10 nm).
Table 4.8. Total enthalpy, $\Delta H_{\text{total}}$, the peak temperature, $T_p$, and Curie temperature, $T_C$, for the samples, and respective Fe concentration and grain size values.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>[Fe] (wt.%)</th>
<th>Grain Size (nm)</th>
<th>$\Delta H_{\text{total}}$ (J/g)</th>
<th>$T_p$ (°C)</th>
<th>$T_C$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>~255</td>
<td>-</td>
<td>-</td>
<td>357</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>81±51</td>
<td>-</td>
<td>-</td>
<td>356</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>44±30</td>
<td>-</td>
<td>-</td>
<td>356</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>37±21</td>
<td>12.49</td>
<td>307</td>
<td>357</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>23±11</td>
<td>14.34</td>
<td>282</td>
<td>357</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>32±18</td>
<td>17.06</td>
<td>379</td>
<td>433</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>12±7</td>
<td>20.03</td>
<td>393</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>10±5</td>
<td>23.20</td>
<td>405</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>10±5</td>
<td>23.76</td>
<td>405</td>
<td>-</td>
</tr>
</tbody>
</table>

al. (1995a), Klement et al. (1995b)]. If the initial heat release is combined with the main grain growth heat release, both “nucleation” and abnormal grain growth processes may be taking place followed by normal grain growth – this was the case for samples no. 4-6 and the combined release was integrated to determine the total enthalpy. If the initial heat release may be distinguished clearly from the grain growth heat release, “nucleation” is likely the dominating process followed by normal grain growth – this was the case for samples no. 7-9 and only the main grain growth peak was integrated to determine the total enthalpy. In addition to determining the total enthalpy, the maximum or peak temperature, $T_p$, of the grain growth peak was reported for each sample. It should be noted that the increase in peak temperature, $T_p$, with increasing Fe is of particular importance to the use these materials in applications where the temperature is relatively high. By alloying, a stabilizing effect is imparted [Erb et al. (2007)] which allows for the use of these materials in various higher temperature applications, for example, wear resistance at elevated temperatures.
In the case of the nanocrystalline Ni samples, the Curie temperatures are relatively constant and agree well with what is reported in the phase diagram (Fig. 4.1). A decrease in grain size increases the measured total enthalpy. This trend is consistent with Turi (1997) who produced anisothermal anneal curves using modulated differential scanning calorimetry (MDSC) with nanocrystalline nickel samples with grain sizes of 10, 20, and 30 nm. In the analysis carried out by Turi (1997), a distinct relationship was made between grain size or intercrystal volume fraction and total enthalpy based on the assumption that the only defects present in considerable quantities were intercrystal defects. Fig. 4.34 shows a plot of the total enthalpy versus grain size for the nanocrystalline Ni samples. The total enthalpy values of the nanocrystalline Ni samples agree well with those of Turi (1997). A direct relationship between the nanocrystalline Ni-Fe samples and grain size cannot be made mainly due to other possible contributing factors, such as ordering to form the FeNi₃ [Turi (1997)]. Instead, the total enthalpy values are plotted as a function of Fe concentration in the deposit (Fig. 4.35).

The Curie temperature for sample no. 6 (Ni-7.3wt.%Fe) was determined to be about 433°C and is slightly lower than what is reported in the phase diagram (Fig. 4.1). Curie temperatures of the remaining Fe containing samples were not detected since they occur at values greater than 500°C which is outside of the upper limit of the scanned range in the DSC measurements. In general, the total enthalpy values for those samples containing Fe are significantly higher when compared to the nanocrystalline Ni samples. This in part due to the Ni-Fe alloys having smaller grain sizes, i.e., samples no. 7, 8, and 9. In addition to this,
### Figure 4.34
Total enthalpy plotted as a function of grain size for the nanocrystalline Ni samples. The dashed line is an approximate trend line.

<table>
<thead>
<tr>
<th>Grain Size (nm)</th>
<th>Total Enthalpy (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>40</td>
<td>13</td>
</tr>
</tbody>
</table>

### Figure 4.35
Total enthalpy plotted as a function of grain size for the nanocrystalline Ni samples. The dashed lines are approximate trend lines.

<table>
<thead>
<tr>
<th>Fe Concentration (wt.%)</th>
<th>Total Enthalpy (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>25</td>
<td>35</td>
</tr>
</tbody>
</table>
non-equilibrium structures are normally observed in electrodeposited Ni-Fe alloys [Fukumuro et al. (2004)]. As a result, the formation of an equilibrium structure from the non-equilibrium structure may represent a significant portion of the measured total enthalpy [Turi (1997)]. Another possible contributing factor in the nanocrystalline Ni-Fe samples is the reduction of growth faults during the grain growth process. As was seen in the HR-TEM image analysis and the XRD analysis, there was a characteristic increase in the occurrence of growth faults with increasing Fe. As a result, there is also more stored energy in the form of lattice defects. Thus, for the nanocrystalline Ni-Fe alloys, it may be said that there is also an alloying effect associated with the total enthalpy released during anisothermal annealing related to a combination of the formation of equilibrium structures and the reduction of lattice defects such as growth faults.

4.6.2. Excess Interfacial Enthalpy

Since the energy released in the nanocrystalline Ni samples can almost be exclusively a result of reducing intercrystal defects [Turi (1997)], a direct relationship between the total enthalpy, $\Delta H_{\text{total}}$, and the intercrystal volume fraction can be derived to determine the excess interfacial enthalpy, $\Delta H_{\text{ic}}$ [Wang et al. (1997)]. The relationship is derived using the model developed by Palumbo et al. (1990) that quantifies the intercrystal volume fraction in polycrystalline materials based on grains having a tetrakaidecahedron shape. The change in intercrystal volume fraction as a result of the anisothermal annealing process is given by,

$$\Delta f_{\text{ic}} = f_{\text{ic}}(d_f) - f_{\text{ic}}(d_i) \tag{4-4}$$
where, $d_f$ and $d_i$ are the final and initial grain sizes and $f_{ic}$ is the intercrystal volume fraction. Substituting the total intercrystal volume fraction equation (Eq. 2-1) given by Palumbo et al. (1990) in to Eq. 4-4, we arrive at the following expression that allows for the determination of the change in intercrystal volume fraction,

$$
\Delta f_{ic} = \left(1 - \frac{\Delta}{d_f}\right)^3 - \left(1 - \frac{\Delta}{d_i}\right)^3
$$

(4-5)

where, $\Delta$ in the expression on the right hand side of the equal sign is the grain boundary thickness and is assumed to be 1 nm. Finally, the relationship used to obtain the excess interfacial enthalpy, $\Delta H_{ic}$, is given as follows,

$$
\Delta H_{total} = \Delta f_{ic} \cdot \Delta H_{ic}
$$

(4-6)

For the final grain size, $d_f$, a reasonable value of 1000 nm was taken. Table 4.9 provides a summary of the values for excess interfacial enthalpy, $\Delta H_{ic}$. The excess interfacial enthalpy or interfacial energy, $\Delta H_{ic}$, may then be multiplied by the density of Ni (8.9 g/cm$^3$) and the grain boundary thickness (1 nm) to determine the grain boundary energy, $\gamma_{gb}$.

Fig. 4.36 shows a plot of the excess interfacial energy with grain size. The grain boundary energy values are also plotted with grain size in Fig. 4.37. In both cases, the plots show a linear decreasing trend for grain boundary energy as a function of grain size which agrees well with the data of Turi (1997) for nanocrystalline Ni, and is consistent with Lu et al. (1993) who studied a nanocrystalline Ni-P system. At grain sizes above 30 nm, the grain boundary energies are comparable to experimentally extrapolated values at their respective
Table 4.9. Calculated excess interfacial enthalpy and grain boundary energy for the nanocrystalline Ni samples. Also shown are the values from Turi (1997).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Grain Size (nm)</th>
<th>$\Delta f_{ic}$</th>
<th>$\Delta H_{total}$ (J/g)</th>
<th>$\Delta H_{ic}$ (J/g)</th>
<th>$\gamma_{gb}$ (J/m²)</th>
<th>$\gamma_{gb}$ † (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>37±21</td>
<td>0.077</td>
<td>12.49</td>
<td>163</td>
<td>1.449</td>
<td>1.216</td>
</tr>
<tr>
<td>5</td>
<td>23±11</td>
<td>0.123</td>
<td>14.34</td>
<td>117</td>
<td>1.039</td>
<td>1.227</td>
</tr>
<tr>
<td>*</td>
<td>30</td>
<td>0.094</td>
<td>12.52</td>
<td>133</td>
<td>1.190</td>
<td>1.234</td>
</tr>
<tr>
<td>*</td>
<td>20</td>
<td>0.140</td>
<td>13.05</td>
<td>93</td>
<td>0.832</td>
<td>1.233</td>
</tr>
<tr>
<td>*</td>
<td>10</td>
<td>0.268</td>
<td>16.63</td>
<td>62</td>
<td>0.553</td>
<td>1.230</td>
</tr>
</tbody>
</table>

* Turi (1997), † Murr (1975)

Figure 4.36. Plot of interfacial free energy ($\Delta H_{ic}$) vs. grain size. The dashed line is a best fit for both sets of data.
peak temperatures determined for conventional polycrystalline Ni [Murr (1975)]. At grain sizes less than 20 nm, there is a clear reduction in the grain boundary energy values. There are several possibilities for the observed reduction in grain boundary energy below 20 nm. Some of the possibilities were considered by Turi (1997): (1) the influence of solute segregation where it is known that the addition of S to grain boundaries can reduce the energy in Ni [Murr (1975)] – in this particular case, the S concentration in the deposit was found to increase with decreasing grain size, (2) the texture of the material which has been shown to be quite different for these two samples may also have an influence whereby grain boundary character distribution may also vary, and (3) the volume fraction of triple junctions and their characteristics (i.e., I-lines or U-lines) may also have a profound effect on the interfacial energy.
4.7. **Summary**

A series of nanocrystalline Ni and Ni-Fe alloys were synthesized using the electrodeposition technique. The nanocrystalline Ni and Ni-Fe alloys were produced with considerable amounts of impurities namely S and C. The S concentration in the deposit was found to be dependent on the amount of Nanovate™ A24 present in the electrolyte. The C concentration in the deposit varied and no relationships with the organics in the electrolyte were noted. In the case of the nanocrystalline Ni-Fe samples, increasing the Fe in the electrolyte resulted in a systematic increase of Fe concentration in the deposit. The deposit quality for all samples was consistent in that they were all smooth, except for the largest grain size sample (no. 1, ~255 nm). There was also no presence of microcracking. Surface oxides were visible on the sample surface which became more prominent with the addition of Fe.

Microstructural characterization was performed on the series of nanocrystalline Ni and Ni-Fe alloys using a variety of analytical techniques. The grain sizes of the samples were initially determined using TEM image analysis. Additional HR-TEM image analysis was performed on selected samples for the purpose of examining the defects present in these materials. Examples of a triple junction, high angle grain boundary, low angle grain boundary and twin boundary were shown. The grain boundaries analyzed all displayed some level of accommodation strain which was consistent with other HR-TEM studies on nanocrystalline materials synthesized using different means. Also present in the HR-TEM images were features in the grain interiors consistent with stacking faults. Since no deformation was imposed on these samples, the stacking faults are likely to be twin faults of
the growth type, or “growth faults”. These growth faults became more prominent with increasing Fe concentration in the deposit.

The lattice parameters determined for all of the samples agreed well with their polycrystalline counterparts. In the case of the nanocrystalline Ni-Fe alloys, increasing Fe was found to increase the lattice parameter consistent with the predictions of *Vegard’s law*. All samples contained various degrees of crystallographic texture. Most samples were found to have a strong (200) fibre texture while others had either a weak (200) fibre texture or a double (111)(200) fibre texture. Grain sizes were determined by XRD pattern analysis and compared with those determined using TEM image analysis. XRD grain sizes that were less than 20 nm were found to agree well with the TEM grain sizes. The XRD method provided significant underestimations at TEM grain sizes greater than 20 nm. The growth fault probability of each sample was quantified by XRD pattern analysis based on peak asymmetries. The growth fault probabilities for the nanocrystalline Ni samples were relatively constant over the grain size range. In the case of the nanocrystalline Ni-Fe samples, the growth fault probabilities increased linearly with the addition of Fe. This trend was found to be consistent with polycrystalline Ni-Fe alloys when comparing to the respective stacking fault energies. The finding also supports the earlier HR-TEM studies which suggested the presence of growth faults and their increased presence with increasing Fe.

Finally, thermal analysis of the nanocrystalline Ni samples provided results that were consistent with previous studies. The total enthalpy (or stored energy) release values
compared well with the increasing trend observed with decreasing grain size and consistent results were also observed for the grain boundary energy estimations. The nanocrystalline Ni-Fe alloys displayed total enthalpy (or stored energy) release values which were consistently higher than those of the nanocrystalline Ni samples when related to grain size, which is also consistent with previous studies. A direct relationship with grain size was not found to be feasible due to other influencing factors which contribute to the heat release event corresponding to grain growth. These factors include ordering of the atomic structure since it is likely that they were deposited in a non-equilibrium state and the reduction of growth faults which are known to be present in increasing quantities with increasing Fe concentration in the deposit.
4.8. References


Chapter 4 – Materials Synthesis and Characterization


Thornton, P.R., T.E. Mitchell and P.B. Hirsch, Phil. Mag. 7 (1962) 1348.


Wang, Z., Phil. Mag. 84 (2004) 351.


5.1. Introduction

One of the objectives of this study was to examine two important properties, namely the hardness and Young’s modulus of nanocrystalline Ni with varying grain sizes and nanocrystalline Ni-Fe alloys as a function of Fe concentration and/or grain size. The study will also consider the effects of other important factors that are known to influence Young’s modulus, especially preferred crystallographic orientation, or texture. A better understanding of the effect of grain size on the Young’s modulus of nanocrystalline Ni-Fe alloys is of particular interest because of the unusual effect of composition observed for these alloys in the polycrystalline form. In contrast to polycrystalline Ni-Cu alloys, which show a relatively linear decrease in Young’s modulus with increasing Cu concentration [Guy (1972)], polycrystalline Ni-Fe alloys show a deep minimum at about 60wt.% Fe (as shown in Fig. 5.1) even though pure Fe and pure Ni have almost the same Young’s modulus values [Ledbetter and Reed (1973)].

It should also be pointed out that although a general trend in Fig. 5.1 is obvious, for any given composition including the pure materials, there are significant variations in the data presented in different studies. The Young’s modulus trend for the Ni-Fe alloys may be explained based on the fact that at greater than 60wt.%Fe, there is a transition from the fcc phase to the bcc phase. On the other hand, the Ni-Cu alloys do not show this behaviour because it remains in the fcc phase over the entire compositional range.

5.2. Results

The hardness and Young’s modulus for each sample were determined using nanoindentation as described in Chapter 3 (Section 3.6). The last elastic unloading curves were analyzed to determine the Young’s modulus using the procedure outlined by Oliver and Pharr (1992). An example of a series of load-unload curves in a force-depth graph is shown
**Chapter 5 – Indentation Behaviour**

Figure 5.2. Force-depth graph showing load-unload curves of sample no. 7 (Ni-16wt.%Fe, 12 nm).

Table 5.1. Characterization, hardness, and Young’s modulus data.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe (wt.%)</th>
<th>Grain Size (nm)</th>
<th>Orientation Indices</th>
<th>Hardness (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$I_{111}$ $I_{200}$</td>
<td></td>
<td>$E_m$ $E_0$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>~255</td>
<td>0.08 4.30</td>
<td>2.7±0.4</td>
<td>151±23 207†</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>81±51</td>
<td>0.33 3.65</td>
<td>4.1±0.6</td>
<td>203±14 207†</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>44±30</td>
<td>1.03 1.57</td>
<td>5.0±0.7</td>
<td>204±20 207†</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>37±21</td>
<td>0.73 2.73</td>
<td>5.3±0.6</td>
<td>194±18 207†</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>23±11</td>
<td>1.32 1.28</td>
<td>6.3±0.7</td>
<td>209±12 207†</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>32±18</td>
<td>0.53 3.21</td>
<td>5.6±0.3</td>
<td>202±10 203‡</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>12±7</td>
<td>0.85 2.46</td>
<td>6.5±0.4</td>
<td>189±8 202‡</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>10±5</td>
<td>0.80 2.56</td>
<td>6.4±0.5</td>
<td>187±10 211‡</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>10±5</td>
<td>0.87 2.39</td>
<td>6.3±0.6</td>
<td>169±5 189‡</td>
</tr>
</tbody>
</table>

† Davis (1990), ‡ Ledbetter and Reed (1973)
in Fig. 5.2 for five different loads (150, 130, 110, 90 and 70 mN) performed at a loading rate of 13.3 mN/s. Table 5.1 summarizes the hardness and Young’s modulus results for each of the samples. The errors reported in the table and figures correspond to one standard deviation. For discussion purposes, the orientation indices that were determined in Chapter 4 (Table 4.5) are also provided in Table 5.1. As expected, the hardness values gradually increase with decreasing grain size. The measured Young’s modulus values, $E_m$, have some noticeable differences when compared to the literature values, $E_0$, for polycrystalline materials. These observations are discussed in the subsequent sections.

### 5.3. Effect of Grain Size on Hardness

A plot of the hardness values with the inverse square root of the average grain size for all materials produced (Fig. 5.3) shows a transition from regular to inverse Hall-Petch behaviour which is in agreement with previous studies [El-Sherik et al. (1992), Erb et al. (1996), Cheung et al. (1995), Ebrahimi et al. (1999), and Li and Ebrahimi (2003)]. The slope for the region representing regular Hall-Petch behaviour was determined to be approximately 24 GPa/nm$^{1/2}$ which is similar to 28 GPa/nm$^{1/2}$ reported by Hughes et al. (1986) for electrodeposited nanocrystalline Ni with grain sizes in the range of 12 to 12,500 nm. It should be noted that solid solution hardening in the Ni-Fe alloys was previously found to be insignificant compared to grain size hardening [Erb et al. (1996), Cheung et al. (1995)].

Several interpretations have been given to explain deviations from the regular Hall-Petch behaviour. When the grain size is sufficiently small, i.e., less than 20 nm, dislocation slip is no longer the dominant deformation mechanism. As a result, deviations from the Hall-
Figure 5.3. Hall-Petch plot for the series of nanocrystalline Ni and Ni-Fe alloys.

Petch relationship are observed and other deformation mechanisms begin to operate. Chokshi et al. (1989) observed a similar behaviour for nanocrystalline Cu and Pd produced using the inert gas condensation technique and suggested that room temperature Coble (Nabarro-Herring) creep occurs and is possible at this temperature because of the relatively high intercrystal volume fraction in these materials. In a study on electrodeposited nanocrystalline Ni-P alloys, Palumbo et al. (1990b) owed deviations from regular Hall-Petch behaviour to the fact that triple lines account for a significant fraction of the bulk volume, especially when the grain size is less than 20 nm. The deformation of electrodeposited nanocrystalline Ni over a broad grain size range of 40 to 6 nm was analyzed by Wang et al. (1997). They demonstrated that at high stress levels, grain boundary sliding is essentially the main room temperature deformation mechanism, although creep mechanisms can contribute
significantly at small grain sizes. Wang et al. (1997) proposed that the deviations from the Hall-Petch relationship are caused by a dynamic creep process due to diffusion mechanisms.

5.4. Effect of Grain Size on Young’s Modulus

Table 5.1 summarizes the Young’s modulus measurement data for each of the samples. Depending on the load and sample, indentation depths ranged between approximately 0.8 and 1.5 μm, i.e., ≤ 3% of the sample thickness. The Young’s modulus for the Ni samples was measured and the values obtained were found to be similar to conventional (randomly oriented) polycrystalline Ni, ~207 GPa [Davis (1990)], down to an average grain size of about 20 nm. The Young’s modulus for the nanocrystalline Ni-Fe alloys was also measured; however, for comparative purposes, values for conventional (randomly oriented) polycrystalline Ni-Fe counterparts with the exact same compositions were not available. Instead, a comprehensive collection of data for the complete range of conventional (randomly oriented) polycrystalline Ni-Fe alloys was compiled earlier by Ledbetter and Reed (1973), shown in Fig. 5.1. For the fcc phase polycrystalline Ni-Fe alloys, there is a notable variation and distinct trend with increasing Fe concentration. From about 0 to 20 wt.%Fe, the Young’s modulus is relatively constant. This is then followed by a decrease down to a minimum average value of ~140 GPa at around 60wt.%Fe. Increasing the Fe concentration in the nanocrystalline Ni-Fe alloys shows a similar trend (Table 5.1). In order to compare the values obtained for nanocrystalline Ni-Fe alloys to their conventional (randomly oriented) polycrystalline counterparts, an average of the Young’s modulus values, was taken from the collection of data [Ledbetter and Reed (1973)] for compositions close to the four alloys obtained in the current study. The measured values were then normalized,
$E_m/E_0$, where $E_m$ is the measured value and $E_0$ is the respective conventional (randomly oriented) polycrystalline counterpart value, and then plotted as a function of grain size (Fig. 5.4). In the case of Ni, $E_0$ is the value of its conventional polycrystalline counterpart value, \(~207\) GPa [Davis (1990)].

Figure 5.4. Normalized Young’s modulus values as a function of grain size. The horizontal solid line represents $E_m/E_0 = 1$, where $E_m$ is the measured value and $E_0$ is the respective conventional (randomly oriented) polycrystalline counterpart value. The dashed lines correspond to the values predicted by the upper bound composite model (Eq. 5-1). The solid lines correspond to the values predicted by the lower bound (Eq. 5-2) composite model.

The effect of decreasing grain size on Young’s modulus was previously investigated by Shen et al. (1995) for nanocrystalline Fe produced by mechanical attrition. Zhou et al. (2003a), Zhou et al. (2003b), and Zhou et al. (2009) also investigated the effect of grain size on the Young’s modulus of electrodeposited Ni-2.5wt.%P. In both cases, the influence of the various structural components (grain interiors, grain boundaries, and triple junctions) in nanocrystalline materials [Palumbo et al. (1990a)] was estimated according to a simple rule.
of mixtures by considering their volume fractions in a composite model and taking into consideration both upper (Eq. 5-1) and lower (Eq. 5-2) bound solutions [Callister (2005)],

\[
E_m = E_g f_g + E_{gb} f_{gb} + E_y f_y
\]  
\[
\frac{1}{E_m} = \frac{f_g}{E_g} + \frac{f_{gb}}{E_{gb}} + \frac{f_y}{E_y}
\]

where, \( E_m \) is the measured Young’s modulus of the material, \( f_g(E_g) \) , \( f_{gb}(E_{gb}) \) and \( f_y(E_y) \) the volume fractions (average Young’s moduli) for grain interiors, grain boundaries and triple junctions, respectively. Note that the upper bound solution (Eq. 5-1) is based on the isostrain condition while the lower bound is based on the isostress condition. Volume fractions were calculated by using a reasonable range for grain boundary thicknesses of 0.7 and 1.1 nm [Kirchheim et al. (1988)] and assuming a three-dimensional tetrakaidecahedral model for the crystal shape [Palumbo et al. (1990a)] using Eq. 2-1, 2-2, 2-3, and, 

\[
f_g = 1 - f_{ic}
\]

where, \( f_{ic} \) is the total intercrystal volume fraction. The value for \( E_g \) is considered to be the same as that of the conventional (randomly oriented) polycrystalline counterparts. The values for \( E_{gb} \) and \( E_y \) are taken to be about 76% and 73%, respectively, of the value for the conventional polycrystalline counterparts [Zhou et al. (2003b)]. Normalized values, for Young’s modulus were then plotted in Fig. 5.4 as a function of grain size along with the composite model predictions for the upper bound (dashed lines) and lower bound (solid lines) solutions using both grain boundary thicknesses.
Chapter 5 – Indentation Behaviour

In general, there is relatively good agreement with the composite model predictions as the grain size of the nanocrystalline Ni and Ni-Fe alloys decreases to below 20 nm. At average grain sizes greater than 20 nm most of the normalized average values are slightly less than $E_m / E_0 = 1$. These samples have a weak to strong (200) fibre texture. Sample no. 1 (Ni, 255 nm) has a very strong preferred (200) fibre texture and a corresponding $E_m / E_0$ value which is much lower than $E_m / E_0 = 1$. Sample no. 5 (Ni, 23 nm), which has a (111)(200) double fibre texture, is slightly greater than $E_m / E_0 = 1$. At average grain sizes less than 20 nm, the normalized values are clearly below $E_m / E_0 = 1$ and lie near or clearly below the lower bounds of the composite model predictions. These samples all have a preferred (200) fibre texture. The general trend for $E_m / E_0$ as grain size decreases is consistent with previous studies [Shen et al. (1995), Zhou et al. (2003a), Zhou et al. (2003b), Zhou et al. (2009)]; however, there is a notable variability when compared to the composite model predictions. This observation introduces a need to analyze the anisotropic elastic behaviour of these materials and consider the influence of texture together with grain size.

5.5. Effect of Texture on Young’s Modulus

As noted in Chapter 4 (Section 4.5.2), the materials in this study were all observed to have some degree of texture. For the purposes of this discussion, the orientation indices for the strongest texture components ($I_{111}$ and $I_{200}$) are also summarized in Table 5.1. To establish an understanding of the anisotropic elastic behaviour of these materials, their dependence on crystallographic orientation is described based on three well known theoretical relationships. Firstly, the extreme situations are considered in order to illustrate
the effect of texture by calculating the values for the principal crystallographic directions in the cubic lattice using [Meyers and Chawla (1998)],

\[
1/E = s_{11} - 2[(s_{11} - s_{12}) - s_{44}/2](l_1^2 l_2^2 + l_2^2 l_3^2 + l_1^2 l_3^2) \tag{5-4}
\]

where, \(s_i\) are the elastic compliances and \(l_1, l_2,\) and \(l_3\) are the direction cosines. In the case of the (111) direction, \(\Sigma l_i^2 l_j^2 = 1/3\), so the equation reduces to,

\[
1/E_{111} = s_{11} - 2[(s_{11} - s_{12}) - s_{44}/2]/3 \tag{5-5}
\]

For the Young’s modulus in the (100) direction, the equation reduces to,

\[
1/E_{100} = s_{11} \tag{5-6}
\]

since \(\Sigma l_i^2 l_j^2 = 0\). For these materials and particularly for the fcc arrangement \(E_{111} > E_{100}\).

Given the elastic stiffnesses \((c_{11}, c_{12},\) and \(c_{44}\)) for single crystal Ni [DeKlerk and Musgrave (1955)] and single crystal Ni-Fe alloys [Kanrar and Ghosh (1983)], the values for the two principal crystallographic directions are calculated for Ni \((E_{111} = 293 \text{ GPa}, E_{100} = 130 \text{ GPa})\), Ni-10wt.%Fe \((E_{111} = 299 \text{ GPa}, E_{100} = 131 \text{ GPa})\), Ni-20wt.%Fe \((E_{111} = 294 \text{ GPa}, E_{100} = 122 \text{ GPa})\), and Ni-40wt.%Fe \((E_{111} = 282 \text{ GPa and } E_{100} = 103 \text{ GPa})\). \(E_{111}\) is relatively constant up

| Table 5.2. Elastic stiffnesses \((c_{ij})\) for single crystal Ni and Ni-Fe alloys (in units of \(10^{11} \text{ N/m}^2\)). |
|-----------------|--------|--------|--------|
| Single Crystal  | \(c_{11}\) | \(c_{12}\) | \(c_{44}\) |
| Ni\(^\dagger\)   | 2.43   | 1.49   | 1.19   |
| Ni-10wt.%Fe\(^\ddagger\) | 2.43   | 1.48   | 1.22   |
| Ni-20wt.%Fe\(^\ddagger\) | 2.32   | 1.44   | 1.21   |
| Ni-40wt.%Fe\(^\ddagger\) | 2.05   | 1.31   | 1.18   |

\(^\dagger\) DeKlerk and Musgrave (1955), \(^\ddagger\) Kanrar and Ghosh (1983)
to Ni-20wt.%Fe and only slightly decreases at Ni-40wt.%Fe. On the other hand, $E_{100}$ is constant up to Ni-10wt.%Fe, but then gradually decreases at Ni-20wt.%Fe and more so at Ni-40wt.%Fe. With the exception of sample no. 5 (Ni, 23 nm), the materials in this study have a weak to strong (200) fibre texture, and corresponding lower Young’s modulus values when compared to $E_m / E_0 = 1$ for grain sizes greater than 20 nm and when compared to the composite model predictions for grain sizes less than 20 nm. In particular, samples no. 8 (Ni-23w.%Fe, 10 nm) and 9 (Ni-32wt.%Fe, 10 nm) are clearly below the composite model predictions which may be owed to $E_{100}$’s decreasing tendency, or sensitivity, with increasing Fe concentration. This is consistent with the findings of Fritz et al. (2003) and Torrents et al. (2010) for Ni, and Auerswald and Fecht (2010) for Ni-W, who also observed that a preferred (200) orientation tends to produce a lower than expected Young’s modulus. In these studies, it was shown that when the orientation was changed by annealing the materials to remove the texture, there was a corresponding increase in the Young’s modulus.

Secondly, the relative degree of anisotropy is determined by calculating the elastic anisotropy factor [Zener (1948)],

$$\eta = \frac{2c_{44}}{(c_{11} - c_{12})}$$  \hspace{1cm} (5-7)

For the isotropic case, $\eta = 1$ but in the case of Ni, $\eta \approx 2.53$; the same can also be shown for Ni-Fe alloys: Ni-10, 20, and 40wt.%Fe, $\eta \approx 2.57, 2.73$, and $3.17$, respectively. In general, these materials have a relatively high elastic anisotropy which increases with increasing Fe concentration.
Finally, the effect of texture is considered by comparing the measured values to the calculated Voigt and Reuss bounds and the Voigt-Reuss-Hill arithmetic average for polycrystalline single-phase materials which are statistically isotropic (quasi-isotropic). The bounds are determined by calculating the bulk and shear modulus using [Grimvall (1999)],

\[ K_V = K_R = (c_{11} + 2c_{12})/3 \]  
\[ G_V = (c_{11} - c_{12} + 3c_{44})/5 \]  
\[ G_R = 5(c_{11} - c_{12})c_{44} /[4c_{44} + 3(c_{11} - c_{12})] \]

where, \( K \) is the bulk modulus and \( G \) is the shear modulus, and subscripts \( V \) and \( R \) are the Voigt and Reuss bounds, respectively. Given the elastic stiffnesses [DeKlerk and Musgrave (1955), Kanrar and Ghosh (1983)], the bounds are determined from the general relation,

\[ 1/E = 1/(3G) + 1/(9K) \]  

Hill (1952) proposed that an arithmetic average of the elastic properties can be determined by calculating the average bulk and shear modulus given by,

\[ K_{VRH} = (K_V + K_R)/2 \]  
\[ G_{VRH} = (G_V + G_R)/2 \]

where, subscript \( VRH \) refers to the Voigt-Reuss-Hill average. By using the same general relation, i.e., Eq. 5-11, \( E_{VRH} \) can then be calculated. The measured values are then plotted as a function of Fe concentration along with the Voigt and Reuss bounds and the Voigt-Reuss-Hill arithmetic average (see Fig. 5.5). The Voigt-Reuss-Hill average for Ni was determined to be 214 GPa. For Ni-10, 20 and 40wt.%Fe, the values were 217 GPa, 209 GPa and 192 GPa, respectively. The observed trend with the addition of Fe is a slight increase at about 10wt.% Fe followed by gradual decrease down to 40wt.% Fe. The Voigt and Reuss bounds
tend to broaden with respect to the Voigt-Reuss-Hill averages as the Fe concentration increases, which is an indicator of increasing anisotropic behaviour. The measured values tend to follow a similar trend with increasing Fe concentration, except that they are consistently lower than the Voigt-Reuss-Hill averages. In the absence of a texture, it would be expected that the measured values lie much closer to the Voigt-Reuss-Hill arithmetic average. In this particular case, sample no. 5 (Ni, 23 nm), who’s measured value is the highest or closest to the Voigt-Reuss-Hill average, has a double (111)(200) fibre texture.

![Figure 5.5. Measured Young’s modulus values for the series of nanocrystalline Ni and Ni-Fe alloys compared with Voigt-Reuss-Hill average values, and Voigt and Reuss bounds.](image)

All other samples, which have a weak to strong (200) fibre texture, are further from the Voigt-Reuss-Hill averages and lie near the Reuss bound. Thus, it is likely that texture is responsible for the lower measured values when compared to the respective Voigt-Reuss-Hill averages. At less than 20 nm, there is likely a combined grain size and texture effect.
When considering the elastic behaviour of these materials, texture is likely to have a strong influence on the normalized value $E_m/E_0$. At greater than 20 nm, the influence of grain size is minimal, so the texture can have a stronger influence. At below 20 nm, both texture and grain size can influence Young’s modulus. Another factor known to strongly influence the Young’s modulus of these materials is their magnetic state [Ledbetter and Reed (1973)]. For example, Engler (1938) demonstrated the effect of magnetic fields on the Young’s modulus of several Ni-Fe alloys. In this current study, no applied magnetic field was present during the nanoindentation measurements. However, the magnetization state of the materials was not further studied. It has also been suggested that internal or residual stresses may also affect the measured Young’s modulus [Ledbetter and Reed (1973)]. In general, electrodeposited Ni and Ni-Fe alloys are intrinsically stressed. For example, there is general agreement that increasing Fe concentration in Ni electrodeposits results in an increased deposit stress [Weil (1971), Sotirova-Chakarova and Armyanov (1990), Grimmett et al. (1993)], i.e., Fe acts as a “stress-intensifier”. The origins of this intrinsic stress in electrodeposited nanocrystalline Ni and Ni-Fe alloys will be discussed in Chapter 6.

A kinematics of polycrystal deformation study has recently predicted an increase in the Poisson ratio at very small grain sizes and shear softening at grain boundaries [Weissmuller et al. (2011)]. Experimentally, this was confirmed using a novel ultrasonic technique which showed a 30% shear softening in nanocrystalline Pd made by the inert gas condensation technique Grewer et al. (2011). It would be interesting to conduct similar experiments on electrodeposited nanocrystals to evaluate whether grain boundary shear softening also occurs in nanomaterials made by another synthesis method.
5.6. **Summary**

The hardness and Young’s modulus values were determined for the series of nanocrystalline Ni and Ni-Fe alloys using nanoindentation. Hardness values showed a transition from regular to inverse Hall-Petch behaviour which is consistent with previous studies. The deviation from regular Hall-Petch behaviour is explained based on the influence of decreasing grain size and increasing intercrystal volume fraction resulting in the operation of deformation mechanisms other than dislocation slip. There was no significant influence of grain size on the Young’s modulus of nanocrystalline Ni and Ni-Fe alloys with grain sizes greater than 20 nm. Nanocrystalline Ni and Ni-Fe alloys with grain sizes less than 20 nm displayed slightly reduced Young’s modulus values when compared to their conventional (randomly oriented) polycrystalline counterparts. Although the general trend with grain size was consistent with the composite model predictions, there was notable variability. In order to explain this variability, the influence of texture was considered. Three theoretical relationships were used to characterize the anisotropic elastic behaviour of these materials: 1. calculated values for the two principal crystallographic directions showed moderate sensitivity for the (111) direction and considerable sensitivity for the (100) direction as the Fe concentration increases, 2. elastic anisotropy factors were relatively high and tend to increase with increasing Fe, and 3. all measured values were below the Voigt-Reuss-Hill average values or near the Reuss bound. As a result, texture is considered to influence the measured Young’s modulus values for the entire grain size range. Moreover, at less than 20 nm, there is likely a combined grain size and texture effect.
5.7. References


Engler, O., Ann. Phys. 31 (1938) 145.


CHAPTER 6
Internal Stress

6.1. Introduction

Electrodeposited metals will nearly always possess some level of internal stress, even when no external load has been applied and dislocation densities are negligible. As a result, these types of stresses are often referred to as “intrinsic stresses”. Internal stresses can be measured on both a microscopic and macroscopic scale. Microstresses are determined based on measurable non-uniform strain (i.e., microstrain) in the material [Cullity and Stock (2001)]. This microstrain is measured from XRD line broadening caused by atomic scale defects [Macherauch and Kloos (1987)]. Earlier reports on measurements of microstrain in nanocrystalline materials have led to the conclusion that there is a strong relationship with grain size [e.g., Eckert et al. (1992), Weissmuller et al. (1995), Eastman et al. (1995), Sanders et al. (1995), Sun et al. (1996), Malow and Koch (1997), Zhao et al. (2001), Li and Ebrahimi (2003), Mishra et al. (2004), Derlet et al. (2005), Qin and Szpunar (2005), and Biju et al. (2008)]. In this study, a systematic approach on the effect of grain size on microstrain is presented for the series of electrodeposited nanocrystalline Ni and Ni-Fe alloy samples.

Macrostresses are determined by measuring strain based on XRD line shifts [Macherauch and Kloos (1987)] which are representative of detectable uniform strain [Cullity and Stock (2001)]. Macrostresses in nanocrystalline materials have been reported on many occasions; however, there are only a few experimental studies which provide some insight into the underlying relationship with grain size [e.g., Czerwinski (1996), El-Sherik et al. (2005), Shamsutdinov et al. (2007)]. Additionally, there are only a few macrostress
measurements using X-ray diffraction (XRD) on nanocrystalline materials, e.g., Sanders et al. (1995), El-Sherik et al. (2005). In particular, the study on nanocrystalline Ni by El-Sherik et al. (2005) demonstrated a significant difference in macrostress values when a polycrystalline sample having a \(~5000\) nm grain size was compared to a nanocrystalline sample having a grain size of \(10\) nm. As a result, it was suggested that this stress could be related to the grain size. In order to elaborate on this observation, a similar systematic approach on the effect of grain size on macrostresses is also presented for the series of electrodeposited nanocrystalline Ni and Ni-Fe alloy samples. The main objective of this study was to develop a relationship with internal stresses based on the microstructural characteristics of these materials identified in Chapter 4.

6.2. Microstrain*

6.2.1. Results

Microstrain is measured based on XRD line broadening [Withers and Bhadeshia (2001)] due to inhomogeneous or non-uniform strain acting over submicroscopic areas, i.e., several atomic distances within a grain [Macherauch and Kloos (1987), Cullity and Stock (2001)]. The microstrain for the series of nanocrystalline Ni and Ni-Fe alloys was analyzed from XRD patterns using the accompanying software package as described in Chapter 3 (Section 3.4.3.5). The respective microstrain values for the series of nanocrystalline Ni and Ni-Fe alloy samples are presented in Table 6.1. For discussion purposes, the growth fault probabilities from Chapter 4 (Section 4.5.4) are also included in Table 6.1.

Table 6.1. Microstrain values for the series of nanocrystalline Ni and Ni-Fe alloys.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Fe (wt.%)</th>
<th>Grain Size (nm)</th>
<th>$f_{ic}$</th>
<th>Microstrain (%)</th>
<th>Growth Fault Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>~255</td>
<td>0.012</td>
<td>0.02</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>81±51</td>
<td>0.037</td>
<td>0.20</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>44±30</td>
<td>0.067</td>
<td>0.11</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>37±21</td>
<td>0.079</td>
<td>0.26</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>23±11</td>
<td>0.125</td>
<td>0.25</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>7.3</td>
<td>32±18</td>
<td>0.091</td>
<td>0.33</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>12±7</td>
<td>0.230</td>
<td>0.42</td>
<td>0.8</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>10±5</td>
<td>0.271</td>
<td>0.47</td>
<td>1.0</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>10±5</td>
<td>0.276</td>
<td>0.54</td>
<td>1.9</td>
</tr>
</tbody>
</table>

6.2.2. Effect of Grain Size on Microstrain

Fig. 6.1 presents a plot of microstrain as a function of grain size. Also included in the plot are the results of other studies on materials produced using electrodeposition synthesis techniques. As seen in Fig. 6.1, there is a distinct trend whereby microstrain tends to increase with decreasing grain size. A best fit (dashed) line is provided for the current data set. The best fit line was determined based on an inverse grain size relationship with microstrain [Weissmuller et al. (1995), Malow and Koch (1997)]. This inverse grain size relationship with microstrain was found to be in relatively good agreement with the data in the present study. To further illustrate the effect of grain size, we also consider the increasing microstrain trend with the corresponding increase in the intercrystal volume fraction (grain boundaries and triple junctions). The intercrystal volume fraction, $f_{ic}$, as a function of grain size, $d$, are related based on Eq. 2-1[Palumbo et al. (1990)].
Figure 6.1. Plot of microstrain vs. grain size (dashed line) and intercrystal volume fraction vs. grain size (solid line).

As grain size decreases, the intercrystal volume fraction in the material increases very rapidly for grain sizes less than 20 nm given by the solid line in Fig. 6.1. The best fit curve for the data (dashed line) in the present study tends to follow a similar increasing trend with intercrystal volume fraction (solid line). This is consistent with the notion that an increased presence of grain boundaries and triple junctions induces lattice strain which results in XRD line broadening [Qin and Szpunar (2005), Stukowski et al. (2009)].

The microstrain values obtained for the nanocrystalline Ni samples are in relatively good agreement with other studies on materials synthesized using the electrodeposition technique. For example, Mishra et al. (2004) reported values which agree very well with the
current results, e.g., 0.25% for electrodeposited nanocrystalline Ni with a grain size of 22 nm, using the Williamson-Hall method described by Suryanarayana and Norton (1998). On the other hand, some differences for the nanocrystalline Ni-Fe microstrain values were observed when compared to results of Li and Ebrahimi (2003). In their study, single peak analysis was used to determine the microstrain which resulted in some higher and lower values when compared to the current study where the grain size and Fe concentration were similar. Thus, it is worth noting that there can be some dependence on the specific plating parameters used to synthesize the materials and the method used to analyze the XRD patterns when determining microstrain values. However, the general trend with grain size is consistent.

The rather significant microstrain which is present in nanocrystalline materials has often been associated with grain size [e.g., Eckert et al. (1992), Weissmuller et al. (1995), Eastman et al. (1995), Sanders et al. (1995), Sun et al. (1996), Malow and Koch (1997), Zhao et al. (2001), Li and Ebrahimi (2003), Mishra et al. (2004), Derlet et al. (2005), Qin and Szpunar (2005), Stukowski et al. (2009)]. This grain size effect has been linked to the HR-TEM observations of localized strains at grain boundaries [Wunderlich et al. (1990), Ping et al. (1995), Li et al. (2000), Valiev et al. (2000)] which are similar to the observations made in Chapter 4 (Section 4.4.2) and proposed to be a result of mainly the local elastic deformation near grain boundaries that is necessary for joining of the crystals [Valiev et al. (1986)]. The quantitative model of Qin and Szpunar (2005) describes the dependence of microstrain on grain size and is based on these physical observations which is essentially a stress field brought on by localized strain at grain boundaries. The origin of the localized strain is thought to be a result of excess free volume (vacancies and vacancy clusters) in the grain.
boundaries Qin and Szpunar (2005). However, as mentioned earlier, electrodeposited metals possess excess free volumes in the grain boundaries with sizes smaller than a vacancy in a perfect lattice Zhou et al. (2009). Thus, the local strain present at grain boundaries resulting from the crystal joining process in these nanocrystalline materials is considered to be the dominant source.

In a closer examination of the current experimental data points in Fig. 6.1, there is some notable variability when compared to the best fit curve (dashed line). Similar observations have also been made in some of the experimental data from the previous studies. Given these observations, a further investigation was carried out to identify the possible causes. In addition to the presence of a significant volume fraction of intercrystal defects (i.e., grain boundaries and triple junctions) in these materials, a contribution of other atomic scale defects resulting in microstrain induced XRD line broadening are considered. Based on the defects analysis carried out earlier, particular emphasis was placed on the possible effects of growth faults since they are known to contribute to microstrain induced XRD line broadening [Paterson (1952)].

When comparing the microstrain values of the pure nanocrystalline Ni samples and the nanocrystalline Ni-Fe samples with respect to grain size, there are some differences that result in the mentioned variability with the best fit curve (dashed line) in Fig. 6.1. In order to elucidate any potential effect of alloying, a plot of microstrain versus Fe concentration is presented in Fig. 6.2. In this plot, there is an increasing trend with the addition of Fe which
Figure 6.2. Plot of microstrain vs. Fe concentration in the deposit showing an increasing trend with increasing Fe.

suggests the presence of an alloying effect in addition to the effect of grain size. When considering their relative microstrain values and grain sizes, the samples containing Fe are consistently higher than the Ni samples. For example, sample no. 6 (Ni-7.3wt.%Fe, 32 nm) has a microstrain value which is noticeably higher than that of sample no. 5 (Ni, 23 nm). In this case, it would have been expected that the smaller grain size sample, i.e., sample no. 5 (Ni, 23 nm), would have the higher microstrain value. Another possible alloying effect can also be seen for samples no. 8 (Ni-23wt.%Fe, 10 nm) and 9 (Ni-32wt.%Fe, 10 nm), whereby each has practically the same grain size but the microstrain for the sample with a higher concentration of Fe, i.e., sample no. 9 (Ni-32wt.%Fe, 10 nm), is greater by about 15%. In the study carried out by Li and Ebrahimi (2003) on a series of nanocrystalline Ni-Fe alloys, the expected grain size dependence for samples containing similar Fe concentrations was
observed. However, where the grain sizes of samples were similar and the Fe concentration increased, the microstrain also increased. Based on this observation, it was suggested to consider other possible contributions to microstrain induced XRD line broadening other than grain size [Li and Ebrahimi (2003)].

6.2.3. Effect of Growth Faults on Microstrain

In Chapter 4, the presence of growth faults was identified qualitatively through HR-TEM image analysis (Section 4.4.2) and quantitatively by determining growth fault probabilities using XRD pattern analysis (Section 4.5.4). Growth faults are known to contribute to microstrain induced (asymmetric) XRD line broadening [Paterson (1952)]. Growth fault probabilities in the nanocrystalline Ni samples were found to be relatively low. This was consistent with the low occurrence of growth faults observed in the HR-TEM image analysis. In the case of the nanocrystalline Ni-Fe samples, the growth fault probabilities increased significantly with increasing Fe. This was also consistent with the high occurrence of growth faults observed in the HR-TEM image analysis.

The increased presence of growth faults supports the typically higher microstrain values noted in the previous section for the Fe containing samples, e.g., when comparing samples no. 5 (Ni, 23 nm) and 6 (Ni-7.3wt%Fe, 32 nm). In addition to this, sample no. 9 (Ni-32wt.%Fe, 10 nm) has a higher microstrain value when compared to sample no. 8 (Ni-23wt.%Fe, 10 nm) although they have the same grain size. This is considered to be a result of the increased presence in growth faults due to the effect of increasing Fe on the stacking fault energy. For the nanocrystalline Ni-Fe alloys, it may be concluded that, in addition to a
grain size effect, there is a contributing alloying effect on microstrain induced XRD line broadening due to the increased presence of growth faults with increasing Fe concentration.

6.3. **Macrostress**

6.3.1. Results

Macrostresses are determined by detecting XRD line shifts [Withers and Bhadeshia (2001)] resulting from homogeneous or uniform strains acting over large areas, i.e., many grains [Macherauch and Kloos (1987), Cullity and Stock (2001)]. The XRD line shifts correspond to a change in interplanar spacing or lattice parameter. The 2D-XRD method used in this study effectively detects distortions of the diffraction cones which are analogous to detecting XRD line shifts using the conventional $\sin^2 \psi$ method. The result of the analysis in both cases is a strain value. In the current study, the (311) ring was analyzed for all samples and the planar component macrostresses, $\sigma_{11}$ and $\sigma_{22}$, and the shear stress component, $\sigma_{12}$ values (Eq. 3-27) were determined. Macrostress determinations were carried out as described in Chapter 3 (Section 3.7) using 2D-XRD.

The samples were analyzed in the “as-deposited” state, having not undergone any surface treatments and/or plastic deformation. An example of the (220), (311), (222) and (400) 2D-XRD diffraction rings on the output screen of the GADDS software for sample no. 4 (Ni, 37 nm) is shown in Fig. 6.3. Shown in Fig. 6.4 is an example of the GADDS software performing an integration of the region along the $\gamma$ (or $\chi$) direction which corresponds to tracing of the ring along the vertical axis of the image. The $2\theta$ value at a given $hkl$ peak
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Figure 6.3. GADDS software output image of diffractions rings for sample no. 4 (Ni, 37 nm) showing the (220), (311), (222), and (400) diffraction rings.

Figure 6.4. GADD software output image of integration along the (311) ring during stress analysis for sample no. 4 (Ni, 37 nm). Embedded within the image is the peak intensity profile as a function of $2\theta$ for the example region that is integrated.
corresponds to the most intense part of the ring which normally occurs in the middle along the horizontal direction of the image. A summary of the macrostress values for each of the stress tensor components (see Section 3.7) is given in Table 6.2. The macrostress values are calculated using the Young’s modulus values, $E_m$, determined from the nanoindentation measurements reported in Chapter 5 (Table 5.1). Given the magnitude of the planar stress components, $\sigma_{11}$ and $\sigma_{22}$, and the relatively low shear stress component, $\sigma_{12}$, it may be concluded that these samples are in a state of biaxial stress, i.e., in-plane. Due to the limited penetration of X-rays, macrostresses measured using XRD normally belong to this stress state [He (2009)].

Macrostresses determined using diffraction methods have two main types of error associated with them: statistical error, which arises from the random arrival of X-ray photons at the detector, causing some variability in the intensity at any $2\theta$ position, and instrumental error, which can be a result of specimen alignment, effect of beam optics, etc.
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[Noyan and Cohen (1987)]. More important are the practical sources of error. Prevey (1986) classifies these practical sources of error as follows: 1. instrumental and positioning errors, 2. effect of sample geometry and microstructure (typically grain size), and 3. X-ray elastic constants.

The instrumental error is normally a result of the high precision required to determine the diffraction line position. Thus, extremely precise positioning of the diffraction apparatus or the sample to accuracies of approximately 0.025 mm is critical but often difficult. Instrumental and positioning issues can result in errors in internal stress measurement of approximately ±14 MPa for high diffraction angle techniques [Prevey (1986)]. The current study made use of a high diffraction angle technique, i.e., the (311) diffraction line, in order to minimize instrumental and positioning errors on the final results. When put in to context, a ±14 MPa error may affect more those samples which have relatively low macrostress values, for example, samples no. 1-6 with grain sizes greater than 20 nm (Table 6.2). In this case, 14 MPa could represent a significant portion of the actual macrostress value. However, samples with high macrostresses, e.g., samples no. 7-9 would not be greatly influenced by this error since 14 MPa is rather small when compared to the experimental values (Table 6.2).

Effects of sample geometry, including roughness, pitting, or curvature of the surface within the irradiated area, can result in systematic error similar to sample positioning. All samples were generally free of roughness or pitting; however, some of the foils (e.g., samples no. 1, 8, and 9) were not without some degree of curvature. In order to minimize the effect
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of the curvature, the samples were affixed to the holder as firmly and as flat as possible. However, there was no guarantee that the curvature was completely eliminated. This factor is likely to have played a role in the noticeable differences between respective planar stress component values for samples no. 1, 8 and 9. Large grain sizes can reduce the number of crystals contributing to the diffraction line resulting in asymmetry and random error in peak location and macrostress measurement. In the current study, all samples had a relatively small grain sizes and thus, such an effect is minimized. Rather, the relatively small grain sizes provided for a good statistical sampling and fairly accurate macrostress measurement.

When analyzing the macrostress in materials that are elastically anisotropic, the use of macroscopic elastic constants is essential for obtaining true values. In this case, the bulk elastic constants should be replaced with X-ray elastic constants that depend on the lattice plane (hkl) where the measurement is performed. Included in the plane specific X-ray elastic constant calculation is a value called the radiocrystallographic anisotropy factor ($A_{RX}$). This value typically ranges between 1 and the single crystal anisotropy factor [Lu (1996)]. For Ni-based (fcc) materials, a value of 1.52 was used [He (2009)]. In the case of the current samples, the anisotropy of the materials was analyzed earlier and shown to increase with the addition of Fe (see Chapter 5). Unfortunately, the absence of elastic constant values for each of the materials containing Fe did not allow for the use of an accurate value for $A_{RX}$.

6.3.2. Effect of Grain Size on Macrostress

In order to investigate a possible dependency of macrostresses on grain size, the three stress components from Table 6.2 are plotted in Fig. 6.5 (shear stress component, $\sigma_{12}$) and
Fig. 6.6 (planar stress components, $\sigma_{11}$ and $\sigma_{22}$) as a function of grain size. The shear stress component, $\sigma_{12}$, tends to have a relatively low value over the entire grain size range. The planar components, $\sigma_{11}$ and $\sigma_{22}$, remain relatively low down to about 20 nm. However, below 20 nm, there is a sharp increase in the compressive macrostress. The results of El-Sherik et al. (2005), who used the $\sin^2 \psi$ method are also plotted in Fig. 6.6. Their values, which were also determined in the as-deposited state, were compressive and fit well with the data points from the current study. The observed trend for the planar components, $\sigma_{11}$ and $\sigma_{22}$, with grain size suggests the presence of an inherent dependency on grain size, especially when it is sufficiently lower than 20 nm.

![Diagram showing macrostress as a function of grain size](image-url)

**Figure 6.5.** Shear stress component, $\sigma_{12}$, for the nanocrystalline Ni and Ni-Fe alloys as a function of grain size.
This dependency on grain size is not consistent with studies of measured macrostresses using XRD techniques on materials produced by other synthesis methods. For example, Sanders et al. (1995) measured the macrostress in nanocrystalline Pd prepared by inert gas condensation and warm compaction using the sin²ψ method and found the macrostress in the as-deposited state to be compressive and in the range of -20 to -40 MPa. The corresponding grain size range was approximately 3 to 26 nm. It should be noted that the nanocrystalline Pd was produced by a method which is known to produce materials with considerable amounts of porosity [e.g., Nieman et al. (1991)]. The presence of porosity was also the root cause of large reductions in the Young’s modulus values [Krstic et al. (1993), Zugic et al. (1997), Sanders et al. (1997)]. The relatively low macrostressed values reported by Sanders et al. (1995) may also be related to the presence of porosity. Although the current
materials were not analyzed for porosity, it is well known that the electrodeposition technique produces materials with relatively low porosity when compared to materials produced by the inert gas condensation technique [Haasz et al. (1995), Van Petegem et al. (2003), Zhou et al. (2009)]. Currently, it is not known what the effects of porosity is on macrostress, however, it is conceivable that long range stress fields in a material could diminish in the presence of sufficient porosity leading to a lower compressive macrostress value due to the presence of free internal surfaces in the grain boundary matrix. That is, stress relaxation may occur on the free internal surfaces associated with porosity in such materials. On the other hand, in fully dense materials, no internal surfaces for stress relaxation are available and therefore, stresses remain cumulative.

As shown in Fig. 6.6, when the grain size decreases below 20 nm, there is a sharp and distinct increase in the compressive macrostress values. Consequently, there is likely a relationship between the measured macrostresses and corresponding increasing intercrystal volume fraction or rather the number of interfaces in the solid. Such solid-solid interfaces are associated with stresses [Brooks (1952), Cahn and Larche (1982)]. According to Cahn and Larche (1982), an interface stress may be defined as: the reversible work per unit area to either elastically deform one phase relative to the other or both phases equally. In this case, phases may be interpreted as neighbouring grains which join to form the solid-solid interface, i.e., grain boundaries. This interpretation of grain boundaries is similar to that of Valiev et al. (1986) who describe the “non-equilibrium” grain boundary. Such grain boundaries have long-range elastic fields since local elastic deformation is necessary for joining of the crystals. This particular interpretation has been used to describe HR-TEM observations of localized
strains at grain boundaries [Wunderlich et al. (1990), Ping et al. (1995), Li et al. (2000), Valiev et al. (2000)] which are similar to the observations made in Chapter 4 (Section 4.4.2).

Considering the concepts of Cahn and Larche (1982), Cammarata and Eby (1991) developed a thermodynamic model which allows for the estimation of internal surface stresses via the determination of strain values. This model was initially used to determine strain values by detecting variations in lattice parameters for lamellar structures. Cammarata and Eby (1991) proposed an extension of the thermodynamic model’s application to very fine-grained metals and ceramics. That is, if the grains are considered to be spheres, the strain will depend on the grain size [Cammarata (1994), Cammarata (1997)],

\[ \varepsilon = -\frac{4f}{3Kd} \]  

(6-1)

where, \( \varepsilon \) is the strain, \( K \) is the bulk modulus, \( f \) is the interface stress associated with grain boundaries, and \( d \) is the grain size.

The current nanocrystalline Ni and Ni-Fe alloys data may be analyzed using the relationship given by Eq. 6-1. The left side of the equation can be rearranged to include the bulk modulus, \( K \). By substituting in the relationship between the bulk modulus, \( K \), and the elastic modulus, \( E \),

\[ K = \frac{E}{3(1-2\nu)} \]  

(6-2)

we arrive at,

\[ \varepsilon E \frac{E}{3(1-2\nu)} = -\frac{4f}{3d} \]  

(6-3)
where, $\nu$ is the Poisson ratio. If it is assumed that Hooke’s law applies, then the macrostress values $\sigma_{11}$ and $\sigma_{22}$ can be substituted and related to the grain size using the thermodynamic model of Cammarata and Eby (1991). By rearranging Eq. 6-3, the following expression is obtained,

$$\sigma_{11/22} = -4f(1 - 2\nu)\frac{1}{d}$$  \hspace{1cm} (6-4)

Using the plot of the macrostress, $\sigma_{11/22}$, with the grain size, $d$, a curve can be fitted based on Eq. 6-4 and the coefficient, $-4f(1 - 2\nu)$, can be determined and used to estimate a value for the interface stress associated with grain boundaries. In the calculation, the Poisson ratio, $\nu$, is taken to be 0.31 [Callister (2005)]. Figure 6.7 shows a plot of $\sigma$ vs. $d$ for nanocrystalline Ni and Ni-Fe alloys with the best fit curve based on Eq. 6-4. In general, the

![Figure 6.7](image-url)

Figure 6.7. Plot of the planar components $\sigma_{11}$ and $\sigma_{22}$ for the nanocrystalline Ni samples as a function of grain size with the best fit (dashed) curve based on Eq. 6-4.
data fits well with the relationship. For illustrative purposes, the total intercrystal volume fraction based on Eq. 2-1 [Palumbo et al. (1990)] is also shown in Fig. 6.7 (solid line) to emphasize the significant increase in these defects (i.e., grain boundaries and triple junctions) with decreasing grain size.

The constant value from the best fit yields an interface stress value, $f$, of approximately 3.56 N/m. There are very few reports on experimental interface stress values. For example, experimental values for surface stress of Ni have been reported to be 4.2 N/m and 2.1 N/m for the [001] and [110] directions, respectively [Lehwald et al. (1987)]. On the other hand, there are a number of calculations for surface stress values which for Ni have been reported to be 1.27 N/m and 0.43 N/m for the (100) and (111) surfaces, respectively. The interface stress value determined for the nanocrystalline Ni and Ni-Fe alloys in the current study is in relatively good agreement with the interface stress value determined by Jiang et al. (2001) who calculated a value of 3.05 N/m for Ni. Jiang et al. (2001) obtained this value by developing thermodynamic equations that relate the interface excess free energy to the interface stress. As described in Chapter 2 (Section 2.1.4) the total enthalpy (stored energy), $\Delta H$, from a strained metal is approximately equal to the excess free energy, $\Delta G$ (Eq. 2-5). The thermal analysis in Chapter 4 (Section 4.6) showed that the total enthalpy (stored energy) measured in the electrodeposited nanocrystalline Ni and Ni-Fe alloys are primarily due to intercrystal defects (i.e., grain boundaries and triple junctions). As the volume fraction of these intercrystal defects increases or the grain size decreases, the total enthalpy (stored energy) in these materials increases accordingly. If interface excess free
energy is related to the interface stress, then in a similar manner, an increase in intercrystal defects would cause an increase in the internal stress.

Weissmuller and Cahn (1997) also emphasized the interaction of grain boundaries and triple junctions and their relationship to interface stress which results from the deformed state of the interface; these interface stresses must be equilibrated by homogeneous bulk stresses or analogously macrostresses. The bulk stresses brought on by interface stresses in polycrystalline materials are rather low; however, when the volume fraction of intercrystal defects is high, as in the case of nanocrystalline materials and especially at grain sizes less than 20 nm, these interface stresses become significant. Birringer et al. (2002) developed a method based on the theory of Weissmuller and Cahn (1997) for experimentally measuring the interface stress, $f$. The calculation relies on the detection of a lattice parameter change which is related to the strain in the material that is induced on the order of $f/d$. Birringer et al. (2002) analyzed nanocrystalline Pd samples produced by the inert gas condensation method and determined an interface stress of 1.2 N/m. The lattice parameters were found to decrease with decreasing grain size which indicates the presence of a compressive bulk stress. This is consistent with the compressive macrostresses identified in the current study for the electrodeposited nanocrystalline Ni and Ni-Fe samples.

The interface stress is brought on through the interaction of solid-solid interfaces and their (elastic) deformations necessary to maintain coherency of the grains; in this case, it is assumed that no atomic bonds are broken in the interface plane [Gurtin and Murdoch (1975), Cahn (1978)]. As a result, it is likely that grain boundary atoms are not in their perfect lattice
position, nor in their lowest energy state. Considering that the grain boundary atoms are not in their perfect lattice position, a qualitative illustration of this effect can be given on an atomistic level. In order to do this, the Lennard-Jones pair potential model is considered [Lennard-Jones (1924)], which according to Wolf (1989a,b) yields results that are similar to the multi-body potential model. The general form of the Lennard-Jones pair potential $U$, for two physical bodies, as a function of the two-body separation $x$ [e.g., Atkins (1997)] is,

$$U = 4\varepsilon \left\{ \left( \frac{\sigma}{x} \right)^{12} - \left( \frac{\sigma}{x} \right)^6 \right\}$$  

where, $\varepsilon$ is the depth potential well and $\sigma$ is the pair separation where $U = 0$. The bond energy, $U$, and bond force, $F = \partial U / \partial x$, curves are shown in Fig. 6.8.

![Figure 6.8. Lennard-Jones pair potential model: (a) bond-energy curve where $a_0$ is the equilibrium interatomic spacing value, $U_a$ is the attractive bond-energy, $U_r$ is the repulsive bond-energy, and $U_t$ is the total energy, (b) bond-force curve where $a_0$ is the equilibrium interatomic spacing value, $F_a$ is the attractive bond-force, $F_r$ is the repulsive bond-force, and $F_t$ is the total force [Lennard-Jones (1924)].](image-url)
In the case of the bond-energy curve, the total energy is at its lowest when the equilibrium interatomic spacing, $a_0$, is achieved. Consequently, the force-energy curve at equilibrium has a net zero force. If the interatomic spacing is increased or decreased, as in the case of the grain boundary atoms, there will be a net attractive or repulsive force respectively, and an overall increase in energy which contribute to the generation of an interface stress in a network of grains leading to the observed macrostresses. Ultimately, it is a net elastic stress field that is generated over the network of grains in the system giving rise to the macrostresses observed in these materials. As the grain size decreases, or the intercrystal volume fraction (i.e., grain boundaries and triple junctions) increases, a corresponding increase in elastic field intensity is generated resulting in an increase in macrostress.

6.4. Elastic Response Due to Internal Stress

The effect of the localized strain at grain boundaries on XRD lines in nanocrystalline materials was investigated by Qin et al. (2008). In addition to XRD line broadening, they proposed that there is a superimposed XRD line shift. In order to illustrate this, Qin et al. (2008) modeled the variation of the lattice parameter in nanocrystalline materials with distance from grain boundaries and determined that conventional XRD lines resulting from lattice planes near grain boundaries will also shift to lower $2\theta$ angles or take on an increased lattice parameter. This is consistent with the presence of internal stresses. Note that conventional XRD produced lines from crystallographic planes which are parallel to the sample plane. Therefore, such XRD line shifts correspond to changes in interplanar spacing, $d$, normal to the sample plane.
Chapter 6 – Internal Stress

If the interplanar spacing increases there is a net tensile strain and if it decreases there is a net compressive strain. The lattice parameter change or resulting change in interplanar spacing is given as follows,

\[
\varepsilon = \frac{d - d_0}{d_0} = \frac{\Delta d}{d_0}
\]

(6-6)

where, \( \varepsilon \) is the strain, \( d \) is the measured interplanar spacing, and \( d_0 \) is the interplanar spacing of the unstressed condition.

The macrostresses measured in this study are bi-axial and result only in the plane of the samples. Since the macrostresses at the smallest grain sizes are predominantly compressive in nature, the net interplanar spacing is bi-axially contracted and thus smaller than that of an unstressed material. On the contrary, there are numerous reports on the effect of decreasing grain size on the lattice parameter or interplanar spacing determined using conventional XRD, e.g., Ni [Liu et al. (1994)] and Fe [Zhao et al. (2001)], whereby it tends to increase, especially at grain sizes less than 10 nm. As mentioned earlier, the modeling of Qin et al. (2008) determined that conventional XRD lines resulting from lattice planes near grain boundaries will contribute to a shifting to lower 2\( \theta \) angles or take on an increased interplanar spacing. Note that in Chapter 4, local strain at grain boundaries was evident in the HR-TEM images (Section 4.4.2) and the lattice parameters for the current nanocrystalline Ni and Ni-Fe samples were observed to be slightly increased when compared to their large grain polycrystalline counterparts (Section 4.5.1). This implies that while the material is undergoing a bi-axial contraction in the plane it is also likely that the material is undergoing an expansion in the normal direction to the plane.
Figure 6.9. Schematic diagram of the sample planar cross-section showing conventional XRD lines from an unstressed lattice with equally spaced atoms and a Bragg angle, $\theta_0$, corresponding to the interplanar spacing, $d_0$.

Figure 6.10. Schematic diagram of the sample planar cross-section showing conventional XRD lines from a lattice in a state of (bi-axial) compressive stress. A contraction of the lattice in the planar direction is accompanied by an expansion that is normal to the plane. The net result is a lower Bragg angle, $\theta$, and increased interplanar spacing value, $d$. 
In order to clarify this, we consider the irradiated area near the surface of the sample in the planar cross-section on an atomic scale shown in Fig. 6.9 for the case where there is no apparent stress in the material and the lattice parameter is equivalent to \( d_0 \) at a corresponding Bragg angle of \( \theta_0 \). In the presence of interface stresses, mechanical equilibrium requires that macrostresses are present in order to compensate [Birringer et al. (2002)] or analogously to equilibrate within the whole body [Macherauch and Kloos (1987)].

If an elastic response can be assumed, then the elastic deformation which takes place will obey the Poisson ratio,

\[
\nu = -\frac{\varepsilon_{11}}{\varepsilon_{33}} = -\frac{\varepsilon_{22}}{\varepsilon_{33}}
\]  

(6-7)

Considering this, a negative value for strain in the planar directions, \( \varepsilon_{11} \) and \( \varepsilon_{22} \), should result in a positive strain in the normal direction, \( \varepsilon_{33} \). If there is a net interplanar spacing contraction in the plane, there must be a net interplanar spacing expansion normal to it. Fig. 6.10 illustrates the result of a bi-axial compressive stress where the lattice contracts in the planar directions but expands in the normal direction causing a diffraction line shift to a lower Bragg angle and thus, an increased interplanar spacing, \( d \), in the normal direction to the sample plane. As a result, there is an inherent relationship between the microscopic and macroscopic strain measurements. Such a relationship can also be seen in the microstrain and macrostress relationship with grain size, i.e., a similar inverse relationship with grain size. If the sources of these stresses are considered to be the same, i.e., the consequences of interface stresses [Cahn and Larche (1982)] or long-range elastic fields since local elastic
deformation is necessary for joining of the crystals [Valiev et al. (1986)], then they are distinguished only by way of the method used to detect them. That is, if microstrain induced XRD line broadening is accompanied by a superimposed XRD line shift [Qin et al. (2008)] then by conventional XRD it is detected as interplanar spacing changes in the direction normal to the plane. Since the macrostresses are resolved bi-axially, they are detected as interplanar spacing changes in the planar directions.

6.5. **Summary**

The microstrain for the series of nanocrystalline Ni and Ni-Fe alloys produced by electrodeposition was determined from XRD pattern analysis based on line broadening. A general increasing trend with decreasing grain size was observed. The microstrain was found to increase dramatically at grain sizes less than 20 nm. This increasing microstrain trend is approximately proportional to the inverse of the grain size and consistent with the increase of intercrystal defects (i.e., grain boundaries and triple junctions) with decreasing grain size. This microstrain is associated with the local strains observed at grain boundaries in the HR-TEM image analysis. The microstrain values for the nanocrystalline Ni-Fe samples were noticeably higher than the Ni samples and showed a distinct increasing trend with both decreasing grain size and increasing Fe concentration. In Chapter 4, both HR-TEM image analysis (Section 4.4.2) and growth fault probabilities determinations (Section 4.5.4) showed an increase of growth faults with increasing Fe concentration. As a result, for the nanocrystalline Ni-Fe alloys, a contributing effect of microstrain induced XRD line broadening is considered to be due to the presence of growth faults in addition to the effect of grain size reduction.
Macrostresses were systematically determined for the series of electrodeposited nanocrystalline Ni and Ni-Fe samples over a broad grain size range based on the detection of strain from the (311) ring using 2D-XRD. At grain sizes below 20 nm, there was a dramatic increase in the compressive macrostress with decreasing grain size. Similar to the microstrain, macrostress was found to be approximately proportional to the inverse of the grain size. The origin of the compressive macrostress is proposed to be an equilibrating response to the presence of interface stresses. These interface stresses arise from elastic deformations at grain boundaries which generate a long-range elastic stress field. The intensity of this elastic stress field is related an increasing intercrystal volume fraction that results in a corresponding increase in the observed macrostresses.

Furthermore, microstrain in these materials was identified to be a result of localized strain near grain boundaries. These localized strains are proposed to be caused by the interface stresses that result in the observed macrostresses. The sources of microstrain and macrostresses are considered to be the same, but detected in different manners. That is, microstrain is detected by XRD line broadening and simultaneously a superimposed XRD line shift. The XRD line shift in this case results in an increased interplanar spacing. On the other hand, macrostresses are detected as XRD line shifts or changes in the interplanar spacing corresponding to the planar directions. In the present study, the macrostresses were found to be increasingly compressive at grain sizes less than 20 nm and thus, there is a decreased interplanar spacing. It follows that the material is undergoing an elastic response that obeys the principle behind the Poisson ratio.
Chapter 6 – Internal Stress

6.7. References


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CHAPTER 7
Conclusions

This research work presents the first comprehensive study on nanocrystalline materials produced in bulk quantities using a novel continuous electrodeposition process. Nanocrystalline Ni and Ni-Fe alloy continuous foils were produced and an intensive investigation into various characteristics and properties was carried out. The main objective was to expand upon the knowledge and understanding around this class of materials. The following are the key findings:

1. In this study, the grain boundary characteristics for electrodeposited nanocrystalline Ni and Ni-Fe was revealed. HR-TEM analysis showed evidence of local strain at different types of grain boundaries, including high and low angle grain boundaries, and twin boundaries. The nature of these local strains at grain boundaries can be explained based on the interpretation of a non-equilibrium grain boundary that results when the conditions of compatibility are not satisfied. Such grain boundaries have long-range elastic fields since local deformation is necessary for joining of the crystals. Due to the presence of a high volume fraction of intercrystal defects in nanocrystalline materials it is conceivable that the occurrence of these local strains is significant.

2. The electrodeposited nanocrystalline Ni and Ni-Fe alloys were not exposed to any external loads, and thus, defects such as dislocations and or deformation stacking faults are present in negligible quantities. However, the presence of twin faults of the
growth type, or “growth faults”, which arise during the synthesis process have been identified. The pure Ni samples were found to have a lower occurrence of growth faults when compared to the Ni-Fe samples. With increasing Fe there was an increased presence of growth faults. The addition of soluble alloying elements in fcc metals, such as Fe in Ni, is known to decrease the stacking fault energy. As a result, an increased presence of growth faults can be expected with increasing Fe concentration.

3. In general, a decrease in grain size is accompanied by an increase in the total enthalpy (stored energy) in electrodeposited nanocrystalline Ni and Ni-Fe alloys. Decreasing grain size and/or increasing Fe was also accompanied by an increase in the peak temperature and thus, thermal stability. The heat released during anisothermal annealing is considered to be almost exclusively a result of reducing intercrystal defects (i.e., grain boundaries and triple junctions). In the case of the nanocrystalline Ni-Fe alloys, a contribution to the heat release was expected from ordering of the lattice structure.

4. The hardness of the nanocrystalline Ni and Ni-Fe alloys was found to follow the regular Hall-Petch behaviour down to about a grain size of 20 nm. Increasing Fe concentration and solid-solution strengthening was not considered to be a contributing factor. Below grain sizes of 20 nm, a deviation from the Hall-Petch behaviour was observed. This deviation was owed to the operation of deformation mechanisms other than dislocation slip.
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5. There was no significant influence of grain size on the Young’s modulus of nanocrystalline Ni and Ni-Fe alloys with grain sizes greater than 20 nm. At grain sizes less than 20 nm there was a slight reduction in the Young’s modulus values when compared to their conventional polycrystalline counterparts. Although the general trend with grain size was consistent with the composite model predictions, there was notable variability. The effect of texture was analyzed and found to influence the measured Young’s modulus values over the entire grain size range. Moreover, at less than 20 nm, there is likely a combined grain size and texture effect.

6. The microstrain for the nanocrystalline Ni and Ni-Fe alloys increased with decreasing grain size in a manner that is consistent with an inverse relationship. This microstrain is associated with the local strains observed at grain boundaries in the HR-TEM image analysis. When lattice defects are considered to be negligible, microstrain induced XRD line broadening is predominantly a result of increasing intercrystal defects, i.e., grain boundaries. However, when the presence of lattice defects is significant, e.g., the high density of growth faults seen in the nanocrystalline Ni-Fe alloys, there is an observable contribution to microstrain induced XRD line broadening.

7. The macrostresses in the nanocrystalline Ni and Ni-Fe alloys were found to be relatively low down to about 20 nm. At grain sizes less than 20 nm, there was a sharp increase in the compressive macrostressed which also followed an inverse grain size relationship. The onset of this increasing macrostress was owed to the corresponding
increase in intercrystal defects or number of interfaces in the solid. Such interfaces are associated with stresses. When the volume fraction of intercrystal defects is high, the interface stresses become significant and must be equilibrated by a homogeneous bulk stress or analogously macrostress. Thus, the origin of the macrostresses in these materials and dependence on grain size is considered to be a result of the interactions at interfaces and their elastic deformations necessary to maintain a coherent network of grains.

8. The origins of microstrain are linked to the macroscopic strains (macrostresses) since they can both result in XRD line shifts. That is, the interface stresses present in these materials induce local strains or elastic deformations near grain boundaries that are homogeneous. For the foils, the macrostresses are bi-axial and result only in the planar directions. Since the macrostresses are compressive, there is a net contraction in the planar directions or decrease in the interplanar spacing. Microstrain in nanocrystalline materials result in XRD line broadening and a superimposed XRD line shift which is consistent with an increased interplanar spacing. This change in lattice parameter is detected in a direction which is normal to the plane. It follows that the material is undergoing an elastic response that obeys the principle behind the Poisson ratio.
CHAPTER 8
Recommendations for Future Work

1. There remains the opportunity to further characterize these materials using various advanced techniques. For example, the presence of porosity in these materials can be better evaluated using positron annihilation spectroscopy. It would also be of significant interest to determine the grain boundary characteristics of these materials with respect to angles of misorientation in order to determine fractions of random and special grain boundaries based on the coincidence site lattice model (CSL). This information could possibly be used to further advance the understanding behind the influence of intercrystal defects (i.e., grain boundaries) on internal stresses and other characteristics.

2. The presence of internal stresses in nanocrystalline materials is intrinsic given that there is a significant volume fraction of intercrystal defects. As seen in this study, there is a tendency for grain boundaries to be in a non-equilibrium state resulting in local strains or elastic deformations. A possibility may exist to minimize the occurrence of these local strains by introducing a grain boundary relaxation process via a heat treatment that does not induce grain growth. Further investigation on this possibility is warranted.

3. The effect of internal stresses on various properties requires further study. In particular, magnetic properties are known to be affected by internal stresses. For example, the inability to obtain coercivity values for the nanocrystalline Ni-Fe alloys
that are comparable with large grained polycrystalline materials could be due in part by the presence of internal stresses. Confirmation of this would be crucial in directing additional work to potentially improve this magnetic property in electrodeposited nanocrystalline materials.

4. Given the macrostress values in the planar directions, one can decipher the principle stresses using Mohr’s circle calculations. Employing this analysis can also help to resolve the reasons for the curvature which has been observed in some of the samples produced in this study. Furthermore, the a directional dependence on the way in which the foil is produced may provide a link to the observed curvature and present an opportunity for optimization with the objective of obtaining flat foils.

5. In this study, the nanocrystalline Ni-Fe alloys were limited to one grain size per Fe concentration. It would be interesting to produce samples with the same Fe concentration and varying grain sizes to eliminate alloying effects and to isolate structural effects.

6. This study was limited to nanocrystalline Ni and Ni-Fe alloys. It would be beneficial to evaluate other fcc phase materials to determine if the conclusions made in this study can be applied to other systems. In addition to this, an analysis of bcc and/or hcp phase materials using the same techniques would also be of particular interest.
7. The smallest grain size in this study was approximately 10 nm. A similar investigation on internal stresses with grain sizes that are less than 10 nm and perhaps amorphous material is recommended. A study on the amorphous material is particularly interesting in that a transition from a state of stress to a minimal stress could be expected due to the loss of crystallinity.
APPENDICES

Appendix A: SEM Images

Figure A.1. SEM image (60,000X) of sample no. 1 (Ni, ~255 nm).

Figure A.2. SEM image (60,000X) of sample no. 2 (Ni, 81 nm).

Figure A.3. SEM image (60,000X) of sample no. 5 (Ni, 23 nm).
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Figure A.4. SEM image (60,000X) of sample no. 6 (Ni-7.3 wt.% Fe, 32 nm).

Figure A.5. SEM image (500X) of sample no. 7 (Ni-16 wt.% Fe, 12 nm).

Figure A.6. SEM image (60,000X) of sample no. 9 (Ni-32 wt.% Fe, 10 nm).
Appendices

Appendix B: TEM BF/DF Images, SAD Patterns, and Grain Size Distributions

Figure B.1. TEM images of sample no. 1 (Ni, ~255 nm): (a) BF image, (b) DF image, and (c) SAD pattern.
Figure B.2. TEM images of sample no. 2 (Ni, 81 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure B.3. TEM images of sample no. 3 (Ni, 44 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure B.4. TEM images of sample no. 4 (Ni, 37 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure B.5. TEM images of sample no. 5 (Ni, 23 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure B.6. TEM images of sample no. 6 (Ni-7.3wt.%Fe, 32 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure B.7. TEM images of sample no. 7 (Ni-16 wt.% Fe, 12 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure B.8. TEM images of sample no. 8 (Ni-23wt.%Fe, 10 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Figure B.9. TEM images of sample no. 9 (Ni-32wt.%Fe, 10 nm): (a) BF image, (b) DF image, (c) SAD pattern, and (d) grain size distribution.
Appendices

Appendix C: XRD Patterns

Figure C.1. XRD pattern (Cu-K\(_\alpha\)) for (calculated) Ni powder standard.

Figure C.2. XRD pattern (Cu-K\(_\alpha\)) for sample no. 1 (Ni, ~255 nm).
Appendices

Figure C.3. XRD pattern (Cu-Kα) for sample no. 2 (Ni, 81 nm).

Figure C.4. XRD pattern (Cu-Kα) for sample no. 3 (Ni, 44 nm).
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Figure C.5. XRD pattern (Cu-K\textsubscript{α}) for sample no. 4 (Ni, 37 nm).

Figure C.6. XRD pattern (Cu-K\textsubscript{α}) for sample no. 5 (Ni, 23 nm).
Figure C.7. XRD pattern (Cu-Kα) for sample no. 6 (Ni-7.3wt.%Fe, 32 nm).

Figure C.8. XRD pattern (Cu-Kα) for sample no. 7 (Ni-16wt.%Fe, 12 nm).
Appendices

Figure C.9. XRD pattern (Cu-K$_\alpha$) for sample no. 8 (Ni-23wt.%Fe, 10 nm).

Figure C.10. XRD pattern (Cu-K$_\alpha$) for sample no. 9 (Ni-32wt.%Fe, 10 nm).