SYNTHESIS AND MECHANICAL PROPERTIES
OF BULK QUANTITIES OF ELECTRODEPOSITED
NANOCRYSTALLINE MATERIALS

by

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Synthesis and Mechanical Properties of Bulk Quantities of Electrodeposited Nanocrystalline Materials

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Abstract

Nanocrystalline materials have generated immense scientific interest, primarily due to observations of significantly enhanced strength and hardness resulting from Hall-Petch grain size strengthening into the nano-regime. Unfortunately, however, most previous studies have been unable to present material strength measurements using established tensile tests because the most commonly accepted tensile test protocols call for specimen geometries that exceeded the capabilities of most nanocrystalline material synthesis processes. This has led to the development of non-standard mechanical test methodologies for the evaluation of miniature specimens, and/or the persistent use of hardness indentation as a proxy for tensile testing. This study explored why such alternative approaches can be misleading and revealed how reliable tensile ductility measurements and material strength information from hardness indentation may be obtained.

To do so, an electrodeposition-based synthesis method to produce artifact-reduced specimens large enough for testing in accordance with ASTM E8 was developed. A large number of 161 samples were produced, tested, and the resultant data evaluated using Weibull statistical analysis. It was found that the impact of electroforming process control on both the absolute value and variability of achievable tensile elongation was strong. Tensile necking was found to obey
similar processing quality and geometrical dependencies as in conventional engineering metals. However, unlike conventional engineering metals, intrinsic ductility (as measured by maximum uniform plastic strain) was unexpectedly observed to be independent of microstructure over the grain size range 10-80nm. This indicated that the underlying physical processes of grain boundary-mediated damage development are strain-oriented phenomena that can be best defined by a critical plastic strain regardless of the strength of the material as a whole.

It was further shown that the \( H_V = 3 \cdot \sigma_{UTS} \) expression is a reliable predictor of the relationship between hardness and strength for electrodeposited nanocrystalline materials, provided the material is ductile enough to sustain tensile deformation until the onset of necking instability. The widely used relationship \( H_V = 3 \cdot \sigma_Y \) was found to be inapplicable to this class of materials owing to the fact that they do not deform in an “ideally plastic” manner and instead exhibit plastic deformation that is characteristic of strain hardening behaviour.
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For my Dad.
# Table of Contents

## Abstract

### ii

## Acknowledgments

### iv

## Table of Contents

### vi

## List of Tables

### viii

## List of Figures

### ix

## List of Appendices

### xvii

### Chapter 1 – Introduction

1.1 Background & Motivation for Study

1.2 Processing of Nanocrystalline Materials

1.3 Mechanical Properties of Nanocrystalline Materials: An Overview

1.3.1 Elastic Properties

1.3.2 Strength

1.3.3 Hardness-Strength Relationships

1.3.4 Ductility

1.3.4.1 Strain Hardening Capacity

1.3.4.2 Specimen Geometry Effects

1.3.4.3 Processing Artifact Effects

1.3.4.4 Closing Remarks on Nanocrystalline Material Ductility

1.4 Research Objectives

1.5 References

### Chapter 2 – Materials Characterization Methods

2.1 Introduction

2.2 Chemical and Structural Characterization

2.2.1 Chemical Composition

2.2.2 X-ray Diffraction (XRD)

2.2.3 Transmission Electron Microscopy (TEM)

2.2.4 Electrodeposit Internal Stress

2.3 Mechanical Testing

2.3.1 Tensile Testing

2.3.2 Vickers Microhardness

2.4 References

### Chapter 3 – Materials Synthesis

3.1 Introduction

3.2 Nomenclature

3.3 Electrodeposition – General Considerations
List of Tables

**Table 2-1** Theoretical peak positions and relative intensities for the first five diffraction lines of a theoretical nickel sample with random crystallographic orientation using Co-Kα radiation, $\lambda = 0.179$ nm, as per Cullity [1].

**Table 3-1** Composition of the Watts-type electrodeposition bath used in the present study.

**Table 3-2** Specimens synthesized.

**Table 5-1** Typical gauge dimensions for tensile tests.

**Table 5-2** Data from other sources.
List of Figures

Figure 1-1 SEM micrographs of a coarse-grained metallic material (left) alongside SEM (centre) and high resolution transmission electron microscope (TEM) (right) images of a chemically similar nanocrystalline material [courtesy of Integran Technologies Inc.].

Figure 1-2 (a) Scanning electron micrograph of a dog-bone-shaped microsample used to evaluate the tensile properties of nanocrystalline Cu produced by inert gas condensation [12]. The 4µm-deep indents (inset) were used as markers for the strain gauge but reportedly did not affect the results. (b) 3mm-length specimens before and after tensile testing of electrodeposited nanocrystalline Ni material batches A and B [13].

Figure 1-3 Schematic illustrations of typical microstructures produced by the pre- eminent nanomaterials synthesis methods (a) nanopowders; (b) consolidated nanopowders; (c) deformation-induced nanostructures; (d) nanograins crystallized from an amorphous phase; (e) nanotwinned material; and (f) electrodeposited nanocrystalline material [courtesy of U. Erb].

Figure 1-4 (a) Young’s Modulus of electrodeposited nanocrystalline Ni and NiP alloys as a function of grain size [79]; (b) Young’s and shear moduli of nanocrystalline Fe produced by mechanical attrition expressed as ratios of the conventionally accepted, coarse-grained bulk values. The dashed and solid curves correspond to a grain boundary thickness of 0.5 and 1nm, respectively. The open circles show the E/Eo values of nanocrystalline Fe versus grain size [76].

Figure 1-5 Three models proposed to explain Hall-Petch behavior. Models due to (a) Cottrell [92], (b) Li [93], and (c) Meyers and Ashworth [94]. Figure from ref. [95].

Figure 1-6 Schematic diagram of the variation of yield strength as a function of grain size [45].

Figure 1-7 Volume fractions of the total interface component, grain boundaries and triple junctions, as a function of grain size, assuming a grain boundary width of 1nm [99].

Figure 1-8 Competition between deformation mechanisms in nanocrystalline materials (schematically). (a) Framework for the grain size dependence of dislocation activity and grain boundary-mediated contributions to nanocrystalline materials, after [117] (b) Lattice dislocation slip and diffusional deformation modes occur in large grains (with dislocation signs) and small (shaded) grains, respectively [106].

Figure 1-9 Elongation-to-fracture data for (a) a variety of metals and alloys produced using a range of synthesis methods [138], and (b) electrodeposited Ni-based materials (figure taken from ref [140]).

Figure 1-10 (a) Deformation and fracture processes in a specimen with a bimodal structure [147], (b) engineering stress–strain curves for pure Cu. Curve A, annealed, coarse grained Cu; B, room temperature rolling to 95% cold work (CW); C, liquid-nitrogen temperature rolling to 93% CW; D, 93% CW . 180 8C, 3 min.; and E, 93% CW . 200 8C, 3 min. Note the coexisting high strength and large uniform plastic strain as well as large overall percentage elongation to failure.
for curve E (bimodal structure) [148]; (c) Tensile curves of extruded nanocrystalline Al–7.5Mg samples with varying concentrations of blended coarse-grained powder to create a bimodal structure [149].

Figure 1-11 (top) Transmission electron microscopy (TEM) observations of the typical microstructure in an as-deposited nanotwinned Cu sample. A bright field TEM image (A) and the electron diffraction pattern (inset in (A)) show roughly equiaxed submicron-sized grains with random orientations separated by high angle grain boundaries; (bottom) a typical tensile stress-strain curve for the Cu sample with nano-twins in comparison with that for a coarse-grained polycrystalline Cu (average grain size >100 µm) and a nanocrystalline Cu sample (mean grain size ~ 30 nm). Inset shows the geometry of the tensile sample for the as-deposited nano-twin sample [19].

Figure 1-12 Typical engineering stress-strain behaviour to fracture, point F. The “ultimate tensile strength” is indicated at point M. The circular insets represent the geometry of the deformed specimen at various points along the curve [61].

Figure 1-13 Illustration of diffuse necking and localized necking in a sheet tensile specimen [152].

Figure 1-14 Photographs of the gauge sections of fractured tensile test coupons from (a) cold rolled steel [155], and (b) cold rolled Al [157], illustrating localized necking and the 55° fracture angle.

Figure 1-15 Schematic diagram of tensile sample geometries used in the current and previous studies (Wang et al. [4], Zimmerman et al. [158], Dalla Torre et al. [13]) on electrodeposited nanocrystalline materials as compared to the ASTM E8 standard subsize tensile test geometry specification [11].

Figure 1-16 Tensile ductility (as measured by reduction in area) of a variety of dual-phase copper alloys as a function of second phase volume fraction [159].

Figure 1-17 Elongation-to-fracture data for metals and alloys produced using a variety of one-step and two-step processing methods, data from [139].

Figure 1-18 Tensile curves obtained for ball milled nanocrystalline Cu and coarse-grained Cu at a strain rate of $10^{-3}$ s$^{-1}$ [138].

Figure 1-19 Representative stress–strain curves for nanocrystalline and coarse-grained cobalt (annealed at 800°C) at strain rates $\varepsilon_1 = 1 \times 10^{-4}$, $\varepsilon_2 = 5 \times 10^{-4}$, $\varepsilon_3 = 2.5 \times 10^{-3}$ [161].

Figure 2-1 Side view schematic of the internal stress measurement apparatus showing the initially flat Cu foil strip onto which the material in question is electrodeposited (shown as the curved black line) clamped by a screw at the top of the fixture and permitted to bend naturally. When the electrodeposited coating exhibits tensile residual stress, the direction of deflection is opposite the case when the electrodeposit stress is compressive in nature (both cases are shown
The amount of deflection of the bottom edge of the foil is measured using a graduated scale at the bottom of the apparatus, with this scale having been calibrated by the manufacturer in such a way that a value for the electrodeposited coating residual stress level may be calculated [2].

**Figure 2-2** Photograph of typical specimens (Ni-6.4 wt% Fe; 18 nm average grain size) before and after tensile testing in conformance with ASTM E8 [3]. Scale in cm.

**Figure 3-1** Schematic diagram showing net-shape manufacturing of an electroformed product [1].

**Figure 3-2** Schematic diagrams showing the experimental set-up for pulsed current plating [2].

**Figure 3-3** Schematic diagram and cross-sectional scanning electron micrograph of a coarse-grained electrodeposit ((a) and (b)) compared to a nanocrystalline electrodeposit ((c) and (d)) [2, 8].

**Figure 3-4** Effect of overpotential ($\eta$) / current density ($I$) on critical crystal nucleation size ($r$) [2].

**Figure 3-5** ‘Processing-structure’ relationship for pulsed electrocrystallization. Fundamental mathematical expressions describing the physical phenomena linking the physically measureable quantities (in ovals) exist as shown by the mechanisms between each oval. The links get progressively weaker down the chain and are replaced by empirical relationships towards the end [10].

**Figure 3-6** Schematic diagram showing nucleation, growth, and surface diffusion during electrocrystallization [11].

**Figure 3-7** Nanocrystalline Ni-Fe electrodeposit grain size as a function of deposit chemical composition, illustrating the significant grain refining effect of alloying in the electrodeposited Ni-Fe binary system [13].

**Figure 3-8** (a) Top-view schematic and (b) photograph of the electroforming apparatus used for the Ni-Fe synthesis component of this work.

**Figure 3-9** Schematic illustration of the square-wave pulsed electrodeposition waveform used in the present study.

**Figure 3-10** Photograph of a typical electroformed plate from which tensile specimens used in this study were cut alongside a single tensile test specimen (scale in cm).

**Figure 3-11** Internal stress of Ni electrodeposited from a standard Watts electrolyte as a function of stress reliever concentration; values from (a) the literature [19]; and (b) the current study.
Figure 3-12 The nature of benzoic acid sulfimide decomposition in the Watts Ni plating electrolyte. Concentration of benzoic acid sulfimide along with two of its decomposition products, o-toluene sulfonamide and benzamide, as a function of bath use as expressed by the amount of electrical charge (Amp-hr) passed through the solution per unit volume [20].

Figure 3-13 Average grain size of electrodeposited nanocrystalline Ni as a function of electrolyte grain refiner concentration as compared to that from a previous study [12].

Figure 3-14 Schematic illustration of common processing artifacts encountered in electrodeposition [20].

Figure 3-15 Cross-sectional optical micrograph of an electroformed plate containing nodular / dendritic growth. Deposit growth direction is from bottom to top.

Figure 3-16 (a,b) SEM Analysis of the fracture face of a nanocrystalline Ni tensile specimen synthesized using an electroforming process replenished with water from a malfunctioning de-ionized water system indicating the presence of particulate contamination; (c) EDX spot analysis of the Ca particulate (images courtesy of Peter Lin, Integran Technologies Inc.).

Figure 3-17 Photograph of representative electroformed nanocrystalline Ni plates produced before and after implementing processing artifact minimization (courtesy of Peter Lin, Integran Technologies Inc.).

Figure 3-18 Cross-sectional optical micrograph of an electroformed plate containing hydrogen pitting. Deposit growth direction is from bottom to top.

Figure 3-19 TEM characterization data of a nanocrystalline Ni (31 ± 9nm average grain size) sample showing a (a) bright field image, (b) selected area diffraction pattern, and (c) grain size distribution.

Figure 3-20 Typical XRD diffraction profiles (Co Kα radiation) for representative pure Ni (38nm grain size) and Ni-46.8wt% Fe (10nm grain size) nanomaterials alongside the calculated random profile for Ni.

Figure 3-21 TEM characterization data of a Ni-47.3%Fe (9nm average grain size) sample showing a (a) bright field image, (b) dark field image, (c) selected area diffraction pattern and (d) grain size distribution [24].

Figure 3-22 TEM bright field image of specimen AE065 indicating an 80nm average grain size and a large concentration of faulted regions [courtesy of G. Cingara].

Figure 4-1 Tensile engineering stress-strain data from six individual specimens cut from a single plate of material produced using (a) an early scale-up stage electroforming process alongside (b) data from six individual specimens cut from an otherwise identical plate of material produced using a later generation process with much stricter processing artifact control.
Figure 4-2 Scanning electron micrograph images of the fracture surfaces of nanocrystalline Ni tensile samples produced using (a) an early scale-up stage electroforming process alongside (b) an otherwise identical plate of material produced using a later generation process with much stricter processing artifact control.

Figure 4-3 Quasi-static tensile strain-to-fracture and uniform plastic strain as a function of plate thickness for nanocrystalline Ni specimens of similar microstructure, areal shape and processing method.

Figure 4-4 Scanning electron microscopy (SEM) images from a typical thin foil (0.05mm thickness) nanocrystalline Ni sample after tensile testing illustrating the combination of (a) brittle macroscopic fracture morphology and (b) highly localized necking.

Figure 4-5 The geometrical dependency of tensile elongation-to-fracture of nanocrystalline Ni (present study) compared to that exhibited by other standard engineering materials (data from ref [21]).

Figure 4-6 (a) Two-parameter Weibull fit to strain-to-fracture data from nanocrystalline Ni specimens varying thickness from 0.030 to 2.5mm; (b) schematic diagram depicting the superposition of the geometrical / surface and volume flaw effects that control the tensile strain-to-fracture variability of electrodeposited nanocrystalline Ni.

Figure 4-7 Photographs of the gauge sections of fractured tensile test coupons from (a) the current study (0.5mm-thick), (b) cold rolled steel [22], and (c) cold rolled Al [23], illustrating the 55° fracture angle resulting from localized necking deformation [24].

Figure 4-8 Optical micrographs (left) of the gauge section of representative specimens illustrating the transition in failure mode from plane strain to plane stress with increasing sample thickness (t) paired with SEM images (right) of the corresponding fracture surfaces: (a) <0.1mm, (b) 0.1 – 0.5mm, (c) 0.8 -1mm, (d) 2-2.5mm. The gauge width (w) of each specimen shown is approximately 6.3mm. Grain size = 25 nm.

Figure 4-9 Representative tensile engineering stress-strain curves with average grain sizes and compositions provided in the legend. All samples electrodeposited except for the Ni-200 standard.

Figure 4-10 Two-parameter Weibull fit to strain-to-fracture data illustrating the differences in statistical variability between the samples of approximately 1mm thickness (crosses) and the samples of varying thickness from 0.030 to 2.5mm (squares).

Figure 4-11 Maximum uniform plastic and non-uniform strain distributions for 116 nanocrystalline Ni-based specimens of equivalent geometry and spanning average grain size values from 10 to 80nm.

Figure 4-12 Maximum uniform plastic strain plotted as a function of yield strength which serves as a proxy for grain size as per the Hall-Petch relationship.
Figure 4-13 Predicted variation of the strain at the onset of necking in uniaxial tension of ferritic steel with different grain sizes along with comparison to experimental results [30].

Figure 4-14 Hardening capacity \( h = \sigma_{UTS} / \sigma_Y \) plotted as a function of yield strength which serves as a proxy for grain size as per the Hall-Petch relationship for 116 nanocrystalline Ni-based specimens of equivalent geometry and spanning average grain size values from 10 to 80nm.

Figure 4-15 Ductile fracture in nanocrystalline materials that occurs through formation of nanocracks, their transformation into pores, growth of pores and formation of local necks between large pores [31].

Figure 5-1 Vickers hardness as a function of ultimate tensile strength data for carbon and alloy steels in the annealed, normalized, and quenched-and-tempered conditions [12].

Figure 5-2 Stress strain curves for typical nanocrystalline Ni-based electrodeposits recorded in conformance with ASTM E8M-01.

Figure 5-3 Hardness as a function of tensile yield strength measured for a wide range of electrodeposited nanocrystalline materials.

Figure 5-4 Hardness as a function of ultimate tensile strength measured for a wide range of electrodeposited nanocrystalline materials.

Figure 5-5 The ratio of hardness to (a) yield strength, and (b) ultimate tensile strength as a function of grain size, as measured by XRD line broadening.

Figure 5-6 The ratio of hardness to (a) yield strength, and (b) ultimate tensile strength as a function of grain size, as measured by XRD line broadening.

Figure 5-7 The influence of the material strain hardening exponent \( n \) on the calculated ratios of hardness to ultimate tensile strength (using the model of Tabor [25]; Equation (5-1)) and hardness to yield strength (using the models of Cahoon et al. [30] (Equation (5-2)) and Gao [28] (Equation (5-3))).

Figure 5-8 The ratio of hardness to ultimate tensile strength as a function of tensile elongation for (a) all specimens analyzed, and (b) only specimens displaying a distinct necking instability failure mode.

Figure 5-9 A comparison of material yield strength estimates generated using \( \sigma_Y = H_V / 3 \) (Equation (1-5)) to the models of Cahoon et al. [30] (Equation (5-2)) and Gao [28] (Equation (5-3)).

Figure 7-1: Minimum specimen thickness required for trustworthy measurement of the plane strain fracture toughness, \( K_{IC} \), of a material as per Equation (7-1).
**Figure A-1** Proposed deformation mechanism of electrodeposited nanocrystalline Ni of 20nm grain size based upon the results of *in situ* TEM tensile testing. Grain boundary sliding transforms into crystal lattice rotation in neighboring grains. a) Before plastic deformation, the materials possessed high angle grain boundaries; b) shear of two nano-sized grains 1 and 2 by gliding grain boundary dislocations, and subsequent occurrence of the crystal lattice rotation in the neighboring nanocrystalline grain 3 by climbing GB dislocations; c) multiple grain rotations leading to grain agglomeration; d) a large grain formed with sub-boundaries (highlighted by dotted lines) due to incomplete grain coalescence [8].

**Figure A-2** Computer generated nanocrystalline Ni sample with a mean grain size of 12 nm synthesized using the Voronoi construction [13].

**Figure A-3** The dislocation mechanism suggested by molecular dynamics for f.c.c. metals: a leading partial is nucleated (a), and a trailing partial follows (b), the dislocation travelling through the grain (c), being finally absorbed in opposite GBs (d) [13].

**Figure A-4** Grain boundary sliding along a bi-crystal boundary with steps and facets. (a) Initial state. (b) Non-accommodated grain boundary sliding results in the formation of regions (grey) where neighbouring grains interpenetrate and regions (white) where voids are formed. (c) Elastic accommodation. (d) Diffusional accommodation. (e) Lattice slip accommodation. (f) Accommodating local migration of grain boundaries [24].

**Figure A-5** 2D schematic of a grain arrangement in a (A) nano- and (B) polycrystalline material. A mesoscopic planar interface can be formed by grain boundary migration. Atoms located in the darker regions have to be re-arranged in the process of grain boundary sliding [25].

**Figure A-6** Twin deformation conducted by regularly arranged partial dislocations emitted from a grain boundary [24].

**Figure A-7** Schematic representation of diffusional creep. Self-diffusion should result in plastic flow if matter is carried from boundaries subject to compressive stress (vertical boundaries) over to boundaries under a tensile stress (horizontal boundaries) [38].

**Figure A-8** A deformation map for pure Ni showing the effect of grain refinement from 32μm to 10nm (finer solid lines) [40].

**Figure A-9** Grain rotation in a polycrystalline solid. (a) Initial state. (b) Non-accommodated grain rotation results in the formation of small regions (black regions near boundaries of rotated grain) where neighbouring grains interpenetrate and small regions (white regions near boundaries of rotated grain) where voids are formed. (c) Accommodation by bulk diffusion. (d) Accommodation by grain boundary diffusion [24].

**Figure A-10** Competition between deformation mechanisms in nanocrystalline materials (schematically). (a) Framework for the grain size dependence of dislocation activity and grain boundary-mediated contributions to nanocrystalline materials, after [47] (b) Lattice dislocation
slip and diffusional deformation modes occur in large grains (with dislocation signs) and small (shaded) grains, respectively [24].
List of Appendices

Appendix A - Plastic Deformation Mechanisms in Nanocrystalline Materials: An Overview
Chapter 1
Introduction

1.1 Background & Motivation for Study

A significant portion of materials science is concerned with the development of synthesis-structure-property relationships. What are the important properties of a material (e.g. mechanical, magnetic, electrical, thermal, etc.) and what is the nature of their dependency on the structure of that material? Equipped with an understanding of synthesis-structure-property relationships for a given material, the engineer may then effectively design methods for fabricating that material so that it can be used in practical applications.

Most metallic materials are comprised of a fully dense aggregate of crystals or grains known as a polycrystalline structure. A scanning electron microscope (SEM) image showing the microstructure of a typical polycrystalline metallic material is shown at the left-hand side of Figure 1-1. The interfaces between the grains near the surface of this particular specimen have been chemically etched to accentuate its polycrystalline character, but otherwise the material is fully-dense. The diameter of the crystals of this material varies between roughly 10-30µm, which is typical for a conventional polycrystalline engineering material. On the other hand, new methods exist to create materials with much smaller crystals. A nanocrystalline material is rather arbitrarily defined as a polycrystalline material that possesses an average grain size below 0.1µm (or 100nm), and an example of such a microstructure is shown on the right-hand side of Figure 1-1.
Introduction

Figure 1-1 SEM micrographs of a coarse-grained metallic material (left) alongside SEM (centre) and high resolution transmission electron microscope (TEM) (right) images of a chemically similar nanocrystalline material [courtesy of Integran Technologies Inc.].

It is well-known that many of the key properties of a material e.g. yield strength, hardness, electrical resistivity, magnetic coercivity, wear resistance and so on, are highly sensitive to the size of the material’s constituent crystals. For example, the Hall-Petch relationship describes the dependency of material yield strength on its grain size:

\[ \sigma_Y = \sigma_0 + kd^{-\frac{1}{2}} \]  

(1-1)

where \(\sigma_Y\) is yield strength, \(d\) is grain size, and \(\sigma_0\) and \(k\) are constants \([1,2]\). The term “yield strength” implies intrinsic resistance to the onset of irreversible or plastic deformation under the influence of an external applied load, and defines the practical upper stress limit to which a material may be loaded without significant change of shape. Examination of Equation (1-1) begs the question of whether grain size refinement can be used as a tool to achieve peak strength in a given polycrystalline solid. As described by Darken \([3]\) and Wang et al. \([4]\), if the Hall-Petch relationship were extrapolated to the smallest grain size imaginable, then the theoretical strength
Introduction

could conceivably be obtained. This hypothesis has been one of the primary drivers behind the immense interest in nanocrystalline materials since Gleiter identified their unique structural character almost 30 years ago [5,6]. In addition, the nature of structure-mechanical property relationships within the nano-regime has received a great deal of attention since that time, most notably the Equation (1-1) Hall-Petch dependency and how it tends to break down as the dominant physical mechanisms that underpin material strength transition from traditional dislocation-based deformation behaviour to grain-boundary mediated mechanisms with grain refinement below 100nm [e.g. 7-9]. This behaviour is reviewed in more detail in Section 1.3.2 and Appendix A.

Unfortunately, however, the vast majority of researchers who have sought to explore the nature of nanocrystalline grain refinement on material strengthening have not, in fact, been able to carry out material strength measurements using established tensile tests because the most commonly accepted standardized tensile test protocols call for specimen geometries that exceeded the capabilities of most nanocrystalline material synthesis processes. This has led to a) the development of non-standard mechanical test methodologies for the evaluation of miniature specimens (see Figure 1-2 for example), and/or b) the persistent use of hardness indentation as a proxy for tensile testing, which is the pre-eminent means to measure material strength. Both of these strategies have numerous inherent issues that have seriously hindered the development of trustworthy structure-mechanical property relationships for nanocrystalline materials [10].

A secondary effect is that the reliable comparison of the properties of nanocrystalline materials to those of other more broadly accepted engineering materials has, in many cases, been
impossible to carry out because the relevant properties have been measured using fundamentally
dissimilar tests. The end result is that the materials selection process in engineering design has
also been rendered unreliable because the standard tests cannot be performed. Therefore, the
primary objective of this work has been the development of a synthesis method to produce
specimens large enough for testing in accordance with ASTM E8 [11], arguably the most widely
used mechanical test in North America. In this manner, the resultant test data might be more
reliably compared to data from other well-known engineering materials. Another objective has
been to evaluate the validity of the hardness-strength relationships most commonly used in the
study of nanocrystalline materials. In doing so, two of the most prevalent issues with effective
mechanical property characterization of nanocrystalline materials (non-standard tensile test
geometries and substitution of hardness indentation for strength testing) could be systematically
addressed.

Figure 1-2  (a) Scanning electron micrograph of a dog-bone-shaped microsample used to
evaluate the tensile properties of nanocrystalline Cu produced by inert gas condensation [12]. The 4µm-deep indents (inset) were used as markers for the strain gauge but reportedly did not affect the results. (b) 3mm-length specimens before and after tensile testing of electrodeposited nanocrystalline Ni material batches A and B [13].
1.2 Processing of Nanocrystalline Materials

Specimen size effects aside, past attempts to obtain a broader picture of the intrinsic mechanical properties of nanocrystalline materials have also been challenging because the process-related material characteristics (e.g. microstructural variability, porosity, impurities, processing artifacts) have generally not been rigorously accounted for in the rationalization of the observed response to deformation. Nanocrystalline materials can be produced using a relatively large number of synthesis routes resulting in a huge diversity of structures from these often fundamentally dissimilar processing methods. For example, “two-step” processes typically involve the production of a nanopowder followed by some sort of consolidation process. See Figure 1-3(a) for a schematic representation of a nanomaterial powder feedstock alongside that of the consolidated structure in Figure 1-3(b). The most common synthesis technique examples for such materials include inert gas condensation methods, mechanical attrition by ball milling, and sol-gel chemical processing. Significant progress has recently been made in the reliable synthesis and consolidation of ball-milled nanomaterials in particular [14,15]. However, after consolidation of the nano-sized particulate, these materials invariably retain some degree of small-scale porosity, which is known to have a marked influence on the mechanical properties, most notably the elastic properties [16].

On the other hand, “single-step” processing techniques output ultrafine-grained material in one step without the need for subsequent powder consolidation. The most popular examples are based upon either severe plastic deformation (e.g. high pressure torsion (HPT), equal channel angular pressing (ECAP), and accumulative roll-bonding (ARB)), crystallization of amorphous precursors or electrodeposition. While severe plastic deformation is capable of producing bulk
Figure 1-3 Schematic illustrations of typical microstructures produced by the pre-eminent nanomaterials synthesis methods: (a) nanopowders; (b) consolidated nanopowders; (c) deformation-induced nanostructures; (d) nanograins crystallized from an amorphous phase; (e) nanotwinned material; and (f) electrodeposited nanocrystalline material [courtesy of U. Erb].

Quantities of material, massive total strains are required to form the ultrafine-grained microstructure, and this often results in very large dislocation densities, dislocations decorating the high angle grain boundaries, and dislocation cells or “subgrains” separated by low-angle
Introduction

boundaries. Moreover, these techniques are typically unable to produce nanocrystalline materials with average grain size values below 100nm. A schematic diagram of a representative ultrafine-grained microstructure is presented in Figure 1-3(c). Methods based upon severe plastic deformation have nevertheless garnered considerable interest, in part because of the ability produce fully-dense structures with bimodal grain size distributions [17]. Bimodal structures offer the potential to achieve an optimum balance between material strength and ductility. Specifically, the successful fabrication of a broad grain size distribution is thought to enable high strength (originating from the small crystals present and their associated strengthening effect as per the Hall-Petch effect, Equation (1-1)) concurrent with good ductility originating from the presence of large crystals that plastically deform in a fashion similar to conventional coarse-grained materials (i.e. strain hardening capacity). Bimodal structures are discussed in more detail in Section 1.3.4.1.

Another technique that has been widely used to produce fully-dense nanocrystalline microstructures is crystallization of amorphous precursors. In this process, an amorphous material is formed by e.g. melt-spinning, rapid quenching, or wire drawing, and then low temperature annealed to induce the formation of small crystals. Unfortunately, there are three notable features of the process that may adversely impact mechanical properties: a) the formation of the highly non-equilibrium amorphous precursor by processes such as rapid solidification typically requires relatively large concentrations of alloying elements (e.g. B, P) in order to depress the eutectic temperature, and the presence of these constituents often results in the undesirable formation of brittle intermetallic secondary phases during processing, b) the resultant post-anneal structure is generally a mixture of nano-sized grains dispersed throughout a retained
amorphous matrix – see Figure 1-3(d), and c) the cooling rates required to achieve the desired microstructure are so high (typically on the order of $10^6 \text{ K/s}$) that only thin foils can be produced. Nanocrystalline materials produced by this route typically exhibit very limited ductility but have found industrial application as soft magnetic materials [18].

Another interesting microstructure is the nanotwinned structure, pioneered by Lu and co-workers [19]. A representative schematic of this microstructure is shown in Figure 1-3(e), and is characterized by a high density of nanoscale growth twins embedded within individual grains. In the case of Cu, the grain sizes are typically on the order of 400-500nm while the twin lamellae thickness ranges from approximately 20-100nm. This structure appears to hold considerable promise for optimizing both strength and ductility [20]. It should also be noted that pulsed current electrodeposition is one of the processing methods that has been used to achieve the nanotwinned structure [21].

Finally, Figure 1-3(f) contains a schematic illustration of the structure employed in the current study, namely single phase structures produced by pulsed current electrodeposition. These microstructures are characterized by an equiaxed grain shape and a relatively narrow log-normal grain size distribution. A notable characteristic is that, unlike most other processes, electrodeposition permits the synthesis of a wide range of grain sizes, in some cases covering the entire structural range from $>10\mu\text{m}$ through to amorphous, from a given metal or alloy system by control of processing parameters. In addition, because electrodeposition is a single-step process that typically yields fully-dense structures, the potential to eliminate or at least minimize processing artifacts such as porosity exists.
1.3 Mechanical Properties of Nanocrystalline Materials: An Overview

Owing to the fact that the Hall-Petch effect is the primary driver behind the interest in nanocrystalline materials, a tremendous amount of work has been directed towards the study of their mechanical properties. The key findings have been summarized in numerous books [e.g. 22-27], conference proceedings [e.g. 28-35], viewpoint sets [e.g. 36-38], and review articles [e.g. 9,17,39-60]. A review of the plastic deformation mechanisms thought to be active in nanocrystalline materials is provided in Appendix A. The objective of this section is to provide a general overview of this literature as it relates to the mechanical properties of nanocrystalline materials, with particular emphasis on materials produced by electrodeposition.

1.3.1 Elastic Properties

By virtue of their ultra-fine grained microstructures, nanocrystalline materials exhibit high strength and this characteristic makes them suitable candidates for load-bearing applications. However, the vast majority of engineering components are intended for continued use over extended time periods, and are therefore designed such that all constituent structural members are safely and predictably loaded strictly within their elastic regimes, and do not experience any permanent change in shape resulting from irreversible plastic deformation in service. Within the elastic regime, the intrinsic capability of a material to withstand deformation is commonly known as its “stiffness”. From this information, one may derive the extent to which the material will deform (“elastic strain”) when loaded under some given stress level within the elastic regime or, conversely, the resistance to deformation (“elastic stress”) upon application of a given elastic
Introduction

strain. Consequently, the elastic stiffness properties of a material represent some of the most practically relevant mechanical characteristics of a structural engineering material.

On an atomic scale, elastic strain is manifested as small changes in the interatomic spacing and the stretching of the interatomic bonds [e.g. 61]. In other words, the macroscopic Young’s modulus is ultimately a reflection of the interatomic bonding forces, assuming no other contributions to measured strain. Given that the values of a material’s elastic constants reflect the bonding nature of its constituent atoms, it seems logical to expect that nanocrystalline materials would exhibit different moduli of elasticity compared to coarse-grained polycrystalline solids because of the high volume fraction of atoms located at or near the grain boundaries, triple junctions, and quadruple nodes. In particular, since the degree of atomic structural disorder is greater within a grain boundary as compared to the crystal lattice, the average atomic distance within it is generally known to be larger [62]. It could then be concluded that the grain boundary as a whole exhibits a lower bond strength and, therefore, have local elastic moduli values lower than those of the lattice. On the other hand, a computer simulation study of a Σ5 Cu grain boundary performed by Wolf and co-workers [63] resulted in exactly the opposite conclusion. Namely, an increase in Young’s modulus was observed across the grain boundary. This was attributed to the asymmetry of the interatomic potential, whereby shortened atomic distances are weighted more heavily than expanded distances and hence the local elastic stiffness of a grain boundary may be enhanced by the relatively low number of interatomic distances smaller than the equilibrium distance.
Introduction

In general, the question of how a material’s internal interfaces contribute to its bulk elasticity has been a matter of intense debate for many years. Most of the early work seemed to suggest that the presence of a significant fraction of interfacial atoms induces a huge effect on the elasticity of polycrystalline solids. Specifically, the Young’s moduli of many nanocrystalline materials were found to be significantly lower than those of their coarse-grained equivalents, up to 50% in some cases [6,64-70]. However, it was subsequently demonstrated that this drop was due in many cases to material porosity, the influence of which is thought to be substantially stronger than that of grain size. One of the first studies that aimed to quantify this effect was carried out by Krstic et al. [16], who developed a model to describe the elastic response of consolidated nanocrystalline powders containing residual porosity resulting from the compaction stage of processing. The aforementioned $E$ drop was deemed by the authors to be a natural result of porosity rather than severe grain refinement, this being corroborated by the fact that electrodeposited fully dense 7 nm grain size Ni-1.2 wt.%P exhibited essentially the same Young’s modulus ($E = 225$ GPa) as that of a coarse-grained Ni reference sample ($E = 221$ GPa) [71].

Several others have followed similar lines of reasoning in an attempt to quantitatively determine the effect of grain size on elastic response. Fougere et al. [72], for example, used both Krstic’s model and that of Boccaccini et al. [73] in order to fit Young’s modulus as a function of pore volume fraction for a large number of Inert Gas Condensed (IGC) Fe samples, ultimately drawing the conclusion that porosity is the dominant microstructural feature in determining the extent of the observed decrement in $E$. Kim and Bush [74] also carried out similar calculations using Budiansky’s method [75] to predict the properties of composite materials comprised of a
random mixture of isotropic constituents, pores being treated as a separate phase of zero-valued bulk and shear moduli. Considering both porosity and grain size effects, they also concluded that the contribution of the grain size could be ignored compared with the influence of porosity.

To further illustrate the problems associated with consolidated nanocrystals, Shen et al. [76] pointed out that the Young’s modulus of nanocrystalline Pd with an 8 nm grain size produced by IGC was reported to be 47 and 88 GPa in two different studies. This variation likely resulted from differences in the sample porosity brought about by variations in the condensation and/or compaction parameters. Upon careful application of nanoindentation to porosity-free locations on their mechanically-milled samples, these researchers observed essentially no difference in Young’s modulus between 17 to 26 nm grain size nanocrystalline Fe, Cu, Ni and Cu-Ni alloys and the corresponding chemically equivalent coarse-grained polycrystalline materials. In another study of the elastic response of nanomaterials, ultrasonic techniques were employed in order to characterize fine-grained (250 nm) Cu synthesized via severe plastic deformation [77]. The authors calculated a Young’s modulus drop and attributed this to non-equilibrium grain boundaries. Subsequently, detailed crystallographic texture studies carried out on the same material revealed that this drop was, in fact, a result of the preferred crystallographic orientation rather than any low modulus non-equilibrium grain boundary phase [78].

Hence, it can be concluded that in any discussion of the elasticity of nanomaterials, the possible effects linked to the chosen synthesis route (i.e. porosity), crystallographic texture, or any other structural feature that could play a role in the interpretation of elastic response measurements must be considered. As it pertains specifically to the effect of grain size, Figure 1-4 captures the
Introduction

present state of knowledge on the subject, which suggests that some modulus of elasticity reductions can indeed be expected for materials with grain diameters less than 10 nm [76,79,80]. However, the intercrystalline contribution to the elastic response for nanocrystalline solids with grain sizes larger than 10 nm appears to be minimal, a conclusion drawn also from computer molecular dynamics simulation studies [81,82].

Figure 1-4 (a) Young’s Modulus of electrodeposited nanocrystalline Ni and NiP alloys as a function of grain size [79]; (b) Young’s and shear moduli of nanocrystalline Fe produced by mechanical attrition expressed as ratios of the conventionally accepted, coarse-grained bulk values. The dashed and solid curves correspond to a grain boundary thickness of 0.5 and 1nm, respectively. The open circles show the E/E₀ values of nanocrystalline Fe versus grain size [76].

1.3.2 Strength

The understanding and practical utilization of mechanisms for strengthening crystalline metallic materials is an important fundamental topic in materials science and engineering. Phenomena such as age hardening, strain or work hardening, solid solution hardening, and grain refinement are commonly used to modify material strength i.e. its ability to resist permanent or non-recoverable plastic deformation. The common theme of these strengthening mechanisms is the formation of barriers to dislocation motion, which is the predominant carrier of plastic flow in
the vast majority of coarse-grained polycrystalline metallic materials at low temperatures. In age hardening, for instance, precipitates are formed within the matrix lattice and the size, density and/or degree of coherency of these secondary phases is controlled in order to optimize their effective resistance to dislocation glide within the lattice of the matrix phase. In the case of strain hardening, the material is plastically deformed or “worked” to generate high concentrations of dislocations within the grain interiors. These dislocations then hinder the motion of other dislocations when the material is mechanically loaded, with the end result being that the strength of the strain hardened material is ultimately dependent upon its dislocation concentration in a fashion analogous to the Hall-Petch relationship as follows:

\[ \sigma = \sigma_i + K\rho^{\frac{1}{2}} \]  

(1-2)

where \( \rho \) is the measured dislocation density in terms of dislocation length per unit volume, \( \sigma \) is the measured flow stress, \( K \) is a constant, and \( \sigma_i \) is the stress obtained when \( \rho^{\frac{1}{2}} \) is extrapolated to zero [83].

It is interesting to note that a relationship similar to Equations (1-1) and (1-2) is also observed for laminate materials consisting of layers with thickness \( t \) [84-87]:

\[ \sigma = \sigma_t + k_i t^{\frac{1}{2}} \]  

(1-3)

where \( \sigma_t \) and \( k_i \) are constants.

In the case of grain refinement, the formation of smaller crystals brings with it a commensurate increase in the volume fraction of interfaces between those crystals, and these interfaces act as barriers to dislocation glide. Thus, finer grained materials possess more barriers to dislocation
motion and are stronger than chemically similar coarser grained materials. Interestingly, the specific mechanisms that underpin the Hall-Petch effect in conventional coarse-grained polycrystalline metallic materials are still a matter of debate some 60 years after the behaviour was first quantified [e.g. 88-91]. However, the effect is generally explained by an external stress-induced pile-up of dislocations in one grain producing a stress concentration that activates a (e.g. Frank-Read) dislocation source in an adjacent grain [92]. Alternative mechanisms involve the activation of dislocation sources at grain boundary ledges [93], elastic/plastic incompatibility stresses between neighbouring grains giving rise to the generation of dislocations that effectively form a hardened reinforcing “second-phase” network [94], and so on. Schematic illustrations of these three models to explain Hall-Petch behaviour are provided in Figure 1-5 [95]. All of these mechanisms involve dislocation motion and its inhibition as a means of material strengthening.

![Figure 1-5](image_url)  
**Figure 1-5** Three models proposed to explain Hall-Petch behavior. Models due to (a) Cottrell [92], (b) Li [93], and (c) Meyers and Ashworth [94]. Figure from ref. [95].

Unfortunately, articulating the specific strengthening / plastic deformation mechanisms that underpin the synthesis-structure-property relationships for nanocrystalline materials has proven quite challenging for two reasons. Firstly, as described earlier, there are a great many ways to fabricate nanostructured materials. The resultant structures and associated mechanical properties
Introduction

are typically quite sensitive to the synthesis parameters and concomitant processing artifacts. De-coupling the effects of the nanostructure from the method used to create it is typically very difficult and so this has impeded the development of our understanding of the operative nanocrystalline material deformation mechanisms which have heretofore been theoretically developed primarily on the basis of structural considerations only. Secondly, because the deformation mechanisms are operating at the near-atomic scale, their direct observation has been difficult to accomplish. For instance, in the case of high resolution TEM evaluation of nanocrystalline materials, the small crystal size results in overlapping of grains in the TEM foil, making \textit{in situ} observations of mechanically loaded nano-sized crystals quite challenging. Even in those cases where individual nano-sized grains can be successfully resolved and plastically deformed in the TEM, the relevance of thin foil deformation mechanisms to bulk deformation may be questionable due to surface effects. Therefore, while numerous attempts to reveal the dominant nanocrystalline material deformation mechanisms have been made, our inability to “see” the deformation mechanisms in operation without great difficulty has definitely impeded the undertaking.

Nevertheless, this topic has received considerable attention and the primary goal of this section is to highlight the most important conclusions drawn so far. Before doing so, it is important to summarize the key macroscale strength and hardness observations that form the basis for this field of study:

1. The yield strength and hardness of nanocrystalline materials are extremely high. The yield strength of a metallic nanocrystalline solid is typically 5-7 times its chemically equivalent coarse-grained counterpart, while its hardness may be 3-10 times greater; and
Introduction

2. Ultrafine-grained materials are known to follow Hall-Petch grain size strengthening behaviour into the nanocrystalline regime. However, at some grain size below 100nm, the dependency of yield strength or hardness on grain size may become weaker, and even reverse at extremely fine-grain sizes. This latter phenomenon is known as the “inverse Hall-Petch effect” and its explanation has generated tremendous attention in the field since it was first observed in the late 1980s [e.g. 6-8,45,60,96]. See Figure 1-6 for a schematic diagram of the yield strength dependency on grain size.

![Figure 1-6](image-url) Schematic diagram of the variation of yield strength as a function of grain size [after 45].

Before proceeding to the discussion of deformation mechanisms, an important structural feature of nanocrystalline materials should be noted. In particular, it may be demonstrated on the basis of geometrical considerations of crystal size and shape that the volume fraction of atoms located at the crystal interfaces (i.e. grain boundaries and triple junctions) of a theoretical polycrystalline aggregate is virtually negligible at grain sizes above 100nm but becomes quite significant at grain sizes below 100nm. This structural characteristic was quantified by Palumbo et al. [98]
Introduction

and is illustrated in Figure 1-7 [99]. The calculation is based upon the assumption of a tetrakaidecahedral crystal shape and a constant 1nm grain boundary width. It may be appreciated from Figure 1-7 that the rate of transition from crystalline to intercrystalline atomic volume fraction increases quite rapidly for grain sizes below 20nm. The significance of this result is that the volume fraction of atoms available for grain boundary-mediated deformation phenomena is negligible for coarser-grained (e.g. grain size >100nm) materials, becomes significant with decreasing grain size within the <100nm nanocrystalline regime and ultimately becomes dominant below 10nm grain size. In the limiting case of a material with a “grain size” of approximately 1-2nm, for instance, the material is comprised wholly of “triple junctions” [99] and one would therefore expect the complete absence of deformation mechanisms based upon the assumption of crystallinity (e.g. dislocation slip) in such circumstances.

Figure 1-7 Volume fractions of the total interface component, grain boundaries and triple junctions, as a function of grain size, assuming a grain boundary width of 1nm [99].

Owing to their extremely fine grain size, nanocrystalline materials are believed to plastically deform via mechanisms that are fundamentally different from those present in their chemically
Introduction

similar coarse-grained counterparts. While there remains considerable debate as to the predominant deformation mechanisms along with when, how and why they carry plastic flow, there is general consensus that at some grain size, dislocation activity should become comparatively less important than other deformation mechanisms mediated by grain boundaries. In other words, there exists a transition from intracrystalline dislocation-based to grain boundary-mediated deformation mechanisms with decreasing grain size. As described by Koch, “At the smallest grain sizes (~10nm) it is believed dislocation activity ceases. At these small grain sizes the dislocation image forces are sufficient to eliminate dislocations by moving them into the grain boundaries. In addition, dislocation multiplication mechanisms such as the Frank-Read source would require stresses of the order of the theoretical strength. It is predicated therefore that dislocations are absent in the smallest nanocrystals and deformation must involve [mechanisms] other than conventional dislocation creation and motion.” [97]

A detailed review of active nanocrystalline material plastic deformation mechanisms is provided in Appendix A. The synopsis of this review is as follows. At the smallest grain sizes (~10nm), there are numerous possible grain boundary-mediated mechanisms that could contribute to plastic flow in nanocrystalline materials, including grain boundary sliding, grain boundary / triple junction diffusional creep, and grain rotation. While the discussion of which ones predominate and why is still a matter of intense study [e.g. 100-104], the overall consensus is that grain boundary processes such as these are indeed dominant below approximately 10nm [49]. Moreover, it may be possible that many or all of the aforementioned deformation mechanisms are operative to some extent in nanostructured metals of the finest grain sizes below ~10nm [105]. Finally, the absence of traditional intracrystalline dislocation activity in lieu of
such grain boundary-mediated deformation mechanisms in such materials likely also underpins the “inverse Hall-Petch” effect illustrated in Figure 1-6.

In the “intermediate” nanocrystalline grain size range above approximately 10nm and below 100nm, it is likely that there exists competition between conventional lattice dislocation slip and diffusional deformation, with the relative contributions of these deformation modes being dependent upon the distribution of grain sizes. This competition is illustrated schematically in Figure 1-8(a). In addition, given that crystalline materials exhibit a distribution of grain sizes, it is likely that in a given nanocrystalline material, the larger grains may exhibit dislocation slip while the smallest crystals plastically deform by grain boundary-mediated mechanisms as discussed earlier [106]. This is illustrated schematically in Figure 1-8(b). How these dislocations are generated, propagated, interact with each other (if at all) and become annihilated (if at all) is currently being debated [e.g. 58,90,96,107-116].
Figure 1-8 Competition between deformation mechanisms in nanocrystalline materials (schematically). (a) Framework for the grain size dependence of dislocation activity and grain boundary-mediated contributions to nanocrystalline materials, after [117] (b) Lattice dislocation slip and diffusional deformation modes occur in large grains (with dislocation signs) and small (shaded) grains, respectively [106].

1.3.3 Hardness-Strength Relationships
As described in Section 1.1, the synthesis of bulk quantities of nanomaterials represents a persistent challenge to researchers. An unfortunate side effect of this inability to produce large specimens is the reliance on hardness indentation as a means to measure the strength of nanocrystalline materials. Hardness testing involves indentation of a test material by a rigid indenter and is therefore a measure of the test material’s resistance to localized plastic
Introduction

deformation. Indentation is typically performed using a standardized indenter geometry and the projected area of indentation is used to calculate a hardness value for the test material:

\[ H = \frac{F}{A} \]  

(1-4)

where \( F \) is the applied force and \( A \) is the resultant projected area of indentation. Of the various types of tests available for hardness measurements of materials, the most commonly used are the Brinell, Vickers, and Rockwell hardness tests which correspond to different indenter shapes and loading conditions.

When a hard indenter is pressed onto the surface of a test specimen, the deformation of the surface is at first elastic and the stresses are given by the Hertzian relationships that describe the elastic interaction of a rigid body with a planar surface [118]. Timoshenko evaluated the onset of plasticity in such a configuration and calculated that the material below the indenter first begins to yield when the measured hardness (for a spherical indenter) reaches a value of approximately \( 1.1\sigma_Y \) where \( \sigma_Y \) is the yield strength of the test material as measured by uniaxial tensile testing [119]. At this early stage, the region of plasticity is very small and the permanent deformation of the test specimen is also very small.

As the load is increased, the region of plasticity grows until it spans the entire domain below the indenter. The resistance to plastic flow under indentation conditions exceeds that measured by uniaxial tensile testing because the plastic zone underneath the indenter is confined within a larger volume of the material which is effectively rigid. In other words, the plastic deformation under the indenter is constrained unlike uniaxial tensile tests. The factor by which the resistance to plastic flow under indentation conditions (i.e. hardness) exceeds the uniaxial flow stress value
is known as the constraint factor [120]. As described by Cottrell [121], this behaviour may be rationalized by consideration of the slip lines along which plastic sliding occurs in the indented material. In particular, as the indenter sinks into the test material, the slip lines must curve to reach the nearest free surface, causing them to lengthen. The test material’s resistance to plasticity is proportional to the length of this slip path, hence the constraint factor. Tabor [122] was the first to point out that the following relationship holds true for metallic materials exhibiting ideally plastic behaviour i.e. materials that do not work harden:

\[ H = 3 \cdot \sigma_y \]  

(1-5)

This experimental observation of a constraint factor of 3 for ideally plastic materials has been substantiated by theoretical analyses of plastic flow based upon the slip line field method for spherical indenters [123,124], for conical indenters [125], and the Vickers pyramidal indenter [126].

Tabor also pointed out that, for the case of work hardenable materials, the process of indentation itself strengthens the material and so Equation (1-5) should be replaced by a relationship of the following form:

\[ H = 3 \cdot \sigma_o \]  

(1-6)

where \( \sigma_o \) represents the uniaxial flow stress at some representative strain value e.g. between 8 and 10% for a Vickers indenter geometry [122]. Consequently, most of the relationships in common use for conventional engineering materials (i.e. materials that work harden) relate hardness to ultimate tensile strength, \( \sigma_{UTS} \), rather than tensile yield strength as used in Equation (1-5). An analysis of ASM handbook [127] hardness and ultimate tensile strength data for a
Introduction

broad range of steels shows that, over a wide range of strengths, there is a fairly good relationship of the following form:

\[ H_V \approx 3 \cdot \sigma_{UTS} \quad \text{(1-7)} \]

where \( H_V \) is the Vickers hardness.

On the other hand, as it pertains specifically to nanocrystalline materials, both experimental studies [e.g. 128-131] and modeling efforts [e.g. 96,132-136] have made extensive use of Equation (1-5), however generally without giving any specific reasoning or references to substantiate this claim. One particular modeling study [137] applied, without any justification, the following relationship when converting previously published hardness values to yield strength data:

\[ H \approx \sigma_y \quad \text{(1-8)} \]

In view of i) the lack of any clear hardness-tensile strength relationships for nanomaterials and ii) the apparent contradiction between the established relationship (1-7) for coarse-grained polycrystalline materials and the wide-spread application of Equation (1-5) for nanomaterials, the goal of Chapter 5 of the present thesis is to present an analysis of hardness - tensile data relationships for a large number of electrodeposited nanocrystalline materials.

1.3.4 Ductility

The natural consequence of the saturation of plastic deformation processes is fracture. Thus, the achievable ductility of a material is an important scientific topic because it demarcates the capacity of the active plastic deformation mechanism(s) to support plastic flow. In Figure 1-9(a), % elongation to fracture in tension has been plotted as a function of grain size for a number of
Introduction

different nanocrystalline metals and alloys synthesized using a wide variety of synthesis methods such as Inert Gas Condensation (IGC), Equal Channel Angular Pressing (ECAP), mechanical milling, and electrodeposition [138]. None of the measurements were carried out in conformance with ASTM E8 and many of these materials exhibit approximately 50% elongation-to-fracture in conventional coarse-grained form. The resultant tensile elongation values of materials with grain size values below 30nm is in line with those exhibited by intrinsically brittle materials, with most exhibiting ductility values in the range of 2-3% [139]. It is not known how much elongation these materials would have exhibited had they been tested according to the ASTM E8 standardized procedure. There is also a great deal of variability in the Figure 1-9(a) data, making it difficult to infer whether grain refinement into the nanocrystalline regime is, in and of itself, the cause of the observations of significantly depressed ductility.

Even for the subset of nanocrystalline Ni-based materials produced using a single processing method, namely electrodeposition, the data scatter is immense with some samples having exhibited greater than 12% elongation-to-fracture in tension while others have exhibited less than 1%, see Figure 1-9(b) [140]. Furthermore, while the measured tensile elongation-to-failure values were oftentimes low, the associated tensile test fracture surfaces generally exhibited dimpling indicative of ductile material flow [13,141-143]. Some have deemed the concurrent observation of fracture surface dimpling (indicative of plasticity) and <1% total macroscopic elongation-to-fracture (indicative of very little plasticity) a “paradox” in the study of the mechanical behaviour of nanocrystalline materials [144,145].
Introduction

This confusion concerning the achievable ductility of nanocrystalline materials stems from the convolution of a number of key factors that contribute to the elongation-to-fracture measured in a tensile test, most notably:

1. Intrinsic material capacity for plastic deformation
2. Specimen geometry effects
3. Processing artifacts

Figure 1-9 Elongation-to-fracture data for (a) a variety of metals and alloys produced using a range of synthesis methods [138], and (b) electrodeposited Ni-based materials (figure taken from ref [140]).
Introduction

It is therefore an important objective of this work to either eliminate or hold the *extrinsic* variables of specimen geometry and processing flaw effects constant in the interest of elucidating the *intrinsic* ductility of nanocrystalline materials. The results of that work are contained in Chapter 4. Beforehand, the goal of section 1.3.4 is to review the current status of nanocrystalline material ductility with particular emphasis on the influence of the three ductility limiting factors listed above.

1.3.4.1 Strain Hardening Capacity

In conventional coarse-grained metallic materials, dislocation processes are the dominant carriers of plastic deformation. Shear stresses acting parallel to the slip plane cause dislocations to move through the lattice. As dislocations travel, they may encounter obstacles such as solute atoms, particles, other dislocations, or grain boundaries, effectively impeding their motion until the local stress is high enough to allow the dislocations to overcome the obstacles. With continued deformation, the dislocation density increases due to dislocation multiplication and/or the formation of new dislocations. With this increasing dislocation density, the distance between them decreases, they encounter each other more often, and it becomes increasingly difficult to deform the material (as per Equation (1-2)). This process is known as strain or work hardening.

Hollomon’s equation is most commonly used to depict the strain hardening phenomenon. The Hollomon relationship describes strain hardening as a power law function of true stress and strain after yielding:

$$ \sigma = K \varepsilon^n $$  

(1-9)
where $\sigma$ and $\varepsilon$ are true stress and strain, $n$ is the strain hardening exponent, and $K$ is the strength coefficient. $n$ is the measure of the ability of a material to strain harden: the larger its magnitude, the greater the strain hardening for a given plastic strain. ASTM has provided a standard test method (ASTM E646) for the measurement of the strain hardening exponent $n$ from tensile engineering stress-strain data [146].

During the process of plastically deforming a typical metallic tensile specimen, strain hardening takes place within the material. Concurrently, the gauge cross-sectional area shrinks as the sample is plastically deformed and the specimen is therefore able to sustain less applied force. This drop in load bearing capacity due to localized thinning and deformation of the specimen is known as *geometrical softening*. Thus, as their names imply, there exists a competition between strain hardening and geometrical softening as the material is plastically deformed. When the strain hardening capacity of the material has been saturated, geometrical softening may become predominate, and plastic flow localization / mechanical instability may occur. In tensile testing, this takes the form of necking in the gauge section of the specimen. Therefore, in order to increase the ductility of the material in question, a common strategy is to promote strain hardening mechanisms since these effectively counteract geometrical softening. In such a fashion, the onset of tensile instability or necking is delayed as long as possible.

Unfortunately, owing to their small grain size, nanocrystalline materials are believed to possess little capacity for intracrystalline dislocation interaction which is the traditional basis of strain hardening in polycrystalline metallic materials. The creation of improved strain hardening capacity as a means to discourage flow localization in nanocrystalline materials has therefore
Introduction

received considerable attention because it offers the potential to achieve an optimum balance between high strength and good ductility in these materials [e.g. 138]. To this end, the two most notable strategies that have been employed to date are a) bimodal grain size distributions, and b) nanotwinning.

A schematic illustration of the bimodal structure is provided in Figure 1-10(a) [147]. In principle, if a broad grain size distribution can be synthesized, then it may be possible for the large grains to provide the strain hardening (related to lattice dislocation accumulation) required for good ductility while the nanocrystalline matrix contributes high strength and hardness. In 2002, Wang et al. demonstrated this strategy for Cu that was prepared by rolling at liquid nitrogen temperatures, see curve E in Figure 1-10(b) [148]. The optimal properties (curve E) were obtained for a material with 1-3µm diameter grains embedded within a matrix of nano- and submicron-sized grains. The ductility was comparable to that of annealed Cu but the yield strength was almost seven times higher (curve A in Figure 1-10(b)).
Introduction

Figure 1-10 (a) Deformation and fracture processes in a specimen with a bimodal structure [147], (b) engineering stress–strain curves for pure Cu. Curve A, annealed, coarse grained Cu; B, room temperature rolling to 95% cold work (CW); C, liquid-nitrogen temperature rolling to 93% CW; D, 93% CW + 180°C/3 min; and E, 93% CW +200°C/3 min. Note the coexisting high strength and large uniform plastic strain as well as large overall percentage elongation to failure for curve E (bimodal structure) [148]; (c) Tensile curves of extruded nanocrystalline Al–7.5Mg samples with varying concentrations of blended coarse-grained powder to create a bimodal structure [149].

Lavernia’s group has made numerous important contributions in the synthesis and characterization of bimodal materials prepared by cryomilling followed by powder compaction by hot isostatic pressing and extrusion [15,149,150]. For example, Figure 1-10(c) contains tensile data recorded from cryomilled nanocrystalline Al-7.5%Mg (Al 5083) powder blended with 15% and 30% of unmilled coarse-grained powder [149]. The addition of larger grains (in
Introduction

the form of unmilled powder) to the nanocrystalline matrix increased the ductility from approximately 1.4% to 5.4% elongation while maintaining a strength value approximately four times higher than conventional Al 5083.

Another technique that may be used to optimize strength and ductility is the formation of nanotwins, this method having been developed by K. Lu and co-workers [19]. The concept relies on the fact that twin boundaries impart material strengthening in a fashion similar to conventional high-angle grain boundaries, namely by blocking dislocation motion. However, unlike conventional nanocrystalline materials, decreasing the twin lamellae thickness also results in an increase in work hardening capacity. Apparently the mechanism for this increased work hardening capacity with increased twin density is that the twin boundaries act as locations for dislocation accumulation [19,151]. Thus, the structure can be both strong and ductile. Lu and co-workers have demonstrated that Cu with a grain size of 400-500nm and twin lamellae thicknesses in the range of 20-100nm provide adequate barriers to dislocation motion for strengthening while creating local sites for nucleating and accommodating dislocations, thereby elevating ductility and work hardening [19]. Characterization data from this structure is provided in Figure 1-11.
Introduction

Figure 1-11 (top) Transmission electron microscopy (TEM) observations of the typical microstructure in an as-deposited nanotwinned Cu sample. A bright field TEM image (A) and the electron diffraction pattern (inset in (A)) show roughly equiaxed submicron-sized grains with random orientations separated by high angle grain boundaries; (bottom) a typical tensile stress-strain curve for the Cu sample with nano-twins in comparison with that for a coarse-grained polycrystalline Cu (average grain size >100 µm) and a nanocrystalline Cu sample (mean grain size ~ 30 nm) [19].

Hence, enhanced strain hardening represents a powerful tool with which the onset of mechanical instability in tension may be delayed. Such work requires modification of the microstructure of the material, which is beyond the scope of the present study. Rather, this study was focused primarily on the effects of processing artifacts and specimen geometry on achievable ductility in nanomaterials possessing fairly narrow grain size distributions, these factors having been largely overlooked in the field.
1.3.4.2 Specimen Geometry Effects

In engineering design, the stimuli imposed upon a particular system of interest are typically mechanical forces, electric fields, temperature gradients, and so on. The responses they cause are deformations, electric charges, amounts of heat, etc. In all of these interactions, there appears a material property that affects the magnitude of the response: modulus of elasticity, dielectric constant, thermal conductivity, etc. Ideally, the material property is defined in such a way as to be independent of the shape and dimensions of the sample used for their determination. In such a way, it depends only upon the nature of the material itself. This allows the component designer to make materials selection decisions without upsetting all the other factors in the design process.

Similarly, the extent to which a material is capable of plastically deforming before fracture is an important feature for consideration in the design of load-bearing structures, such as those in which high material strength may be exploited, for instance. Unfortunately however, unlike modulus of elasticity or thermal conductivity, the ductility of a material cannot be quantitatively expressed independent of specimen shape and size. In other words, it is dependent both upon the “intrinsic ductility” of the material itself and the dimensions of the sample used to make the measurement. As a result, the utility of tensile percentage elongation at fracture as a quantitative measure of material ductility has been a matter of some debate for over 100 years, yet it nevertheless remains the most commonly used method to evaluate this important material characteristic [127].

In a tensile test of a typical metallic material, the overall measured tensile extension consists of contributions from elastic strain, uniform plastic strain up to the onset of necking (located at the
point on the stress-strain curve commonly known as the “ultimate tensile stress”, point $M$ in Figure 1-12), and the localized or non-uniform plastic strain after the onset of necking until final fracture (strain between points $M$ and $F$ in Figure 1-12).

![Figure 1-12](image.png)

**Figure 1-12** Typical engineering stress-strain behaviour to fracture, point $F$. The “ultimate tensile strength” is indicated at point $M$. The circular insets represent the geometry of the deformed specimen at various points along the curve [61].

As discussed in section 1.3.4.1, the extent of uniform elongation that is achievable is dictated primarily by the work hardening capacity of the material. However, the measured elongation-to-fracture also typically includes a contribution from non-uniform strain arising from localized deformation of the specimen after the onset of necking. In particular, there is a strong dependency of achievable post-uniform linear strain on sample size and shape because these geometrical factors play a key role in the process of neck formation during tensile extension. In general, for metallic specimens of similar geometry in terms of dimensional proportionality (ratios of specimen width to length to thickness and so on), the larger the specimen gauge cross-sectional area, the more necking the sample is able to sustain before fracture. Hence, a sample
Introduction

with a larger cross-sectional gauge area will exhibit greater post-uniform elongation in tensile extension than an otherwise identical, geometrically similar sample with a smaller area because of the ability of the larger sample to form a better developed neck. The effect of gauge area on tensile ductility can be described by the Unwin equation, also known as Barba’s Law [127]:

\[ \varepsilon_f = \frac{B \sqrt{A_o}}{L_o} + \varepsilon_u \]  \hspace{1cm} (1-10)

where \( \varepsilon_f \) is the total elongation to fracture, \( \varepsilon_u \) is the uniform elongation, \( A_o \) is the initial gauge cross-sectional area, \( L_o \) is the initial gauge length, and \( B \) is a constant. The importance of proper consideration for the ratio \( A_o^{1/2}/L_o \) when tensile elongation measurements from different test series are compared may be readily appreciated by inspection of Equation (1-10).

In addition to its size, the shape of the specimen also plays an important role in the process of neck development. For example, necking in cylindrical tensile specimens is typically symmetrical around the tensile axis. However, a different type of necking behaviour may be found for a tensile specimen with rectangular cross-section. In such a configuration, materials with a large capacity for strain hardening typically exhibit diffuse necking, labeled as such because the necking development is gradual and diffused over a relatively large zone of the sample (see Figure 1-13). This is analogous to neck formation in a cylindrical test sample. The condition of instability leading to diffuse necking is known as the Considère criterion which may be expressed as:

\[ \frac{d\sigma}{d\varepsilon} = \sigma \]  \hspace{1cm} (1-11)
where $d\sigma/d\epsilon$ is the true hardening rate and $\sigma$ is the corresponding true stress. This relationship applies to scenarios where diffuse necking is the predominant mode of non-uniform plastic elongation [152].

![Illustration of diffuse necking and localized necking in a sheet tensile specimen](image)

**Figure 1-13** Illustration of diffuse necking and localized necking in a sheet tensile specimen [152].

In specimens of rectangular cross-section, diffuse necking may end in fracture but is oftentimes followed by localized necking. In this mode, the neck becomes localized over a very small zone of length of the order of the specimen thickness (Figure 1-13). In localized necking there is no change in width measured along the trough of the localized neck, so that localized necking corresponds to a state of plane strain deformation in the trough [152]. The corresponding Considère relationship for the onset of localized necking instability is as follows:

$$\frac{d\sigma}{d\epsilon} = \frac{\sigma}{2}$$

(1-12)

Inspection of Equations (1-11) and (1-12) reveals that the condition for the onset of diffuse necking occurs at a hardening rate value of $\sigma$ whereas the onset of localized necking instability occurs at a hardening rate value of $\sigma/2$. In localized necking, the specimen area decreases less rapidly than in diffuse necking. Thus, during localized necking, more strain may be accumulated before the geometrical softening will cancel the strain hardening.
Introduction

Furthermore, in materials with little strain hardening capacity (e.g. cold rolled strip) the condition of instability, and hence the strain at both diffuse and localized necking, may both approach zero strain. Specimens of rectangular cross-section cut from material with little strain hardening capacity may therefore exhibit a distinct localized necking mode before fracture.

Another prominent feature of localized necking is the oblique fracture angle of approximately 55° relative to the loading axis. The tendency for wide bars of strain hardened metals to fracture in this manner was first recognized by Koerber and Siebel in 1928 [153], and Bijlaard subsequently provided a first principles calculation of the 55° angle based upon principal stresses [154]. Further commentary on the plastic instability of wide flat tensile specimens and the 55° angle may be found in [155,156]. Figure 1-14 contains photographs of cold rolled Al and steel sheet illustrating the predominant localized necking mode and oblique 55° fracture.

![Photographs of the gauge sections of fractured tensile test coupons from (a) cold rolled steel [155], and (b) cold rolled Al [157], illustrating localized necking and the 55° fracture angle.](image)

**Figure 1-14** Photographs of the gauge sections of fractured tensile test coupons from (a) cold rolled steel [155], and (b) cold rolled Al [157], illustrating localized necking and the 55° fracture angle.
Introduction

To address the ductility sensitivity to sample geometry, materials scientists and engineers have established standardized protocols for the measurement of ductility wherein mechanical test specimen dimensions are prescribed for common use. In this manner, ductility data from one material may be systematically recorded and compared to data gathered from another material. One widely used test specification is ASTM E8 [11], which provides a guideline for the tension test, the most commonly accepted method of measuring ductility. Unfortunately, the ASTM standard test geometries are much larger and thicker than the thin sheets or small coupons of feedstock nanocrystalline materials that have been synthesized by or made available to most researchers in the field. For illustrative purposes, Figure 1-15 contains schematic drawings of some of the tensile sample geometries found in the electrodeposited nanomaterials literature alongside the ASTM standard subsize tensile coupon geometry [11] and that used in the current study. Interestingly, the smallest sample geometry in Figure 1-15, of 3mm in total length, was heavily used in one of the most cited papers on the topic, namely the work of Dalla Torre et al. [13]. See Figure 1-2(b) for a photograph of these specimens. Upon examination of Figure 1-15 in conjunction with Equation (1-10), it may be readily appreciated that ductility measurements recorded using miniature samples may be unsuitable for comparison to those of other well-known engineering metallic materials characterized in conformance with the standard ASTM specification. On the other hand, note that the gauge section of the specimens for the current study is identical to that of ASTM E8, the only notable difference being the tab width which was widened to provide increased gripping area after slipping problems owing to the extremely high material strength were experienced. The sensitivity of electrodeposited nanocrystalline material ductility to specimen geometry is explored in Chapter 4.
In addition to the effects of specimen geometry, the situation is further complicated by our lack of understanding of the influence of processing artifacts on nanostructured material ductility. Processing artifacts play an important role because the linear extension that may be sustained by a typical mechanical test specimen loaded in tension is not a deterministic material-specific property but instead reflects both an intrinsic material ductility and a concentration of flaws present in the material in addition to specimen size and shape dependencies discussed earlier. As first pointed out by Edelson and Baldwin in 1962 [159] and illustrated in Figure 1-16, tensile strain-to-fracture of a metallic material may be highly sensitive to the volume fraction of second phase particles present in the material. This behaviour originates from the observation that second phase particles act as initiation sites for damage. While the specific mechanisms of
Introduction

damage formation are also influenced by particle size, shape, and particle-matrix interfacial strength, Edelson and Baldwin demonstrated that the influence of these factors (for the Cu-based materials they studied) was relatively minor compared to the role played by particle volume fraction [159].

Figure 1-16 Tensile ductility (as measured by reduction in area) of a variety of dual-phase copper alloys as a function of second phase volume fraction [159].

To a large extent, past attempts to obtain a broader picture of the intrinsic ductility of nanocrystalline materials have been unsatisfactory largely because the process-related material characteristics (e.g. microstructural variability, porosity, impurities, processing artifacts) have not been rigorously accounted for in the rationalization of the observed response to deformation.

The tensile elongation to fracture of a number of nanocrystalline materials from the literature has been plotted in Figure 1-17, with the data separated by “one step” vs. “two step” material
Introduction

synthesis processes [139]. The material synthesis techniques based upon severe plastic deformation (SPD) e.g. equal channel angular pressing (ECAP), and high pressure torsion (HPT) are typical “one step” processes while methodologies wherein the nanocrystals are formed and subsequently consolidated comprise the “two step” class e.g. inert gas condensation (IGC). A value of 5% elongation, often used by structural engineers, is used to separate “ductile” from “brittle” behaviour [139]. 13 of the “one step” data points correspond to electrodeposited nanocrystalline Ni, although it should be noted that these were all thin foils of less than 0.25mm thickness. While the two-step processes are capable of producing extremely fine-grained (<30nm) structures, the majority are unable to exceed the 5% engineering ductility threshold. The materials processed via single step synthesis techniques exhibit greater ductility, although the overall variability is enormous.

![Graph](https://via.placeholder.com/150)

**Figure 1-17** Elongation-to-fracture data for metals and alloys produced using a variety of one-step and two-step processing methods, data from [139].
On the other hand, there are some indications that elongation-to-fracture values in excess of 5% can be achieved with flaw-free nanocrystalline materials. For example, Figure 1-18 contains tensile data from a 23nm grain size nanocrystalline Cu sample synthesized by ball milling followed by *in situ* consolidation [138]. In this case, the optimization of both strength and ductility was attributed to a lack of processing artifacts and the ability of the sample to exhibit significant strain hardening. The authors attributed the observed strain hardening to dislocation accumulation and storage [160]. The processing artifact content was not quantified.

![Figure 1-18](image)

**Figure 1-18** Tensile curves obtained for ball milled nanocrystalline Cu and coarse-grained Cu at a strain rate of $10^{-3}$ s$^{-1}$ [138].

Another example of combined high strength and good ductility was for 12nm grain size electrodeposited nanocrystalline Co [161]. As seen in Figure 1-19, the hexagonal close-packed nanocrystalline Co exhibited 6-9% elongation-to-fracture in tension, which was roughly comparable to conventional coarse-grained Co. Of particular interest is the observation of increased strain rate sensitivity of the nanocrystalline specimens, which the authors attributed to twinning being the dominant deformation mechanism in this material.
Observations such as those in Figures 1-17 through 1-19 have led Koch to conclude that, “minimization or elimination of processing artifacts is the key to revealing the inherent mechanical properties of nanocrystalline materials and potentially optimizing high strength and good ductility” [97]. This was also one of the main conclusions drawn by Ma in his series of papers directed towards improving the ductility of bulk nanostructured materials. In particular, “the paramount requirement, or the foremost strategy [to achieve enhanced ductility], is…to strive for truly flaw-free materials” [53]. Hence, any attempt to optimize the ductility of these high strength materials must necessarily address the elimination of processing artifacts. This synthesis challenge is the focus of Chapter 3 and its impact on ductility is discussed in Chapter 4.
Introduction

1.3.4.4 Closing Remarks on Nanocrystalline Material Ductility

In conclusion, it may be readily appreciated that, in addition to specimen geometry effects, the fact that nanocrystalline materials can be created using a wide variety of fundamentally dissimilar processing techniques that result in tremendously varying microstructures and processing artifacts has hindered the development of our understanding of the intrinsic ductility of this important material class. A strong emphasis has been placed on improving ductility by structural control (bimodal structures, twin formation, etc) whereas relatively little headway has been made in eliminating processing artifacts, arguably a more critical contributor. In addition, while plastic flow instability is influenced by microstructure (competition between strain hardening and geometric softening), it is also sensitive to specimen geometry (as will be demonstrated in Chapter 4). Again, this has received little attention in the community. Therefore, as it relates to material ductility, a focused study to elucidate the effects of electroforming processing artifacts and specimen geometry on nanocrystalline material ductility is required. It is therefore an important objective of this work to produce a very large number of bulk samples synthesized from a gross artifact-reduced, steady state electroforming process, test them in conformance with ASTM E8, and then quantify the distributional variability in intrinsic ductility of the materials using Weibull distributional analysis.
1.4 Research Objectives

Objective #1
As described in Section 1.3, a great deal of work has been devoted to the study of nanocrystalline materials and their mechanical properties. However, some of the most important mechanical properties (most notably ductility and elastic modulus) are known to be highly sensitive to the presence of processing artifacts. It is therefore the first objective of this work to *synthesize artifact-reduced nanocrystalline materials*. This is addressed in Chapter 3.

Objective #2
An inability to produce bulk quantities of nanocrystalline materials has prevented tensile testing according to standardized test protocols such as ASTM E8. The persistent use of non-standardized specimen geometries has resulted in considerable confusion concerning the intrinsic mechanical properties of nanocrystalline materials. It is therefore the second objective of this study to *synthesize bulk quantities of electroformed nanocrystalline materials suitable for testing in conformance with ASTM E8*. This work is also presented in Chapter 3.

Objective #3
With bulk quantities of artifact-reduced feedstock material in-hand, tensile testing in conformance with ASTM E8 was then performed. The specific focus of Chapter 4 is ductility, including an *examination of the influence of processing artifacts and specimen size and shape on the achievable tensile elongation of nanocrystalline materials*. 
Introduction

Objective #4

Because the linear extension that may be sustained by a typical mechanical test specimen loaded in tension is not a deterministic material-specific property but instead reflects a distribution (size and orientation) of flaws present in the material in addition to the intrinsic material ductility and specimen size and shape dependencies, a thorough analysis of nanocrystalline material ductility requires a statistically significant set of specimens. In particular, the fourth objective is the synthesis of a large number of samples to enable a statistical evaluation of achievable ductility by Weibull distributional analysis. This is presented in Chapter 4.

Objective #5

The inability to synthesize bulk quantities of nanocrystalline material has forced many researchers to rely on hardness indentation as a proxy for strength. Unfortunately, there has been little consensus concerning which hardness-strength relationships can or should be applied, and this has resulted in misleading information concerning the intrinsic strength of nanocrystalline materials. Hence, it is the objective of Chapter 5 to elucidate those conditions under which hardness may be reliably used to evaluate the strength of electrodeposited nanocrystalline materials.
1.5 References

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Introduction

Introduction


Introduction

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Introduction


Chapter 2
Materials Characterization Methods

2.1 Introduction

A detailed description of the synthesis conditions used to fabricate the materials of the current study follows in Chapter 3, while Chapters 4 and 5 present the outcomes of subsequent mechanical tests that were performed on the resultant specimens. As a preface to those discussions, this chapter describes the tools and techniques that were used to derive the structural, chemical, and mechanical property characterization data.

2.2 Chemical and Structural Characterization

2.2.1 Chemical Composition

In the case of alloy deposits, the chemical composition was measured using an energy dispersive X-ray spectroscopy (EDS) system attached to a JEOL JSM-840 scanning electron microscope (SEM). The EDS system was an e2v Scientific Instruments model Sirius 10/UTW. All data presented in this study regarding compositional analysis using the SEM / EDS was an average of at least five readings.

2.2.2 X-ray Diffraction (XRD)

X-Ray Diffraction (XRD) patterns were collected with a Rigaku Miniflex diffractometer using Co-Kα (λ = 0.179 nm) radiation. XRD was used primarily to identify the grain size and preferred crystallographic orientation of the electrodeposits. The theoretical peak positions and
relative intensities for the first five diffraction lines of a theoretical nickel control sample with random crystallographic orientation were calculated using the structure factor technique as per Cullity [1] and are presented in Table 2-1. This served as the randomly oriented benchmark for the current study.

Table 2-1 Theoretical peak positions and relative intensities for the first five diffraction lines of a theoretical nickel sample with random crystallographic orientation using Co-Kα radiation, \( \lambda = 0.179 \) nm, as per Cullity [1].

<table>
<thead>
<tr>
<th>hkl</th>
<th>( 2\Theta )</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>52.2°</td>
<td>100.0</td>
</tr>
<tr>
<td>(200)</td>
<td>61.1°</td>
<td>46.2</td>
</tr>
<tr>
<td>(220)</td>
<td>91.9°</td>
<td>26.8</td>
</tr>
<tr>
<td>(311)</td>
<td>114.8°</td>
<td>33.9</td>
</tr>
<tr>
<td>(222)</td>
<td>123.3°</td>
<td>10.5</td>
</tr>
</tbody>
</table>

In addition to preferred crystallographic orientation, XRD is a useful tool that is commonly used for grain size measurement in nanocrystalline materials. Through measurement of the diffraction peak width, the average grain size may be estimated using the Scherrer formula:

\[
d = \frac{0.9\lambda}{B \cos \Theta_B}
\]  

(2-1)

where \( d \) is the average grain diameter of the material (Å), \( \lambda \) is the wavelength of the radiation used (Å), \( B \) is the true broadening (radians), \( \Theta_B \) is the Bragg angle (degrees), and

\[
B^2 = B_M^2 - B_S^2
\]  

(2-2)

where \( B_M \) is the measured broadening (radians) and \( B_S \) is the standard (intrinsic) broadening due to equipment used [1]. Peak broadening is measured as Full Width at Half Maximum (FWHM) in radians. The true broadening, \( B \), is dependent upon the equipment used, and is typically
corrected by first measuring a standard peak width, $B_S$. In most cases, a structurally similar (i.e. Ni) large-grained powder is used for this purpose, as was the case for the current study.

### 2.2.3 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) allows one to make direct measurements of the grain size and other relevant microstructural features. However, due to the large number of samples synthesized as part of the current study, TEM was not possible for every electrodeposit. Instead, representative samples were selected and TEM characterization performed. TEM foils were obtained by mechanically grinding bulk nanocrystalline material coupons down to a thickness of approximately 100$\mu$m. 3mm diameter discs were then mechanically punched from the foil and electropolished using a Struers TenuPol-5 twin-jet electropolisher. The electrolyte consisted of 90% methanol and 10% perchloric acid held at a temperature of -40°C to -50°C. Electropolishing was carried out at 15V and 74-95mA for a duration of 75 seconds. A Philips CM12- LaB6 TEM with an operating accelerating voltage of 200kV was then used to obtain bright field and dark field images as well as diffraction patterns.

### 2.2.4 Electrodeposit Internal Stress

The electrodeposit internal stress measurements were made using the copper strip technique that is commonly employed in industrial electroplating (see Figure 2-1 [2]). The specific apparatus used was the SM683 Stress Analyzer Scale and SM223 Stress Analyzer Strips from Larry King Corporation, a supplier of electrodeposition equipment. The measurements were performed before and after each electroforming run, and the average of the two calculated internal stress values was taken as an estimate of the internal stress value of the electroformed specimen.
synthesized chronologically between. In other words, the internal stress values presented for each nanocrystalline specimen are not direct measurements made of the specimen itself, but are instead the average of the two witness samples carried out immediately before and after the specimen of interest. The electroplating / electroforming convention for the directionality of internal stress has been maintained, with “tensile” stress referring to the propensity for each layer of the growing electrodeposit to cause progressive macroscopic plate contraction – see Figure 2-1(b).

Figure 2-1 Side view schematic of the internal stress measurement apparatus showing the initially flat Cu foil strip onto which the material in question is electrodeposited (shown as the curved black line) clamped by a screw at the top of the fixture and permitted to bend naturally. When the electrodeposited coating exhibits tensile residual stress, the direction of deflection is opposite the case when the electrodeposit stress is compressive in nature (both cases are shown in the figure). The amount of deflection of the bottom edge of the foil is measured using a graduated scale at the bottom of the apparatus, with this scale having been calibrated by the manufacturer in such a way that a value for the electrodeposited coating residual stress level may be calculated [2].
2.3 Mechanical Testing

2.3.1 Tensile Testing

Based upon practical limitations regarding tank size, 152mm x 152 mm Ti cathode plates were used as the temporary substrates for the electroformed nanocrystalline materials produced for this study. Each 152mm x 152mm electroformed plate was large enough to yield six individual tensile coupons. In some cases all six samples were tested, while in the majority of cases only three specimens from each plate were pulled. All tensile coupons produced for this study were cut using Electrical Discharge Machining (EDM) with a constant machining template. In other words, the areal shape of all the tensile specimens produced for this study was identical with a 125mm overall length, 25mm gauge length, 6mm gauge width, 35mm grip section length and 20mm grip section width. This geometry was based upon the ASTM standard E8/E8M-09 subsize specimen geometry [3] with the only notable deviation from the standard being the grip section geometry. The grip section width dimension was increased from 10 to 20mm and the grip length was increased from 30 to 35mm as a means to prevent slippage in the sample grips; owing to the relatively high hardness and strength of the materials studied, it was found that an increased grip section area was essential for proper specimen clamping. Specimen width and thickness dimensions were measured with an inside micrometer caliper with a resolution of 0.025 mm. Caliper calibration was periodically performed using a 25 mm reference gauge bar. The micrometer zero was reset at the start of each measurement session. The machined edges of the samples were not polished after cutting, and the free surfaces of all samples were kept in the as-deposited surface condition. 2D surface roughness measurements across an 8mm scan length on the outer surface of a typical 1mm-thick plate revealed an arithmetic average of the absolute
values ($R_a$) of approximately 1 micron. See Figure 2-2 for a photograph of typical specimens before and after tensile testing.

![Figure 2-2](image)

**Figure 2-2** Photograph of typical specimens (Ni-6.4wt%Fe; 18nm average grain size) before and after tensile testing in conformance with ASTM E8 [3]. Scale in cm.

All tensile tests were performed at Engineering Materials Research Inc. (Toronto, Ontario) using a 67 kN capacity servo hydraulic load frame configured with a MTS controller. The load frame was calibrated annually using load standards traceable to United States National Institute of Standards and Technology (NIST). A pair of hydraulically actuated wedge grips was installed in the load frame to grip the specimen.

Tensile tests were conducted using displacement control and a ramp waveform at a rate of approx. 0.1 mm/min in lab air and 20-25°C. All tensile tests were carried out at a strain rate of $5 \times 10^{-4}$ s$^{-1}$ and were typically performed until the specimen fractured. Results were recorded by a computer data acquisition system. Prior to each test, the data acquisition system was calibrated using a voltmeter which was calibrated at approximately 1 year intervals. All samples were tested to fracture and the elongation to fracture, $\varepsilon_f$, was measured using both a calibrated extensometer and also by measurement of the gauge length before and after testing. An MTS
Model 632.11C-20 extensometer with a 25 mm gauge length and a maximum measuring range of 3.5 mm was used to measure specimen gauge length displacement. The extensometer was calibrated by following the ASTM Standard Practice for Verification and Classification of Extensometers and met the requirements of Class B-1 [4]. The extensometer was mounted at approximately the center of the specimen's gauge length.

Several methods have been used to determine the maximum uniform strain including the graphical method, the Considère criterion, and the point of peak load on the stress-strain curve [5]. In the case of the Considère criterion, different relationships are used depending on whether plastic instability occurs by diffuse necking \( (d\sigma/d\epsilon = \sigma) \) such as in the case of round bar, or by localized necking \( (d\sigma/d\epsilon = \sigma/2) \) such as in the case of thin flat sheet [6,7]. These two necking modes are illustrated in Figure 1-13. Many of the samples of the present study exhibited a mixed mode of necking failure. Consequently, the peak load method was used to designate the onset of plastic instability in order to determine the maximum uniform strain. The elastic component of the maximum uniform strain was assumed to be equivalent to the strain measured from the onset of loading until the 0.2% offset yield point [3] with elastic strain values typically falling within the range of 0.5 to 1%. The difference between the measured maximum uniform strain (at peak load) and the elastic strain term was then termed the maximum uniform plastic strain.

The strain hardening exponent was calculated using ASTM E646, “Standard Test Method for Tensile Strain-Hardening Exponents (n-Values) of Metallic Sheet Materials” [8]. This method involves fitting the plastic portion of the true stress-true strain curve to the power law relationship Equation (1-9). While this exercise may be performed over any portion of the
plastic flow curve, fitting of the present study was carried out from the 0.2% offset yield point until the onset of necking.

2.3.2 Vickers Microhardness

Hardness measurements were performed using the Vickers microhardness technique by measuring the averages of at least 10 indentations each at several locations on each electrodeposit. The applied loads were 50-200 g depending on the deposit thickness. In all cases, the sample thickness was at least 20 times the depth of individual indentations. Samples were mounted into epoxy before measurements were made in order to ensure proper specimen support and therefore provide accurate readings.

2.4 References

Chapter 3  
Materials Synthesis

3.1 Introduction

As described in Chapter 1, the characteristics of the nanostructured material synthesis method can play a major role in the observed response to subsequent mechanical deformation. This has made it difficult, and in many cases impossible, to de-convolute the effect(s) of nanocrystalline grain refinement from those originating from other concomitant structural characteristics such as porosity, particulate contamination, chemical contamination, secondary phases, internal stress, and other side effects of the technique used to create the nano-sized crystals. Therefore, one main objective of this study was the elimination or minimization of synthesis artifacts in the nanocrystalline material electrodeposition process.

The second objective of this study was to answer the question of whether it is possible to synthesize bulk quantities of electrodeposited nanocrystalline materials to enable tensile testing in conformance with ASTM E8 since, prior to this study, reproducible nanomaterial thick plate electroforming had not been possible. Thus, the main contributions of this chapter are the description of the issues associated with electrodeposition-based synthesis of bulk quantities of artifact-reduced nanocrystalline materials and how they were overcome.
3.2 Nomenclature

A few remarks on nomenclature are appropriate to begin. “Electrodeposition” refers to the electrochemical reduction of one or more dissolved metallic species from an electrically conductive electrolyte, as will be described in Section 3.3. “Electroplating” is the term most commonly used to describe industrial-scale electrodeposition processes, and refers specifically to the coating of a substrate with a layer of electrodeposited material. Generally, this layer is relatively thin (say, 1-50µm) and is used for superficial purposes e.g. 10µm layer of Zn as a galvanic corrosion protection coating on steel, 15µm of duplex Ni/Cr on steel for corrosion resistance, surface hardness, and aesthetic quality, 5µm Cu throughhole plating to electrically connect the laminates in a printed circuit board panel, and so on. In other words, “electroplating” refers to coating a substrate using an electrodeposition-based process.

On the other hand, it may be desirable to create structures comprised wholly of the electrodeposited material. In this case, one would electrodeposit for a much longer period of time in order to create a much thicker layer of material e.g. >200µm. The material would be electrodeposited onto a temporary substrate, and then subsequently removed for use. This process is commonly known as “electroforming” and may also be considered a subset of “electrodeposition”. For the present study, the objective is to evaluate the properties of the electrodeposited material itself without any influence of the substrate. Hence, all specimens discussed here have been “electroformed” onto temporary commercial grade pure Ti cathode substrates from which they were subsequently stripped to yield free-standing sheets to be cut into specimens for characterization and mechanical testing. The removal of the nanocrystalline plate was accomplished by lifting the nanocrystalline plate from the temporary Ti cathode substrate.
A schematic illustration of net-shape manufacturing of an electroformed Ni object is shown in Figure 3-1.

![Figure 3-1 Schematic diagram showing net-shape manufacturing of an electroformed product][1]

### 3.3 Electrodeposition – General Considerations

As mentioned, electrodeposition is the electrochemical reduction of one or more dissolved metallic species from an electrically conductive electrolyte. Most electroplating solutions are aqueous, although organic-based solutions are becoming increasingly prevalent for the electrodeposition of metals and alloys that are not easily reducible from water-based electrolytes e.g. aluminum. An electroplating apparatus in its most basic form is shown in Figure 3-2. The electrolyte is contained in a vessel such that it can be heated. Temperatures between room temperature and 90°C are typical for electroplating processes, depending on the desired metal reduction reaction. All the Ni-based specimens of the current study were electrodeposited from a solution held at 60°C. In addition to heating, the solution vessel contains the mechanism to agitate the solution, which is important for both temperature and chemical homogeneity within the plating cell, as well as to promote diffusion of the cationic species to the cathode surface.
Materials Synthesis

This function is carried out by a magnetic stirrer in the small-scale apparatus of Figure 3-2, while in large-scale industrial electroplating, air agitation and mechanical solution agitation through pumps contained either within or outside the vessel is more commonplace. Finally, the vessel must also be constructed from a material that is chemically resistant to the electrolyte.

**Figure 3-2** Schematic diagrams showing the experimental set-up for pulsed current plating [2].

The solution must be electrically conductive since the reduction of metal on the cathode surface is accomplished electrochemically. In the case of Ni reduction, the cathodic reaction is usually expressed as:

\[ \text{Ni}^{2+} + 2e^{-} \rightarrow \text{Ni} \]  \hspace{1cm} (3-1)

However, it is more likely that deposition involves the following reactions [3,4]:

\[ \text{Ni}^{2+} + \text{H}_2\text{O} \rightarrow \text{NiOH}^+ + \text{H}^+ , \]  \hspace{1cm} (3-2)

\[ \text{NiOH}^+ + e^- \rightarrow (\text{NiOH})_{\text{ads}} \]  \hspace{1cm} (3-3)

\[ (\text{NiOH})_{\text{ads}} + \text{H}^+ + e^- \rightarrow \text{Ni} + \text{H}_2\text{O} . \]  \hspace{1cm} (3-4)
Materials Synthesis

Current is supplied by an external power source (shown with an ammeter in series for the particular example shown in Figure 3-2) and the circuit is completed by the anode-cathode electrode couple immersed in the electrolyte. In principle, the negatively-polarized cathode may be any electrically conductive material that is chemically resistant to the plating solution, while the positively-charged anode may be either a non-consumable dimensionally stable anode such as Pt-clad Nb or a consumable anode that oxidizes as electrodeposition proceeds. For the current study, the predominant anode material was “R-rounds”, a form of pure Ni manufactured by INCO mainly for the specific application of plating anodes. INCO R-rounds are perhaps the most commonly used anode material in industrial Ni electroplating and electroforming. The R-rounds were held in a Ti basket as is conventional plating practice. As the electrodeposition process proceeds, metallic Ni from the R-rounds continuously oxidizes and enters the solution in cationic form, while any unoxidized Ni particulate is captured in a cloth anode bag that encapsulates the Ti basket. Electrodeposition using a dimensionally stable anode, on the other hand, requires the continuous external replenishment of the cationic species to be reduced. In the case of Ni electrodeposition, this may be accomplished by the addition of NiCO$_3$ dissolved in water, for instance. Electrodeposition using a dimensionally stable anode was not performed as part of the current study.
3.4 Electrodeposition for the Production of Fine-Grained Microstructures

It is possible to create materials across a very broad spectrum of microstructures using the electrodeposition synthesis method. Metals such as tin, lead and zinc may exhibit average grain size values on the order of 10µm or larger when deposited from an additive-free bath. On the other hand, metals from the iron-group (Ni, Fe, Co), some of the precious metals e.g. Au, Pt, Rh, and a number of others can be electrodeposited in nanocrystalline form through proper control of the chemical and electrical processing parameters [5,6]. In fact, with some systems, microstructural refinement through to the amorphous regime can be accomplished if so desired. A notable example includes electrolytic Ni-P deposition under conditions where the deposit chemical composition exceeds approximately 6wt%P [7]. Many Cr electrodeposits are also known to be amorphous. Cross-sectional images and accompanying schematics corresponding to a typical coarse-grained electrodeposit compared to a chemically similar nanocrystalline electrodeposit are shown in Figure 3-3. With increasing grain refinement, the crystal morphology typically transitions from columnar (e.g. Figure 3-3(a)) to fibrous (i.e. a finer, more narrow columnar grain shape) to equiaxed (e.g. Figure 3-3(b)). This grain shape transition from columnar to fibrous to equiaxed is a general trend for many electrodeposited materials such as Cu and Ni. In other words, through control of the material synthesis parameters, it is possible to achieve a Cu deposit, for instance, that exhibits a columnar morphology of 10µm average grain size, or through grain refinement, an equiaxed nanocrystalline one that exhibits microstructure orders of magnitude finer.
Figure 3-3 Schematic diagram and cross-sectional scanning electron micrograph of a coarse-grained electrodeposi((a) and (b)) compared to a nanocrystalline electrodeposi((c) and (d)) [2,8].

It is understood that the applied current density has two important effects on electrocrystallization, namely it increases the rate of metal ion reduction on the surface and reduces the critical crystal nucleation size by increasing the applied overpotential. The critical
crystal nucleation size, \( r_c \), is inversely proportional to overpotential, \( \eta \)/current density, \( I \), as shown by the Gibbs-Kelvin equation [9]:

\[
    r_c = \frac{2 \cdot \Phi \cdot M}{\rho \cdot z \cdot F \cdot \eta}
\]  \hspace{1cm} (3-5)

where \( \Phi \) is the interfacial tension of the metal/solution interface, \( M \) the molecular weight, \( \rho \) the density and \( z \cdot F \) the molar charge. The effect of overpotential/current density on the critical crystal size is shown schematically in Figure 3-4 in the form of free energy for nucleation versus crystal size [2]. It may be seen from Figure 3-4 that higher current density results in smaller crystal sizes.

**Figure 3-4** Effect of overpotential (\( \eta \)) / current density (\( I \)) on critical crystal nucleation size (\( r \)) [2].
In addition to current density effects, electrolyte additives can have a drastic effect on the surface diffusion behaviour of the adatom once it has deposited onto the cathode surface. In other words, bath additives designed to discourage adatoms from diffusing to “join” a pre-existing crystal on the deposit surface in lieu of nucleating a new crystal are powerful tools with which to influence the overall extent of microstructural refinement.

Unfortunately, the theoretical relationships between the input synthesis conditions (chemical and electrical plating parameters) and the output resultant microstructure are very poorly understood. This is captured in Figure 3-5, where the “processing-structure” relationship for pulsed electocrystallization has been illustrated [10]. Fundamental mathematical expressions describing the phenomena linking physically measurable quantities (in ovals) exist as shown by the mechanisms between each oval. However, as described by Choo et al., the links become progressively weaker down the chain and are replaced by purely empirical relationships towards the end [10]. As a result, the creation of ultrafine-grained electrodeposits has generally been accomplished by largely empirical means overall. Nevertheless, there are two fundamental characteristics of the electocrystallization process that are well-established and form the basis for the systematic electrochemical synthesis of nanocrystalline materials:

1. High current densities are required for massive nucleation on the substrate, as per Equation (3-5). Massive nucleation rates that overwhelm the crystal growth rates encourage the formation of finer grains [9]. This is the underlying motivation for the use of pulsed current electrodeposition, as it permits the utilization of much higher peak current densities; and
2. Electrolyte additives directed towards reducing the diffusion of adatoms over the surface of the growing deposit are typically applied in nanomaterial electrodeposition.

![Diagram of processing-structure relationship for pulsed electrocrystallization.](image)

**Figure 3-5** ‘Processing-structure’ relationship for pulsed electrocrystallization. Fundamental mathematical expressions describing the physical phenomena linking the physically measureable quantities (in ovals) exist as shown by the mechanisms between each oval. The links get progressively weaker down the chain and are replaced by empirical relationships towards the end [10].

To summarize, electrical parameters that maximize the driving force for grain nucleation throughout electrocrystallization, combined with inhibition of adatom surface diffusion by chemical means, represent the methodology for the production of nanocrystalline materials by electrodeposition. These phenomena are illustrated schematically in Figure 3-6.
3.5 Electroforming of Bulk Quantities of Nanocrystalline Materials

3.5.1 Chemical and Electrical Processing Parameters

The creation of materials with nanocrystalline microstructures by electrodeposition is well-established [5,6]. However, previous studies on the topic have largely been restricted to thin coatings or freestanding foils. In order to extend beyond “thin sheets” and into the geometrical regime of “bulk plate” specimens, deposition must be sustained for much longer periods of time. For example, a pure nanocrystalline Ni electrodeposit thickness of 1mm requires approximately 10-20 hours of sustained deposition run time to achieve. From a practical perspective, there are two main obstacles to achieving sustained deposition. Firstly, the internal stress of the deposit must be minimized in order to alleviate the risk that excessive build-up of residual stress will result in exfoliation (internal stress-induced peeling) of the growing deposit from the substrate before the synthesis run is complete. Secondly, large processing flaws can limit sustained
deposition. Preventing the formation of processing flaws in the growing electrodeposit for such a lengthy material processing duration has been found to be extremely challenging, as will be described in detail in this section. Hence, the main focus of the materials synthesis component of this work was a) internal stress control, and b) the elimination of electrodeposition processing artifacts as a means to achieve bulk quantities of flaw-free material.

For this particular study, Ni-based metals and alloys were studied primarily. Throughout the current study, the standard aqueous Watts-type Ni electroplating solution was used as the base electrolyte formulation and its composition is included in Table 3-1 below. To prepare the Watts-type electrolyte, standard analytical grade chemicals from Alfa Aesar and Fisher Scientific, an Integrān proprietary organic residual stress-relieving grain refiner (A-21), and an Atotech USA Inc. proprietary wetting agent (NPA-91) were added to heated distilled water. The primary role of the NiSO$_4$·6H$_2$O and NiCl$_2$·6H$_2$O salts is to provide Ni cations to the solution, as well as electrically conductive SO$_4^{2-}$ and Cl$^-$ anions for solution conductivity and to promote anode dissolution. Boric acid is used as a pH buffer. The electrolyte pH was maintained in the range of 1.5-2.5. Use of the Watts-type solution for the synthesis of pure nanocrystalline Ni is a mature process, and is described in more detail in the work of El-Sherik et al. [e.g. 5,6,12].

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO$_4$·6H$_2$O</td>
<td>260-300</td>
</tr>
<tr>
<td>NiCl$_2$·6H$_2$O</td>
<td>45</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>45</td>
</tr>
<tr>
<td>FeCl$_2$·4H$_2$O</td>
<td>0-35</td>
</tr>
<tr>
<td>Na$_3$C$_6$H$_5$O$_7$·2H$_2$O</td>
<td>0-30</td>
</tr>
<tr>
<td>Proprietary grain refiner A-21</td>
<td>0.1-10</td>
</tr>
<tr>
<td>Proprietary wetting agent NPA-91</td>
<td>0-15 mL/L</td>
</tr>
</tbody>
</table>
While many of the electrodeposits produced for the current study were pure Ni, a large number of Ni-Fe alloy deposits were also produced and characterized. The primary motivation for iron alloying was to refine the electrodeposit grain size to values much smaller than are achievable with the pure Ni system. Alloying is well-known to induce grain refinement in some electrodeposited systems and the magnitude of this effect for the Ni-Fe system is shown in Figure 3-7 [13]. In this way, the range of microstructures available for study could be broadened.

![Figure 3-7](image.png)

**Figure 3-7** Nanocrystalline Ni-Fe electrodeposit grain size as a function of deposit chemical composition, illustrating the significant grain refining effect of alloying in the electrodeposited Ni-Fe binary system [13].

The synthesis of Ni-Fe alloys was accomplished by the addition of iron chloride to the electrolyte along with a chelating agent such as sodium citrate (Na₃C₆H₅O₇·2H₂O) to maintain the deposit chemical composition at the desired level and discourage the oxidation of Fe²⁺ to Fe³⁺.
Materials Synthesis

(see Table 3-1). As described by Cheung et al., Fe$^{3+}$ tends to form iron oxide (Fe$_2$O$_3$) precipitate in the presence of dissolved oxygen in the electrolyte, the end result being that Fe-containing plating solutions may be short-lived [13]. In addition to dissolved iron salts and chelating agents, electrolytic Fe was added as an anode material so that the solution could be continuously replenished with both Ni and Fe cations during the electrodeposition process. A schematic diagram and photograph of the apparatus developed for the materials synthesis in this study are shown in Figure 3-8 below. Nanocrystalline Ni-Fe electrodeposition is also a mature process and more information is provided by Cheung et al. [13-16].

In addition to pure Ni and Ni-Fe alloy electrodeposits, some Co-based materials along with data from past studies in the literature were added to the Chapter 5 study of hardness-strength relationships in order to broaden the data set. The synthesis of these materials will not be described here, but more information can be found in the individual works cited in Chapter 5.
Figure 3-8 (a) Top-view schematic and (b) photograph of the electroforming apparatus used for the Ni-Fe synthesis component of this work.
Materials Synthesis

For the current study, pulsed electrodeposition was carried out galvanostatically using cathodic square wave pulses with complete current cut-off during the intervals between the pulses. See Figure 3-9 for a schematic diagram showing the experimental pattern of current versus time for pulsed current plating. The important electrical parameters during pulse plating include the pulse frequency, $f$, the duty cycle, $\Theta$, and the average current density, $I_{ave}$:

$$f = \frac{1}{T_{on} + T_{off}}$$  \hspace{1cm} (3-6)

$$\Theta = \frac{T_{on}}{T_{on} + T_{off}}$$  \hspace{1cm} (3-7)

$$I_{ave} = I_{peak} \cdot \Theta$$  \hspace{1cm} (3-8)

For the present study, cathodic current on-time values ranged from 1-20ms, off-time values ranged from 0-100ms, and peak current density values ranged from 0.2-1A/cm$^2$. However, most of the samples of the current study were produced using an average current density of 0.05A/cm$^2$.

![Schematic illustration of the square-wave pulsed electrodeposition waveform used in the present study.](image)

**Figure 3-9** Schematic illustration of the square-wave pulsed electrodeposition waveform used in the present study.

152mm x 152 mm Ti cathode plates were used as the temporary substrates for the electroformed nanocrystalline materials produced for this study and each electroformed plate was large enough
to yield six individual tensile coupons. A photograph of a typical electroformed nanocrystalline material plate from which six tensile specimens were cut is included in Figure 3-10. One of the tensile specimens cut from the plate is positioned alongside it while the remaining five specimens are not shown.

As mentioned earlier, there are two pre-requisites for the successful synthesis of bulk quantities of electrodeposited material:

1. The internal stress level of the deposit must be controlled. Excessive residual stress levels in the deposit specimen may result in its partial or complete exfoliation from the temporary substrate before the end of the deposition run. This is discussed in Section 3.5.2; and

2. Processing artifacts must be minimized. A flaw on the surface of a growing electrodeposit may preferentially build up relative to the remainder of the plate and
eventually inhibit or prevent sustained deposition altogether. Processing flaws are discussed in detail in Section 3.5.3.

3.5.2 Internal Stress Control

Internal stress is a common characteristic of electrodeposited materials (irrespective of grain size) and can limit the upper plate thickness that may be achieved. There are several structural causes of this electrodeposit internal “macrostress”, as outlined by Weil [17]: “If the interatomic spacing of an epitaxial deposit is different from that of the substrate on which it is forced to fit, macrostresses develop. If the coefficients of thermal expansion of the substrate and deposit differ and plating is carried out at elevated temperatures, macrostresses develop in cooling. Codeposited hydrogen can affect the internal stress by diffusing into the substrate and expanding it while the deposit tries to contract. Diffusion of hydrogen from the near-surface region toward the substrate can also result in a tensile macrostress. Recrystallization and decomposition of hydrides or other compounds are also possible causes of macrostresses.” Regardless of its origin, internal stress-relieving electrolyte additives are commonly employed in industrial electroforming i.e. where the production of thick freestanding electrodeposits is desired. A commonly used rule of thumb is that the internal stress of an electroform to exceed 2mm in thickness must be maintained below approximately 7MPa in order to avoid gross dimensional non-conformity due to residual stress-induced deflection [18].

For the Watts Ni system, electrolyte grain refiner concentrations in the range of 0.1 – 0.5 g/L are typically used to minimize deposit stress, a common practice in thick plate electroforming, see Figure 3-11(a) [19]. Using the standard Watts-type Ni electrolyte of Table 3-1, the stress-
relieving grain refiner (A21) of the present study was varied between 0 and 10g/L in order to compare its stress-relieving effectiveness to the other bath addition agents shown in Figure 3-11(a). The results are presented in Figure 3-11(b), and it can be seen that the stress-relieving grain refiner of the current study behaves in a similar fashion to the other addition agents from the literature on Watts-type Ni electrolytes [19]. In particular, deposits produced from the additive-free Watts Ni exhibit approximately 60MPa residual tensile stress, and the addition of only 0.1g/L A21 induces a marked transition to approximately 20MPa compressive stress. Further additions increase the magnitude of the compressive stress, and eventually the behaviour plateaus beyond 4g/L or so.

Figure 3-11 Internal stress of Ni electrodeposited from a standard Watts electrolyte as a function of stress reliever concentration; values from (a) the literature [19]; and (b) the current study.
One notable characteristic of Figure 3-11(b) is the steep slope of the curve in the proximity of 0 MPa internal stress. The significance of this high slope is that, in an attempt to achieve a state of zero stress, small changes in the effective stress-relieving grain refiner concentration may induce significant changes in the observed residual stress of the resulting electrodeposit. Unfortunately, the maintenance of a steady-state stress-relieving bath addition agent concentration is non-trivial, as will be explained below.

Typical organic stress-relievers, such as the one employed in the current study, actively participate in the electrocrystallization process and tend to become at least partially co-deposited within the Ni deposit as it grows [20]. In other words, the additive is continuously consumed by the process. Moreover, there is a well-known tendency for organic electroforming bath additives to decompose in service wherein the intermediate compounds (or breakdown products) are in fact the predominant species with respect to modification of the electrodeposit properties [20]. For instance, Figure 3-12 contains the results of a study of the decomposition products of benzoic acid sulfimide in Ni electrodeposition [20]. The “age” of the bath is represented by the total amount of electrical charge passed through the system per unit electrolyte volume. The original additive molecule, benzoic acid sulfimide, decomposes into numerous sub-species as electrodeposition proceeds. Two of these decomposition products, o-toluene sulfonamide and benzamide, were monitored and attempts were made to correlate their concentration to electrodeposit internal stress and other properties, with limited success. Numerous such attempts have been made to differentiate between the individual decomposition product species and their effects on the resultant electrodeposit microstructure [20]. Unfortunately, the complexity of the electrocrystallization process (e.g. [10]) combined with the numerous possibilities for
decomposition products of the addition agents in common use has made a rigorous analysis of the effects of each decomposition product extremely challenging.

Nevertheless, for the purposes of the current study, the combined effect of the tendency for organic addition agents to chemically decompose as per Figure 3-12 along with the sensitivity of internal stress to the effective bath addition agent concentration as per Figure 3-11(b) results in a scenario wherein the production of electrodeposits that are completely devoid of internal residual stress is rendered extremely challenging via grain refiner / stress relieving additive control alone [20].

![Figure 3-12](image)

**Figure 3-12** The nature of benzoic acid sulfinamide decomposition in the Watts Ni plating electrolyte. Concentration of benzoic acid sulfinamide along with two of its decomposition products, o-toluene sulfonamide and benzamide, as a function of bath use as expressed by the amount of electrical charge (Amp-hr) passed through the solution per unit volume [20].

Furthermore, in addition to deposit stress relief, organic electrolyte additives often serve a grain-refining dual purpose role. This is also the case for the present study, where the A21 bath additive is employed for both stress relief and grain refinement. To illustrate this effect, the
average grain size of the specimens of Figure 3-11 (Watt-type pure Ni bath with an A21 concentration varying between 0 to 10g/L) are provided in Figure 3-13. It may be appreciated from Figure 3-13 that the grain size of the materials produced was found to be strongly sensitive to the electrolyte stress-relieving grain refiner concentration, consistent with previous work on the topic [12]. The pure Ni electrodeposits shown in Figure 3-13 span the grain size range of 28 to 80nm.

Figure 3-13 Average grain size of electrodeposited nanocrystalline Ni as a function of electrolyte grain refiner concentration as compared to that from a previous study [12].

Ideally, a method should be used to achieve grain refinement without a concomitant change in internal stress, or vice versa. In this manner, the impact of electrodeposit internal stress on the resultant material properties might be de-convoluted from that of grain refinement. At present, a method to vary grain size independent of electrodeposit internal stress is not known. Indeed, it has been suggested that high internal stress may even be an intrinsic property of ultrafine-grained solids such as nanocrystalline metallic materials [21]. This is the topic of on-going study in our research group [22] and is beyond the scope of the present study. In light of this issue, most of
the electrodeposits of the current study were produced with the stress-relieving grain refiner concentration held as close to 1g/L as possible. This concentration level was selected because it represents a trade-off between desired grain refinement and undesired residual stress as per Figures 3-11(b) and 3-13. Pure Ni deposits produced from the Watt-type electrolyte of Table 3-1 with 1g/L A21 were typically found to exhibit approximately 35-45MPa compressive residual stress and an average grain size of approximately 30-40nm. However, due to local cathodic current density and effective grain refiner concentration fluctuations during lengthy electroforming runs of a large number (>50) of samples, a broader average grain size range of 15-50nm is a more appropriate description of the pure Ni microstructures produced as part of the current study.

Finally, it may be appreciated from Figure 3-11(b) that the pure Ni specimens fabricated using the extreme processing conditions of 0 and 10g/L grain refiner exhibited approximately 9-10 times the level of residual stress deemed acceptable in industrial electroforming (7MPa) wherein post-synthesis process sample warping is unacceptable [18]. As a result, these electrodeposits were observed to exhibit pronounced bending upon removal from the temporary Ti cathode substrate. In contrast, specimens produced using 0.1-0.5g/L of grain refiner exhibited little curvature upon removal from the substrate.

3.5.3 Processing Artifact Control

In addition to internal stress, processing artifacts may inhibit sustained deposition for long periods of time. The nature of electrodeposition is such that electrodeposited materials almost
always contain various types of inclusions and/or impurities, see Figure 3-14 [20]. Some typical sources of this contamination include [23]:

1. Chemicals added to the solution to achieve various effects e.g. brightness, leveling, low internal stress;

2. Particulate e.g. atmospheric dust, particles intentionally added to the solution (e.g. for composite coatings), anode corrosion by-product;

3. Cathodic products e.g. complex metal ions

4. Hydroxides

5. Hydrogen bubbles

**Figure 3-14** Schematic illustration of common processing artifacts encountered in electrodeposition [20].

One key focus of the materials synthesis component of this work was the minimization of processing artifacts such as hydrogen pits, nodular deposit growth and co-deposited fine particulate matter. Elimination of electroforming process flaws was found to be particularly
Materials Synthesis

challenging for two reasons. Firstly, in order to extend beyond “thin sheets” and into the geometrical regime of “bulk plate” specimens, the target electroform thickness was typically 1mm, which requires approximately 20 hours of deposition run time to achieve. From a practical perspective, keeping the electrolyte free from contamination for such a lengthy duration was found to be non-trivial. A good example is atmospheric dust. If the electroforming tank was left partially uncovered during material synthesis, the probability of dust entering the electrolyte was found to be relatively high. In such a scenario, the lengthy run time gives the dust particle ample opportunity to make contact with the cathode plate and thereby become entrapped within the steadily growing electrodeposit. The isolated co-deposited dust particle is not, in and of itself, a major issue. However, because the plate is formed by a deposition process whereby the metal is formed atomic layer upon layer, this initially imperceptibly small geometrical heterogeneity on the deposit surface gradually and continuously grows into a protrusion through the following mechanism. Since the particle protrudes from the otherwise smooth cathode surface, this protrusion causes a minor distortion in the cathodic electric field wherein the local current density at the top of the defect is slightly higher than the remainder of the smooth cathode surface. By way of the multiplicative action of layer upon atomic layer of electrodeposited material, the protrusion grows in size faster than the remainder of the smooth cathode surface, the end result being a pronounced nodule on the deposit surface. Such macroscopic defects are less common in electroforming runs of short 1-4hr duration, but commonplace in production runs that exceed 10hrs. Figure 3-15 contains a cross-sectional image of an electrodeposit containing particulate contamination and a concomitant nodule defect. The particle from which the nodule emanates is too small to be resolved, while the nodule itself is massive.
Based upon an examination of Figure 3-15, it may be appreciated that when tensile testing the material with a loading direction oriented perpendicular to the deposit growth direction, the presence of such gross nodular/dendritic growth features could have a marked impact on its tensile properties, most notably ductility for instance. Therefore, since ductility as measured by strain-to-fracture in quasi-static tensile extension of a typical high strength material is strongly influenced by the presence of pre-existing flaws and second phase particulates in the sample as per Figure 1-16, the electrodeposition processing parameters used to fabricate the nanocrystalline material play a key role because they typically dictate the type, size, orientation, and concentration of processing artifacts that are created as the material is formed. This is explored in more detail in Chapter 4.

By way of preliminary pilot material production runs carried out before the specimens for this study were produced, the processing parameters that enabled the elimination of most of the gross
Materials Synthesis

Macroscopic surface defects were identified. Throughout the current study, however, the most persistent and problematic processing artifacts encountered were co-deposited particulates. In some instances, these particulates could be characterized in a rigorous manner. This was typically the case only when severe contamination of the electrolyte from some extrinsic source had taken place i.e. not originating from the process itself, but rather from an external contamination source. A notable example is Ca contamination from a malfunctioning de-ionized water replenishment system. The fracture surface of a tensile specimen produced from such a Ca-contaminated process is shown in Figure 3-16. Lower magnification SEM revealed regions of brittle and ductile fracture on the fracture faces, with Ca particulate dispersed throughout the deposit. By combined use of SEM and EDX, the size, shape, and concentration of this particulate contamination might be described and its effect on tensile ductility quantified in a fashion similar to Figure 1-16. The success of subsequent systematic removal of the contaminating species could also be monitored in this manner.
The second synthesis challenge relates to the presence of not only external contamination such as foreign particulate matter but unavoidable contamination resulting from the process itself. Consumable pure Ni “R-rounds” from INCO were used as anodes throughout this work. Over the course of a lengthy (greater than approximately 8hrs) electroforming run, the continuous oxidation of the Ni anode is accompanied by physical breakdown of its surface, resulting in fine Ni particulate contamination of the electroforming bath. This is the main reason most anode

![Figure 3-16](image-url) (a,b) SEM Analysis of the fracture face of a nanocrystalline Ni tensile specimen synthesized using an electroforming process replenished with water from a malfunctioning de-ionized water system indicating the presence of particulate contamination; (c) EDX spot analysis of the Ca particulate (images courtesy of Peter Lin, Integran Technologies Inc.).
baskets are bagged in industrial electroplating and electroforming. Metal hydroxides are also known to form on the surface of electroplating anodes and these represent another possible particulate contamination source. Regardless of its origin, any solution-borne particulate may become entrapped in the electroform, causing defects similar in character to the nodule in Figure 3-15. Because particulate originating from the continuously corroding consumable Ni anode material was chemically identical to the matrix material being reduced on the cathode surface, the co-deposited particulate could not be resolved by conventional EDX or Back-Scattered Electron Diffraction (BSED) techniques as per Figure 3-16. Moreover, no co-deposited nano-sized particles originating from the anodes were ever detected on the fracture surfaces of the subsequent tensile test specimens. In fact, to the best of the author’s knowledge, there exist no conventional methods or previous studies that have rigorously characterized electroforming anode particulate contamination and its effect on material properties. Thus, the rigorous characterization of the particulate matter of primary interest to the current study was not possible.

A number of practical strategies to combat the issue of internally-generated particulate contamination were nevertheless evaluated and the failures will not be described in detail here. However, the most effective method to prevent co-deposition of the anode particulate within the cathode plate was found to be a combination of proper tank enclosure, anode bagging (filter bag encapsulating the anode basket), continuous electrolyte filtration, and solution flow pattern control. This was largely an empirical exercise, with the dependent variables being macroscopic plate defect inspection and, more rigorously, testing of multiple tensile samples cut from each plate. In other words, for the specific case of second phase particulate chemically identical to the
matrix, it was not possible to detect and therefore quantify the level of contamination. Therefore, observations of appearance and ductility measurements were used as indirect particle content indicators instead. A photograph of plates produced before and after introducing specific processing strategies to address the specific issue of particulate contamination were implemented can be seen in Figure 3-17. There was a clear empirical correlation between particulate contamination and macroscopic plate roughness. In turn, the impact of this decrease in the processing flaw content of the electrodeposits on ductility was evaluated and the results are presented in Chapter 4.

The identification of a method to quantify the co-deposited anode particulate content would greatly assist in the development of a ductility-particulate concentration relationship for this material class, similar to that presented in Figure 1-16. This is suggested for future study.

![Figure 3-17](image-url) Photograph of representative electroformed nanocrystalline Ni plates produced before and after implementing processing artifact minimization (courtesy of Peter Lin, Integran Technologies Inc.).
In addition to particulate, another prevalent intrinsic processing artifact source is evolved hydrogen. In aqueous electrodeposition, the preferred cathodic metal reduction reactions are rarely 100% efficient and so some portion of the electric charge is almost always consumed by hydrogen reduction. If the resultant hydrogen outgas fails to detach from the surface of the cathode, then there exists some risk that the bubble will become encapsulated in the growing electrodeposited. This phenomenon is known as “hydrogen pitting” and an example of such a gross defect is found in Figure 3-18. Best practices in electroplating, and especially electroforming, prescribe the use of wetting agents such as sodium lauryl sulfate (SLS) to lower the surface tension of the electrolyte so that hydrogen bubbles are encouraged to leave the cathode surface as the deposit grows. Such techniques are typically effective and pit-free plates are readily producible. For the present study, steady-state electrolyte surface tension control using the Atotech proprietary wetting agent NPA-91 was implemented as a means to control hydrogen pitting. Using the Watts-type electrolyte of Table 3-1, the electrolyte surface tension was continuously maintained below 0.03 N/m to accomplish this.

Figure 3-18 Cross-sectional optical micrograph of an electroformed plate containing hydrogen pitting. Deposit growth direction is from bottom to top.
3.5.4 Resultant Thick Plate Microstructures

Figure 3-19 contains TEM characterization data for a typical nanocrystalline Ni electrodeposit of 31nm average grain size. As discussed elsewhere [7,12], the microstructure of nanocrystalline electrodeposits typically exhibits a log-normal grain size distribution.

Figure 3-19 TEM characterization data of a nanocrystalline Ni (31 ± 9nm average grain size) sample showing a (a) bright field image, (b) selected area diffraction pattern, and (c) grain size distribution.

The crystal structure, preferred crystallographic orientation, and grain size of electrodeposited nanomaterials is dependent upon the chemical composition and plating parameters of the
Materials Synthesis

electrodeposition process. A representative nanocrystalline Ni X-ray diffraction pattern is shown in Figure 3-20. It may be seen that electrodeposited pure nanocrystalline Ni of 38nm grain size is face-centered cubic and exhibits a strong (111) (200) fibre texture.

![X-ray diffraction pattern](image)

**Figure 3-20** Typical XRD diffraction profiles (Co Kα radiation) for representative pure Ni (38nm grain size) and Ni-46.8wt% Fe (10nm grain size) nanomaterials alongside the calculated random profile for Ni.

In addition, alloying nanocrystalline Ni with Fe has been used in the present study to induce grain refinement beyond what is achievable with pure Ni. Ni-Fe specimens in the compositional ranges of 0 - 15wt% Fe and 47 - 49wt% Fe were synthesized and chemical composition measured using energy dispersive X-ray spectroscopy (EDS). Figure 3-21 contains TEM characterization data of a Ni-47.3%Fe sample with a 9 nm average grain size and relatively narrow log-normal grain size distribution [24]. As studied in detail by Cheung et al. [13], Fe alloying of nanocrystalline Ni electrodeposits may induce a transition towards a more random
crystallographic texture with increasing iron content / decreasing grain size in the deposits. See Figure 3-20 for an XRD pattern taken from a representative Ni-Fe specimen. It can be seen that the Ni-Fe specimen exhibits a (200) texture but is more random than that of the pure Ni deposit. A detailed description of nanocrystalline Ni-Fe electrodeposition is provided by Cheung et al. [6,13-16].

Figure 3-21 TEM characterization data of a Ni-47.3%Fe (9nm average grain size) sample showing a (a) bright field image, (b) dark field image, (c) selected area diffraction pattern and (d) grain size distribution [24].
3.6 Summary of Materials Produced for This Study

The aforementioned processing considerations were used to synthesize a large number of processing artifact-reduced plate specimens, the descriptions of which are listed in Table 3-2.

Table 3-2 Specimens synthesized.

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Plate Label</th>
<th>Thickness (mm)</th>
<th>[Fe] (wt%)</th>
<th>Grain Size XRD (nm)</th>
<th>Hardness (HVN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3</td>
<td>A044</td>
<td>0.03</td>
<td>0</td>
<td>20</td>
<td>461</td>
</tr>
<tr>
<td>4-6</td>
<td>A043</td>
<td>0.05</td>
<td>0</td>
<td>21</td>
<td>456</td>
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<tr>
<td>7-9</td>
<td>A046</td>
<td>0.07</td>
<td>0</td>
<td>22</td>
<td>451</td>
</tr>
<tr>
<td>10-12</td>
<td>A045</td>
<td>0.10</td>
<td>0</td>
<td>21</td>
<td>455</td>
</tr>
<tr>
<td>13-15</td>
<td>A054</td>
<td>0.19</td>
<td>0</td>
<td>20</td>
<td>462</td>
</tr>
<tr>
<td>16-18</td>
<td>A055</td>
<td>0.52</td>
<td>0</td>
<td>22</td>
<td>458</td>
</tr>
<tr>
<td>19-21</td>
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<td>0</td>
<td>23</td>
<td>446</td>
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<td>24</td>
<td>424</td>
</tr>
<tr>
<td>28-29</td>
<td>C0028</td>
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<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>30-32</td>
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<td>n/a</td>
<td>n/a</td>
</tr>
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<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>36-38</td>
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<td>0.92</td>
<td>0</td>
<td>27</td>
<td>391</td>
</tr>
<tr>
<td>39-41</td>
<td>SA020</td>
<td>1.05</td>
<td>0</td>
<td>25</td>
<td>410</td>
</tr>
<tr>
<td>42-44</td>
<td>SA022</td>
<td>1.05</td>
<td>0</td>
<td>24</td>
<td>417</td>
</tr>
<tr>
<td>45-47</td>
<td>J005-D</td>
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<td>0</td>
<td>25</td>
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<tr>
<td>48-50</td>
<td>J012-D</td>
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<td>0</td>
<td>25</td>
<td>400</td>
</tr>
<tr>
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<td>0</td>
<td>23</td>
<td>440</td>
</tr>
<tr>
<td>54-56</td>
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<td>1.13</td>
<td>0</td>
<td>23</td>
<td>440</td>
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<tr>
<td>57-59</td>
<td>R330</td>
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<td>0</td>
<td>22</td>
<td>450</td>
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<tr>
<td>60-62</td>
<td>R327</td>
<td>0.98</td>
<td>0</td>
<td>22</td>
<td>450</td>
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<tr>
<td>68-70</td>
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<td>0</td>
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<tr>
<td>71-73</td>
<td>J100</td>
<td>1.08</td>
<td>6.4</td>
<td>18</td>
<td>485</td>
</tr>
<tr>
<td>74-76</td>
<td>J101</td>
<td>0.98</td>
<td>6.5</td>
<td>17</td>
<td>431</td>
</tr>
<tr>
<td>77-79</td>
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<td>1.18</td>
<td>4.6</td>
<td>18</td>
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</tr>
<tr>
<td>80-82</td>
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<td>19</td>
<td>457</td>
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<tr>
<td>86-88</td>
<td>J114</td>
<td>1.06</td>
<td>11.7</td>
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<tr>
<td>89-94</td>
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<td>1.08</td>
<td>13.9</td>
<td>14</td>
<td>563</td>
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<tr>
<td>98-100</td>
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<td>1.08</td>
<td>12.7</td>
<td>16</td>
<td>560</td>
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<tr>
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<td>3.4</td>
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<td>2.6</td>
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<tr>
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<td>C065</td>
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<td>8.5</td>
<td>16</td>
<td>491</td>
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<tr>
<td>110-112</td>
<td>C066</td>
<td>1.22</td>
<td>7.5</td>
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<td>439</td>
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<td>113-115</td>
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<td>1.21</td>
<td>14.5</td>
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<td>543</td>
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<tr>
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<td>1.20</td>
<td>14</td>
<td>17</td>
<td>532</td>
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<tr>
<td>119-121</td>
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<td>1.18</td>
<td>9.6</td>
<td>19</td>
<td>539</td>
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<td>122-127</td>
<td>C071</td>
<td>1.21</td>
<td>11.9</td>
<td>15</td>
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<tr>
<td>128-130</td>
<td>C067</td>
<td>1.16</td>
<td>13.4</td>
<td>17</td>
<td>545</td>
</tr>
</tbody>
</table>
It should be noted that there exists general consistency between the XRD-based grain size values and those based upon application of the Hall-Petch relationship to the measured hardness values listed in Table 3-2 with one notable exception. Specimens 66-70 cut from plates labeled AE065 and AE066 exhibited XRD peak broadening that resulted in calculated average grain size values of 21 and 22nm, respectively. However, the hardness and strength properties of these specimens were indicative of a much coarser microstructure. For example, the average hardness and yield strength values of the two samples cut from plate AE065 were only 344 VHN and 702 MPa, respectively, values that would be expected from Ni with a grain size much larger than 21nm. In order to explain this unexpected result, TEM analysis was performed on specimen AE065 and a representative bright field image is presented in Figure 3-22. It was found that the average grain size of this specimen was 80nm and that the material exhibited an unexpectedly large concentration of faulted regions and microtwins. These faulted regions are likely the origin of the anomalously high XRD peak broadening upon which the 21nm grain size calculation was based. From a synthesis perspective, the origin of this microstructure is unknown.
3.7 Summary

As described in Chapter 1, the characteristics of the nanostructured material synthesis method can play a major role in the observed response to subsequent mechanical deformation. This has made it difficult, and in many cases impossible, to de-convolute the effect(s) of nanocrystalline grain refinement from those originating from other concomitant structural characteristics such as porosity, particulate contamination, chemical contamination, secondary phases, internal stress, and other side effects of the technique used to create the nano-sized crystals. Therefore, one main objective of this study was the minimization or elimination of synthesis artifacts in the nanocrystalline material electrodeposition process. As described by Koch, “minimization or
elimination of processing artifacts is the key to revealing the inherent mechanical properties of nanocrystalline materials and potentially optimizing high strength and good ductility” [25]. In this chapter, it was demonstrated that electroformed specimens substantially reduced in defects such as hydrogen pitting, chemical contamination, and particulate contamination could be reproducibly synthesized through adoption of specific strategies such as steady state chemical control, fine particulate filtering, improved feedstock chemical quality, and so on. As will be described in Chapter 4, the “quality” criteria throughout this work were macroscopic plate defect inspection and, more rigorously, achievable tensile elongation-to-fracture of multiple samples cut from each individual plate produced. In other words, it was found that artifact-reduced specimens were more ductile and showed less sample-to-sample variability in elongation-to-fracture than specimens produced from a defect-rich process. Owing to the inability to rigorously characterize the artifacts themselves due to the identical chemical character of the matrix and second phase particles in question, these strain-to-fracture tests effectively served as indirect measurements of the co-deposited material particle content.

The second objective of this study was to answer the question of whether it is possible to synthesize bulk quantities of electrodeposited nanocrystalline materials to enable tensile testing in conformance with ASTM E8 since, prior to this study, reproducible nanomaterials thick plate electroforming had not been possible. It was found that processing artifact minimization and electrodeposit internal stress control enabled the systematic production of a large number of artifact-free 152mm x 152 mm plates of 1mm thickness and beyond.
3.8 References


Chapter 4
Ductility


4.1 Introduction

While much has been written concerning the relationship between grain size and strength [e.g. 1-3] and hardness [e.g. 4-6], the literature contains a great deal of conflicting data regarding the intrinsic ductility and toughness of nanocrystalline materials [e.g. 7-9]. Ductility is defined as the ability of a material to undergo plastic deformation without fracture [10] and is not only a key piece of information that must be considered in material formability considerations and the design of reliable load bearing structures, but is also a very useful measure in the broader assessment of material quality and damage tolerance. In the case of nanocrystalline materials, there are a number of factors that have contributed to a lack of clarity on the topic, as will be discussed below. It is the goal of this chapter to elucidate some of the causes of past ambiguity and to employ data gathered using a very large set of electrodeposited nanocrystalline material specimens to study the intrinsic ductility of this important material class.

4.2 Experimental Details

4.2.1 Material Synthesis and Characterization

As discussed in Chapter 3, the nature of electrodeposition is such that electrodeposited materials typically contain various types of inclusions and/or impurities, and one primary objective of the
materials synthesis component of this thesis was the minimization of processing artifacts such as hydrogen pits, nodular deposit growth and co-deposited fine particulate matter in the production of bulk, thick plate specimens for testing in conformance with ASTM E8 [11]. This was largely an empirical exercise, with the dependent variables being macroscopic plate defect inspection and, more rigorously, testing of multiple tensile samples cut from each plate.

4.2.2 Mechanical Testing
As described in Chapter 2, all samples were tested to fracture using a calibrated load cell and the elongation to fracture, $\varepsilon_f$, was measured using both a calibrated extensometer and also by measurement of the gauge length before and after testing. The peak load method was used to designate the onset of plastic instability in order to determine the maximum uniform elongation. The elastic component of the maximum uniform strain was assumed to be equivalent to the strain measured from the onset of loading until the 0.2% offset yield point [11] with elastic strain values typically falling within the range of 0.5 to 1%. The difference between the measured maximum uniform strain (at peak load) and the elastic strain term was then termed the maximum uniform plastic strain.

4.2.3 Data Analysis
Two-parameter Weibull distributional analysis was used to quantify the variability in the ductility data. Weibull analysis is one of the most commonly used tools in reliability analysis, and is based upon a probabilistic “weakest link” depiction of the scatter in the time-to-failure of engineering components. Its basic assumptions are the existence of statistically distributed defects throughout the volume and on the surfaces of the material and that the structure can be
considered as a link series in which the failure of the weakest link generates the fracture of the whole structure [12]. The principles of Weibull distributional analysis [13] are commonly used to interpret fracture stress data from brittle ceramics [14]. However, the method has also been used to characterize the distribution of tensile elongation data taken from aluminum test specimens containing casting defects [15-17] and brittle intermetallic phases [18] from which the ultimate sample fracture is thought to originate. For the present study, overall strain-to-fracture, $\varepsilon_f$, was chosen as the continuous random variable for the statistical analysis. This was done in order to permit the utilization of a two-parameter Weibull distribution to fit the data as opposed to a three-parameter Weibull distribution with a correction factor, also known as a location parameter, applied to account for elastic strain. For the present study, it is assumed that Weibull’s two-parameter mathematical formalism is able to describe the strain-to-fracture probability distribution of the samples under examination. The cumulative distribution function of the two-parameter Weibull distribution is given by:

$$F = 1 - e^{-(\varepsilon_f / \eta)^\beta}$$

(4-1)

where $F$ is the failure probability for a given strain-to-fracture $\varepsilon_f$, $\eta$ is the scale parameter, and $\beta$ is the Weibull modulus. In order to minimize the statistical uncertainty of the analysis, a large set of 116 specimens was used for the study of samples of approximately constant geometry while 31 samples were prepared for the study of data recorded using specimens of varying thickness.
4.3 Results and Discussion

The first problem addressed in Section 4.3.1 is the effect of processing artifacts on tensile ductility. A largely empirical process of artifact minimization was then performed, and a material synthesis protocol was established that was as consistent and artifact-free as possible with the quality control parameter throughout being tensile tests of multiple samples cut from a single plate. Once a consistent sample-to-sample tensile elongation value that exceeded the onset of tensile necking instability was achieved, all relevant process parameters were locked in place and strictly controlled for every subsequent plate produced. The first study thereafter focused upon the effect of tensile specimen thickness on elongation measurements, and the results of this work comprise Section 4.3.2 of this chapter. Finally, to eliminate the geometry effect from further consideration and to explore the statistical variability in intrinsic achievable tensile elongation, a statistically significant number of 116 specimens of fixed sample thickness cut from relatively thick (approximately 1mm) monolithic nanocrystalline Ni-based electrodeposits produced using a well-controlled, steady state electroforming process were then evaluated and the results are discussed in Section 4.3.3.

4.3.1 Effect of Processing Artifacts

Since ductility as measured by strain-to-fracture in quasi-static tensile extension of a typical high strength material is strongly influenced by the propagation of pre-existing flaws in the sample, the electrodeposition processing parameters used to fabricate the nanocrystalline material play a key role because they typically dictate the type, size, orientation, and concentration of processing artifacts that are created as the material is formed. As discussed in Chapter 3, the processing parameters that enable the reduction of gross macroscopic defects were identified as part of this
Ductility

study. The most persistent and problematic processing artifacts encountered throughout this work were co-deposited particulates. A photograph of plates produced before and after processing strategies to address the specific issue of particulate contamination were implemented was presented in Figure 3-17. There was a clear empirical correlation between particulate contamination and macroscopic plate roughness.

The correlation between macroscopic plate roughness and co-deposited particulate content was also found to extend to specimen ductility. In order to quantify this effect, tensile tests were performed. Figure 4-1(a) contains tensile engineering stress-strain curves corresponding to six individual tensile bars cut from a single nanocrystalline Ni plate produced using an early scale-up stage electroforming process alongside data gathered from an otherwise identical plate produced using the later generation process with much stricter processing artifact control (Figure 4-1(b)).
Both lower absolute values and higher variability in tensile strain-to-failure measurements were typical of samples cut from macroscopically rough plates where more defects originating from the process are thought to have formed. In particular, the average elongation-to-fracture value for the six test specimens in Figure 4-1(a) was 2.8% as compared to 6.8% for the otherwise
Ductility

identical samples in Figure 4-1(b). The Weibull probability distribution function shape parameter, $\beta$, for the Figure 4-1(a) elongation-to-fracture data was 4.4 as compared to 17.2 for the Figure 4-1(b) data, indicative of significantly increased variability in ductility data for samples thought to contain more processing artifacts. In addition, fractography revealed that the less ductile specimens (Figure 4-2(a)) often showed signs of flat fracture (teardrop-shaped feature in Figure 4-2(a)) combined with areas of more pronounced ductile material flow whereas samples synthesized from a later generation process (Figure 4-2(b)) exhibited few signs of brittle fracture or processing flaws throughout the volume or along the surfaces.

Figure 4-2 Scanning electron micrograph images of the fracture surfaces of nanocrystalline Ni tensile samples produced using (a) an early scale-up stage electroforming process alongside (b) an otherwise identical plate of material produced using a later generation process with much stricter processing artifact control.
Ductility

It is unreasonable to expect that the electroforming process improvements developed as part of this study were successful in completely eliminating all processing artifacts. However, the fact that all thick, artifact-reduced samples were intrinsically ductile enough to surpass a point of peak load indicates that the processing artifact content was sufficiently low for final fracture to be initiated by plastic instability. Past the onset of plastic necking instability at the ultimate tensile stress point, it is very likely the case that further improvements in processing artifact control might yield increased elongation before fracture, as will be discussed in more detail in the following section. However, for the purposes of the current study, once a consistent sample-to-sample tensile elongation value that exceeded the onset of tensile necking instability was achieved, all relevant process parameters were locked in place and strictly controlled for every subsequent plate produced. All specimens produced for the subsequent sections of this chapter were substantially free of major electroforming artifacts such as large hydrogen pit holes, localized dendritic growth, and other prominent surface and volume flaws.

4.3.2 Effect of Sample Geometry

Figure 4-3 shows the relationship between specimen thickness and total achievable strain-to-fracture (based upon measurement of the gauge length before and after tensile testing) for 31 nanocrystalline Ni specimens of varying thickness processed in an identical fashion in order to yield similar microstructures and processing defect contents. In other words, the sole processing difference between the specimens from which the Figure 4-3 data originates is that the thicker plates were electrodeposited for a longer duration than the thinner ones.
Figure 4-3 Quasi-static tensile strain-to-fracture and uniform plastic strain as a function of plate thickness for nanocrystalline Ni specimens of similar microstructure, areal shape and processing method.

In the region of lowest thickness between 0.03 and 0.1mm, the detrimental effect of any minor surface defects (e.g. roughness) or non-uniformity in plate thickness becomes increasingly magnified as the relative size of these defects versus the cross-sectional thickness becomes greater with decreasing thickness. Scanning electron microscopy (SEM) images from a typical tensile specimen, in this case one of 0.05mm thickness, are shown in Figure 4-4. Macroscopically brittle fracture with highly localized necking was observed for specimens in this low thickness regime. Generally, most samples exhibited a sharp approximately 55-60° (relative to the loading direction) oblique crack path originating from one or both sides of the gauge section followed by a wider crack path running perpendicular to the sample length, as shown in Figure 4-4(a).
Beginning at approximately 0.1mm thickness, the tensile elongation-to-fracture of the plates becomes much less sensitive to changes in sample thickness. For these specimens, uniform plastic strain (plastic strain at the point of peak load on the engineering stress-strain curve, see Section 2.3.1) values were recorded and are also presented in Figure 4-3. It should be noted that samples too thin to sustain linear extension past the point of peak load (or “ultimate tensile stress”) were omitted from this analysis as the measurement of an overall uniform plastic strain value was not possible. The maximum amount of uniform plastic strain achievable in a tensile test may be considered one measure of a material’s intrinsic ductility and is typically dictated by the microstructure of the material from which it is made. In addition, there is a contribution of loading mode wherein sheet specimens may be expected to begin necking later than thicker

**Figure 4-4** Scanning electron microscopy (SEM) images from a typical thin foil (0.05mm thickness) nanocrystalline Ni sample after tensile testing illustrating the combination of (a) brittle macroscopic fracture morphology and (b) highly localized necking.
samples of otherwise identical feedstock material (see Section 1.3.4.2) [19,20]. In Figure 4-3, the average uniform plastic strain value exhibited by the 10 samples between 0.1 and 0.5mm-thickness was 5.16±0.30% whereas the average uniform plastic strain value exhibited by 13 samples of thickness 0.8mm and above was 4.68±0.35%. The uniform plastic strain values of the thin (0.1 – 0.5mm thick) samples were therefore, on average, approximately 7% higher than the 13 samples of thickness 0.8mm and beyond. Hence, the thinner (0.1 – 0.5mm thick) samples appear to exhibit slightly increased uniform plastic strain, likely originating from the fact that these particular samples failed by localized necking (see Section 1.3.4.2).

Apart from the influence of necking mode, the uniform plastic strain of the specimens under consideration appears to be relatively invariant across the sample set. The observation of a constant uniform plastic strain indicates that microstructure does not play a critical role in the geometrical dependence of overall tensile ductility as expressed by total strain-to-fracture in Figure 4-3. This observation is consistent with the work of Zhao et al., who carried out similar experiments on ultrafine-grained (100nm-1μm grain size) Cu and found that the achievable tensile uniform elongation was independent of specimen thickness [9]. Finally, the fact that all samples greater than 0.1mm thickness in Figure 4-3 were intrinsically ductile enough to surpass a point of peak load indicates that the processing artifact content was sufficiently low for final fracture to be initiated by plastic instability.

In Figure 4-5, the nanocrystalline Ni strain-to-fracture data has been re-plotted as a function of $A_o^{1/2}/L_o$ as per Equation (1-10):

$$\varepsilon_f = \frac{B\sqrt{A_o}}{L_o} + \varepsilon_u$$  \hspace{1cm} (1-10)
Ductility

where $\varepsilon_f$ is the total elongation to fracture, $\varepsilon_u$ is the uniform elongation, $A_o$ is the initial gauge cross-sectional area, $L_o$ is the initial gauge length, and $B$ is a constant. This relationship is known as the Unwin equation or Barba’s Law, and reflects the sensitivity of tensile ductility to specimen gauge dimensions [10]. The nanocrystalline Ni data in Figure 4-5 is plotted alongside the raw data from Kula and Fahey’s study on the topic of tensile specimen size and shape effects [21]. Their sample set is useful because the metals examined (copper and steels) are well-known and encompass a broad range of intrinsic tensile properties. Note that the general behaviour of nanocrystalline Ni is comparable to that of H-11 tool steel, another high strength material.

![Graph](image)

**Figure 4-5** The geometrical dependency of tensile elongation-to-fracture of nanocrystalline Ni (present study) compared to that exhibited by other standard engineering materials (data from ref [21]).

It can be seen that the samples of large cross-sectional area roughly follow Equation (1-10). However, regardless of the material studied, this relationship has a tendency to break down for...
Ductility

smaller samples of cross-sectional area below approximately 2 mm², or 0.04 mm/mm (Ao½/Lo) on Figure 4-5. The observations of the present study are consistent with those of Kula and Fahey and indicate that regardless of the intrinsic ductility of the material under examination, the achievable tensile elongation-to-fracture of thin tensile samples is inherently less predictable as neck development becomes increasingly geometry/surface-flaw sensitive with decreasing thickness.

The relationship between total elongation-to-fracture and sample geometry of the nanocrystalline Ni samples was also observed to become more unpredictable at the other end of the thickness spectrum (>2mm, Figure 4-3), this time in contrast to the behaviour of the conventional engineering material benchmarks. Of the five nanocrystalline Ni samples from the highest thickness (>2mm) regime, four exhibited signs of appreciable ductile material flow (εf = 7-10%), as expected from a relatively defect-free high strength metallic engineering material, while the fifth fractured soon after the onset of post-uniform elongation (indicative of the presence of critical defects). This indicates that, in the case of the thickest nanocrystalline Ni plates, the probability of encountering a critical “ductility controlling” volume defect may become less predictable, and possibly even increase, with increasing plate thickness. On the other hand, it is reasonable to assume that the type, size, orientation and concentration of flaws distributed throughout the volume of the Figure 4-5 benchmark engineering material specimens is relatively constant across the entire sample set because all specimens were taken from a common piece of bar stock material prepared by conventional metallurgical means, with individual tensile samples sliced to the desired thickness thereafter [21]. This is in contrast to the nanocrystalline
Ductility

specimens of varying thickness from the current study, which were not cut from a common stock but rather deposited for varying times in the material synthesis process.

These observations invoked the use of Weibull distributional analysis to quantify the variability in ductility data. Figure 4-6(a) contains the two-parameter Weibull plot produced using the tensile strain-to-fracture data from the 31 sample set of nanocrystalline Ni tensile specimens of varying thickness and Equation (4-1). Two marked transitions in slope indicate that the geometry-dependent strain-to-fracture data regimes possess unique probability distribution functions. In particular, the probability distribution function shape parameter of the <0.1mm-thick nanocrystalline Ni plate strain-to-fracture values ($\beta = 1.3$) was much smaller than those in the 0.1 – 1.25mm thickness regime ($\beta = 5.9$), indicative of a significant drop in ductility reliability for the thinnest specimens. This is the regime where surface flaws play a key role i.e. slant localized fracture at the expected 55° angle may not necessarily span the entire specimen width, but rather proceed only in the initial stages of plastic deformation with brittle fracture perpendicular to the loading direction accompanied by negligible necking proceeding thereafter, as was shown in Figure 4-4. Here tensile plasticity is highly sensitive to specimen thickness and is relatively unpredictable. Therefore, the practical implication is that one must design on the basis of elastic limit for freestanding, monolithic plates of nanocrystalline Ni from this geometrical regime when loaded in tension, with minimal capability for plastic flow to be expected. Moreover, it can also be concluded that work to improve the mechanical reliability of these materials should be focused primarily upon surface defects, namely improved process control to increase the overall plate thickness uniformity over the entire sample surface and to minimize the formation of surface asperities such as hydrogen pits, nodular deposit growth, etc.
Ductility

In contrast, the specimens in the 0.1 – 1.25mm thickness regime were far more reliable with a β value of 5.9. This sub-set of data is the central region in the Figure 4-6(a) Weibull plot and corresponds to the following fracture morphology: oblique fracture spanning the entire gauge width and transitioning to fully flat fracture with increasing thickness in a manner nearly

Figure 4-6 (a) Two-parameter Weibull fit to strain-to-fracture data from nanocrystalline Ni specimens varying thickness from 0.030 to 2.5mm; (b) schematic diagram depicting the superposition of the geometrical / surface and volume flaw effects that control the tensile strain-to-fracture variability of electrodeposited nanocrystalline Ni.
Ductility

identical to that previously observed with cold worked steel [22] and cold-worked Al [23], see Figure 4-7. Here the plate ductility is less sensitive to surface flaws as the transition from plane stress to plane strain deformation proceeds. The Weibull slope in this region represents the region of highest material reliability explored in the present study.

![Figure 4-7](image)

**Figure 4-7** Photographs of the gauge sections of fractured tensile test coupons from (a) the current study (0.5mm-thick), (b) cold rolled steel [22], and (c) cold rolled Al [23], illustrating the 55° fracture angle resulting from localized necking deformation [24].

On the other end of the thickness spectrum, data pairs from only five samples from the high thickness (>2mm) regime were unfortunately not sufficient to calculate a trustworthy Weibull shape parameter, but the drop-off in reliability is nevertheless apparent at the right-hand side of Figure 4-6(a) where this data has been plotted. In this geometrical regime, the specimen size-dependent material behaviour is similar to that observed with engineering ceramics: the larger
Ductility

the specimen, the greater the probability of a critical “ductility controlling” flaw, and the less ductile it is likely to be.

This superposition of the geometrical / surface and volume flaw effects that control the achievable tensile elongation of this electrodeposited material system is captured in schematic form in Figure 4-6(b). Here the reliability of the tensile strain-to-fracture data has been arbitrarily represented on the ordinate axis as a function of sample thickness. Thin samples exhibit highly localized deformation behaviour with ultimate fracture being governed by surface flaws and inhomogeneous plate thickness effects. The reliability increases with sample thickness until volume artifacts associated with the electroforming process begin to dominate. One implication of this behaviour is that the region of highest reliability in Figure 4-6(b) can very likely be extended to much higher thickness values (with a commensurate increase in overall achievable tensile elongation as per Equation (1-10)) via further improvements in electroforming processing flaw elimination. In other words, it would be reasonable to expect that nanocrystalline Ni plates with $A_o^{1/2}/L_o$ values that exceed approximately 0.04 mm/mm and produced using a process free of gross volume defects would predictably follow a relationship of the form of Equation (1-10). More importantly, as depicted in Figure 4-6(b), it is anticipated that such processing improvements might also increase the overall mechanical reliability in tensile loading, manifested in even higher Weibull shape parameters than those observed in the present study.

In conclusion, it is apparent from an examination of Figure 4-6 that, as compared to the 0.1 – 1.25mm thickness range, one can expect much less predictability in the tensile ductility of either
Ductility

extremely thin monolithic plates of electrodeposited nanocrystalline Ni where the samples are highly sensitive to the presence of surface flaws or in extremely thick (greater than approximately 2mm) samples where the presence of critical ductility controlling volume flaws during lengthy electroforming runs may become significantly more problematic.

Unfortunately, due to sample availability, it is difficult to better define the reliability regions on the basis of thickness. Most notably, more samples from the 0.2 to 0.5mm and 1 to 2mm thickness regimes would be required to do so. Nevertheless, based upon the data in-hand, it can be concluded that if monolithic plates of nanocrystalline Ni electroformed from a process similar to that of the present study are to be used in structural applications with tensile loading perpendicular to the deposit growth direction, 0.1 to 1-2mm is the most reliable thickness regime as indicated by tensile strain-to-fracture statistical variability.

Optical micrographs of representative nanocrystalline Ni samples after fracture spanning the entire range of specimen thicknesses are shown in Figure 4-8. The thinnest samples showed fracture along an oblique plane inclined at 55° with respect to the loading axis, gauge width reductions of approximately 2% and gauge thickness reductions of approximately 30 to 45% (Figure 4-8(a)). This localized necking mode was predominant for the specimens with a width-to-thickness ratio (w/t) greater than 8 (Figures 4-8(a),(b)). On the other hand, the thicker samples showed a transition towards diffuse necking. In particular, the specimens with a width-to-thickness ratio less than 8 exhibited flat fracture after necking down symmetrically around the section normal to the loading direction (Figures 4-8(c),(d)), with the thickest samples (Figures 4-8(d)) exhibiting gauge width reductions of approximately 15% and gauge thickness reductions of
Ductility

Figure 4-8 Optical micrographs (left) of the gauge section of representative specimens illustrating the transition in failure mode with increasing sample thickness (t) paired with SEM images (right) of the corresponding fracture surfaces: (a) <0.1mm, (b) 0.1 – 0.5mm, (c) 0.8 -1mm, (d) 2-2.5mm. The gauge width (w) of each specimen shown is approximately 6.3mm. Grain size = 25 nm.
Ductility

approximately 30%. The samples of the present study therefore exhibited varying amounts of localized and diffuse necking depending on the sheet thickness. These observations are consistent with the fracture behaviour of wide, flat tensile specimens cut from cold worked steel and Al sheet (Figure 4-7) and ultrafine-grained Cu produced by equal-channel angular pressing [9]. As the gauge width-to-thickness ratio increases, there is increased restraint in the width direction such that the contribution of thickness versus width strain to the measured linear extension becomes increasingly asymmetrical and this geometrical constraint plays an important role in the development of the neck [21]. Further commentary on the plastic instability of wide flat tensile specimens may be found in [22,24].

Higher magnification SEM examination of the nanocrystalline Ni fracture surfaces (see Figure 4-8, right-hand side) revealed dimpling indicative of localized ductile plastic flow for all specimens examined, regardless of geometry. The fact that all samples studied exhibited such similar signs of local plasticity, independent of whether the macroscopic failure mode was brittle or ductile in appearance, supports the view that the observed dependence of overall ductility on plate thickness is a mechanics effect associated with the size of the deformation zone relative to the plate thickness as the stress state transitions away from combined diffuse / localized necking and towards predominantly localized necking with decreasing specimen thickness. Also of interest in Figure 4-8 is the observation that the dimples increase in size with plastic strain sustained before fracture. This correlation substantiates the progressive void coalescence aspect of the underlying plastic deformation mechanism(s) [e.g. 25] that ultimately results in dimple formation upon fracture.
Ductility

4.3.3 Intrinsic Ductility

To restrict study to a unimodal failure sample set of high mechanical reliability as per Figure 4-6 and minimize the geometry effect in any further considerations, a statistically significant number of 116 specimens were tested. Samples of fixed thickness were cut from relatively thick (approximately 1mm) monolithic nanocrystalline Ni-based electrodeposits produced using a steady state electroforming process. This thickness regime was also selected because the gauge width-to-thickness ratio was sufficiently low (≤8) to ensure relatively symmetrical necking along a section normal to the loading direction, as discussed earlier. As described in Chapter 3, Fe alloying was implemented as a means to broaden the range of grain sizes available for study. XRD line broadening measurements on all samples and TEM analysis of selected samples was used to determine that the tests encompassed an average grain size range of approximately 10nm to 80nm. Figure 4-9 contains stress-strain curves from representative nanocrystalline samples from this study alongside coarse-grained pure Ni benchmarks. It should be noted that solute hardening in the electrodeposited Ni-Fe system is known to be small compared with grain size hardening [26]. In other words, the significant strengthening behaviour apparent from Figure 4-9 is primarily a grain size effect.
Ductility

**Figure 4-9** Representative tensile engineering stress-strain curves with average grain sizes and compositions provided in the legend. All samples electrodeposited except for the Ni-200 standard.

The Weibull plot of the strain-to-fracture data from all 116 tensile specimens is shown as crossed symbols in Figure 4-10 alongside the data from the specimens of varying thickness discussed earlier (shown as squared symbols) for comparative purposes. Upon examination of the 116 data pair Weibull fit, the first conclusion that can be drawn is that the use of the Equation (4-1) is sound, with no obvious curvature or marked cusps in the data. Typically, concave curvature in a Weibull plot is a clue to indicate that the three-parameter Weibull should be used instead of the two-parameter [27]. This is not the case for the analysis in question; hence the selection of the two-parameter Weibull distribution to fit the data is considered valid. Secondly, the Weibull slope of the 116 specimens of constant thickness ($\beta = 6.4$) is similar to that of the 0.1 – 1.25mm thickness regime ($\beta = 5.9$) as discussed earlier. This is to be expected since the failure mode and processing method of the 0.1 – 1.25mm thick subset of samples is similar to that of the 1mm-thick specimens.
Figure 4-10 Two-parameter Weibull fit to strain-to-fracture data illustrating the differences in statistical variability between the samples of approximately 1mm thickness (crosses) and the samples of varying thickness from 0.030 to 2.5mm (squares).

From the perspective of reliability analysis and the design of reliable components, the 116 data pair set in Figure 4-10 is of practical interest because it indicates the strain at which a given percentage of samples will fail under quasi-static tensile loading in conformance with ASTM standard E8. Weibull coined these values the “B lives” [28]. For instance, the B1 life for this particular material data set is approximately 2.2%, which implies that 1% of the samples will fail by the time they reach 2.2% elongation in tension. Similarly, the Weibull scale parameter or characteristic strain-to-fracture, $\eta$, denotes the strain at which 63.2% of the samples have fractured and is commonly used in Weibull analyses because its value is independent of the slope $\beta$ [27]. For this particular data set $\eta = 6.38\%$ strain-to-fracture.

Following the Weibull analysis, an examination of the achievable maximum uniform plastic strain and non-uniform (necking) strain values for all 116 tensile tests was carried out. As seen
Ductility

in Figure 4-11, it was found that the achievable non-uniform strain values recorded from the point of ultimate tensile stress, $\sigma_{UTS}$, until final fracture exhibited considerable variability ($\beta = 2.3$) across the 116 sample set, indicating that the processes of damage development during necking are strongly sensitive to the sample-to-sample defect and geometrical variations described earlier. On the other hand, the corresponding maximum uniform plastic strain values were relatively constant at 4.3% ($\beta = 11.3$).

![Histogram of uniform and non-uniform strain](image)

**Figure 4-11** Maximum uniform plastic and non-uniform strain distributions for 116 nanocrystalline Ni-based specimens of equivalent geometry and spanning average grain size values from 10 to 80nm.

Figure 4-12 contains the same data re-plotted as a function of 0.2% offset yield stress, used as the abscissa because it represents the intrinsic resistance to the onset of plastic deformation of the specimens examined and serves as a proxy for grain size as per the Hall-Petch relationship. The observation of relatively constant maximum uniform plastic strain holds true for this large set of samples despite a relatively broad dispersion in grain size and associated yield strength. This is somewhat surprising given that microstructural refinement typically results in increasingly
limited dislocation storage capacity in the grain interiors of polycrystalline metals, hindering their ability to strain harden.

Figure 4-12 Maximum uniform plastic strain plotted as a function of yield strength which serves as a proxy for grain size as per the Hall-Petch relationship.

For conventional coarse-grained materials, the manifestation of this progressively inhibited strain hardening capacity with increased grain refinement is that the achievable maximum uniform plastic strain also scales with grain size. Bouaziz [29] and Massart and Pardoen [30] have studied this effect using data recorded on pure Fe, single phase ferritic steels and interstitial free steels with grain sizes in the range of 150 to just below 0.1µm and their key findings have been included in Figure 4-13. Their results indicated that the maximum achievable uniform plastic strain tended to diminish throughout this microstructural range, and began to plateau with grain refinement below 0.8µm. Unfortunately, extrapolation into the nanocrystalline regime was not possible with the aforementioned steels. The present study suggests that there is indeed a plateau in the maximum achievable uniform plastic strain for grain sizes in the range of 10-80nm.
To further explore this effect, the strain hardening capacity of the nanocrystalline specimens, \( h = \sigma_{UTS} / \sigma_Y \), has been plotted in Figure 4-14. It can be seen that the strain hardening capacity was found to decrease with decreasing grain size, as might be expected from the behaviour of conventional coarse-grained polycrystalline materials. Yet despite this correlation, the hardening capacity has no apparent impact on the intrinsic ductility as measured by uniform plastic strain. Such differences in strength parameters among the tested samples have made the observation of constant maximum uniform plastic strain for this large sample set even more significant.
In ductile polycrystalline metals, the onset of plastic instability may be considered a signpost for the beginning of micro-damage formation followed by pronounced strain localization as the sample is deformed beyond the point of peak tensile loading. In coarse-grained materials, such damage usually takes the form of voids that typically develop at the interfaces between second phase particles and the matrix material, or at the grain boundaries. For the present case, the synthesis conditions are such that damage formation originating primarily from second phase particles is unlikely. On the other hand, the underlying physical processes that govern the plastic flow, damage development, and subsequent fracture of nanocrystalline materials are primarily grain boundary- and/or triple junction-mediated, see Figure 4-15(b) [31].
Ductility

Figure 4-15 Ductile fracture in nanocrystalline materials that occurs through formation of nanocracks, their transformation into pores, growth of pores and formation of local necks between large pores [31].

In the case of macroscopically “brittle” fracture, for instance, small-scale damage takes the form of nanovoids that nucleate and converge at the crystal interfaces, ultimately resulting in brittle,
intergranular fracture. On the other hand, if plastic flow and diffusion are intense in the proximity of the interfaces, the as-formed flat interfacial nanovoids gradually transform into pores, and with continued external loading, these pores progressively coalesce to form the dimples that we ultimately observe on the fracture surfaces of macroscopically “ductile” specimens, e.g. Figure 4-8. In other words, regardless of whether the macroscopic failure mode is “ductile” or “brittle”, the first stage of nanocrystalline material damage formation remains the same: localized interfacial decohesion leading to the formation of nanovoids situated at the grain boundaries and/or triple junctions [31]. While the specific physical mechanisms that contribute to deformation-induced damage nucleation and growth in ductile nanocrystalline materials are currently a matter of intense debate [32-34], the present results indicate that, within the grain size range of 10 to 80nm, this interfacial damage formation seemingly does not strongly depend on grain size nor bulk material strength (as governed by grain size) but is instead a strain-controlled phenomenon that can and would be better defined by a critical plastic strain, namely the maximum uniform plastic strain level.

4.4 Summary and Conclusions

1) The impact of electroforming process control on both the absolute value and variability of achievable tensile elongation is strong. High variability in tensile strain-to-failure was seen in samples cut from plates where more defects originating from the process were thought to have formed in the electrodeposit. On the other hand, samples originating from a more strictly controlled electroforming process were not only more ductile overall, but were more consistent from a sample-to-sample tensile strain-to-failure perspective.
2) The effect of specimen thickness on achievable tensile elongation was studied via fractography and Weibull distributional analysis of plastic strain-to-failure data of tensile specimens taken from a set of pure nanocrystalline Ni plates of varying thickness between 0.025 and 2.5 mm. As compared to the 0.8-1.25 mm thickness range, one can expect much less predictability in the tensile ductility of either extremely thin monolithic plates of electrodeposited nanocrystalline Ni where the samples are highly sensitive to the presence of surface flaws or in extremely thick (greater than approximately 2 mm) samples where the presence of critical ductility controlling volume flaws during lengthy electroforming runs becomes significantly more problematic.

3) The observed dependency of nanocrystalline Ni tensile ductility on sample thickness was compared to that of a previous study [21] performed using common engineering metallic materials encompassing a broad range of mechanical properties. All samples of large cross-sectional gauge area followed Unwin’s Equation (1-10). However, it was found that, regardless of the material studied, Unwin’s equation has a tendency to break down for smaller samples exhibiting a $A^{1/2}/L$ value below approximately 0.04 mm/mm wherein neck development becomes increasingly geometry/surface-flaw sensitive with decreasing thickness. Hence, it is concluded that artifact-reduced electrodeposited nanocrystalline materials behave in a manner similar to other conventional engineering materials with respect to the dependence of tensile ductility on specimen shape.

4) Tensile necking elongation in electrodeposited nanocrystalline materials obeys similar processing quality and geometrical dependencies as in conventional engineering metals.
Ductility

5) Unlike conventional engineering metals, intrinsic ductility (as measured by maximum uniform plastic strain) is unexpectedly independent of microstructure over the grain size range 10-80nm. This indicates that the underlying physical processes of grain boundary-mediated damage development are strain-oriented phenomena that can be best defined by a critical plastic strain regardless of the strength of the material as a whole.

6) The “paradox” between extremely low values of macroscopic elongation-to-fracture in tension and microscopic ductile fracture surfaces in nanocrystalline materials [35] is mainly a mechanics (geometry) effect.

7) The prediction of ductility and/or toughness properties using thin samples can be risky and it is better to carry out mechanical testing on the scale and in the loading mode intended for component application than to extrapolate based upon material availability. This sensitivity of tensile elongation to specimen geometry is one of the factors that led Dieter to conclude that, “At our present degree of understanding, ductility is a qualitative, subjective property of a material” [10].

4.5 References


Ductility


Ductility

Chapter 5
Hardness-Strength Relationships

The key findings contained in this chapter were previously presented in the following refereed article: I. Brooks, P. Lin, G. Palumbo, G.D. Hibbard, U. Erb, “Analysis of hardness–tensile strength relationships for electroformed nanocrystalline materials”, Materials Science and Engineering A 491 (2008) 412.

5.1 Introduction

A good understanding of the relationships between the hardness and tensile properties of materials is of considerable importance for several reasons. First, reliable hardness-strength correlations allow for rapid overall mechanical property evaluations using fast and inexpensive hardness testing instead of elaborate tensile testing. Second, in contrast to tensile tests, the hardness of a material can be measured non-destructively in situ on fully assembled components and devices, thus allowing for structural integrity tests in service, for example in elevated temperature applications. Third, during the development of new materials, hardness testing is often the only choice when materials are available in relatively small quantities, insufficient to perform extensive tensile testing, for example as per ASTM standards. The latter was clearly the case during the development over the past two decades of the majority of the many nanocrystalline metals, alloys and composites made using synthesis methods such as inert gas condensation, vapour phase deposition, electrodeposition, mechanical attrition or crystallization of amorphous precursors. Most previous studies presented mainly hardness data. Whenever tensile properties were measured, they were usually obtained on subsize specimen geometries not in accordance with ASTM standard tests (e.g. ASTM E8). So far, however, no systematic
Hardness-Strength Relationships

studies have been carried out on nanocrystalline metals to investigate the relationship between their hardness and critical mechanical properties obtained from the tensile test.

To reiterate the equations introduced in Chapter 1, one widely used assumption in the nanomaterials literature is that there is a relationship between the hardness, $H$, and yield strength, $\sigma_y$, of the following form:

$$H \approx 3 \cdot \sigma_y \quad (1-5)$$

Both experimental studies [e.g. 1-4] and modeling efforts [e.g. 5-10] have made extensive use of this relationship, however generally without giving any specific reasoning or references to substantiate this claim. One particular modeling study [11] applied, without any justification, the following relationship when converting previously published hardness values to yield strength data:

$$H \approx \sigma_y \quad (1-8)$$

On the other hand, for conventional coarse-grained polycrystalline materials, most relationships describe the proportionality of hardness to ultimate tensile strength, $\sigma_{UTS}$, rather than tensile yield strength as used in Equation (1-5). An analysis of ASM handbook [12] hardness and ultimate tensile strength data for a broad range of steels shows (Figure 5-1) that, over a wide range of strengths, there is a fairly good relationship of the following form:

$$H_v \approx 3 \cdot \sigma_{UTS} \quad (1-7)$$

where $H_v$ is the Vickers hardness.
The relationship given in Equation (1-5) has also previously been discussed for coarse-grained polycrystalline materials [13,14]. However, as pointed out by Ashby and Jones [13] in their derivation, this relationship is only valid for materials that do not work-harden, i.e. for ideally plastic materials. In other words, Equation (1-5) should only be used for cases in which the strength does not change when the hardness indenter is pushed into the surface of the materials. When a material exhibits work hardening, the proportionality constant, also known as the “constraint factor”, of 3 is no longer applicable and a correction factor must be applied [13]. Such a scenario has important practical design engineering implications since the continued use of Equation (1-5) for work hardening materials would effectively result in a potentially significant over-estimation of the material strength.

Figure 5-1  Vickers hardness as a function of ultimate tensile strength data for carbon and alloy steels in the annealed, normalized, and quenched-and-tempered conditions [12].
In view of i) the lack of any clear hardness-tensile strength relationships for nanomaterials and ii) the apparent contradiction between the established relationship (1-7) for coarse-grained polycrystalline materials and the wide-spread application of Equation (1-5) for nanomaterials, this study examines the hardness - tensile data relationships for a large number of electrodeposited nanocrystalline nickel and cobalt-based materials.

5.2 Experimental Details

Data was extracted from all material lots for which Vickers hardness and tensile tests were carried out on the same test pieces or lots of materials. The data set used for this analysis comprises a total of 198 individual tensile / hardness tests and includes both materials synthesized as part of the current study along with data collected from previous members of the same research group. With respect to experimental details the following should be noted:

i) All materials were synthesized using the electrodeposition method [15,16]. For pure metals, the plating bath contained only one metallic species (e.g. Ni, Co), while alloys were deposited from solutions containing two or more ionic species (e.g. Ni-Mo, Ni-Fe, Co-P). Nanocrystalline Ni-SiC composites were made from a bath containing sub-microcrystalline SiC particles in the plating solution [17]. All metals were deposited onto Ti cathodes from which they were subsequently stripped by mechanical means to yield free-standing sheets of varying thicknesses (0.1 – 3.4 mm) to be cut into suitable specimens for hardness and tensile testing.
ii) The grain sizes of all materials were determined from X-ray line broadening measurements using the Scherrer approach [18]. For many of the deposits the grain size was also determined from dark field transmission (TEM) electron micrographs. The grain sizes in the materials chosen for the current analysis ranged from 80 nm for some of the pure Ni deposits to 7 nm for the smallest grain sized Ni-Fe deposits. Most of the grain sizes were in the 10-40 nm grain size range.

iii) Hardness measurements were performed using the Vickers microhardness technique by measuring the averages of at least 10 indentations each at several locations on each electrodeposit. The applied loads were 50-200 g depending on the deposit thickness.

iv) Tensile testing was performed on samples with varying gauge dimensions (Table 5-1), which depended largely on the overall sizes of the available electrodeposit sheets. Most of the tensile specimens were based upon ASTM standard E8M-01. However, some of the earlier tests used considerably smaller samples with 5 mm gauge length. The range of gauge volumes was from 2.5 to 535 mm³. The majority of tensile tests were carried out at a strain rate of 5x10⁻⁴ s⁻¹ although some measurements were performed at other strain rates. The range of 5x10⁻⁵ to 2.5x10⁻³ s⁻¹ encompasses all the test results analyzed in the present study. All samples were tested to fracture so that yield strength, \( \sigma_Y \) (0.2% offset), ultimate tensile strength, \( \sigma_{UTS} \), and elongation to fracture, \( \varepsilon_f \), could be recorded.

| Table 5-1 Typical gauge dimensions for tensile tests. |
|----------------|----------------|----------------|
| Width [mm]     | Length [mm]    | Thickness [mm] |
| 2.5-3.0        | 5              | 0.1-0.3        |
| 6.0-6.5        | 25.0-59.5      | 0.1-3.4        |
v) Some of the data for Ni, Ni-SiC and Co have been published elsewhere [19-21] and are included here for the purpose of establishing statistically meaningful trends. However, most of the data was collected as part of the current study.

vi) Many of the early tensile samples failed with relatively low elongations to fracture ($\varepsilon_f < 2\%$), likely as a result of processing flaws (hydrogen pit holes, codeposited bath impurity particulates, other surface flaws) introduced into the materials during electrodeposition in a small-scale plating system. However, as discussed in Chapter 4, with improvements of the electrodeposition process upon scaling up from 1L to 40L tanks, for instance, much higher ductility values were obtained.

vii) Figure 5-2 contains typical engineering stress-strain curves for some of the samples that were considered. As discussed in Chapter 4, the elongation of the specimens synthesized as part of the current study typically fell within the range of 5 to 12%. However, some of the coarser-grained (~80nm) nanocrystalline materials from earlier studies exhibited elongation-to-fracture values as high as 15-20%.

viii) The strain hardening exponents for a number of the samples were calculated in conformance with ASTM standard E646-00 and all fell within the range of 0.07-0.20. As will be discussed in the following sections, the tendency for electrodeposited nanocrystalline materials to exhibit work hardening behaviour impacts their hardness-tensile strength relationships.
5.3 Results and Discussion

5.3.1 Strength Hardness Correlations

In Figure 5-3 Vickers hardness, $H_V$, has been plotted as function of 0.2% offset yield strength, $\sigma_y$, for each of the 198 electrodeposited nanocrystalline specimens that were analyzed for this study. In general, there is no simple correlation between $H_V$ and $\sigma_y$. In addition, the widely used hardness-strength relationship given by Equation (1-5) with a proportionality constant of 3 has been superimposed onto Figure 5-3, and it can be readily observed that there exists no good fit with the recorded experimental data. In general, the material 0.2% offset tensile yield strength is always substantially less than 1/3 its hardness. The practical engineering implication of this finding is that strength estimates made solely on the basis of indentation data using Equation (1-
5) significantly over-estimate the actual yield strength of electrodeposited nanocrystalline materials.

![Hardness-Strength Relationships](image)

**Figure 5-3** Hardness as a function of tensile yield strength measured for a wide range of electrodeposited nanocrystalline materials.

In Figure 5-4, hardness, $H_V$, has instead been plotted as a function of ultimate tensile strength, $\sigma_{UTS}$, for this same set of materials. Again, $H_V$ does not correlate very well with $\sigma_{UTS}$. When Equation (1-7) is superimposed (dotted line) onto the experimental data, it is apparent that while the $H_V = 3\cdot\sigma_{UTS}$ linear relationship holds true for many of the samples, there is also a large number that deviate quite significantly from Equation (1-7). The cause of this deviation will be elucidated in section 5.3.4 of this chapter.
5.3.2 Hardness to Strength Ratio as a Function of Grain Size

In an attempt to reveal whether the discrepancy between Equations (1-5) and (1-7) and the recorded experimental mechanical property data is a result of the nanocrystalline microstructure, the ratios of $H_V/\sigma_Y$ and $H_V/\sigma_{UTS}$ have been plotted as a function of grain size in Figure 5-5. From Figure 5-5(a), it is readily apparent that over the entire range of alloy systems and grain sizes studied (7-80nm), the scatter in the $H_V/\sigma_Y$ data was consistently broad, ranging in magnitude from less than 4 to as high as 8.6. Hence, the degree of refinement of the microstructure over the range of grain sizes studied is likely not the origin of the marked deviation from Equation (1-5).
Figure 5-5 The ratio of hardness to (a) yield strength, and (b) ultimate tensile strength as a function of grain size, as measured by XRD line broadening.

Similarly, for the case of Figure 5-5(b), in which the ratio of $H_v/\sigma_{UTS}$ has been plotted as a function of electrodeposit grain size, the deviation from Equation (1-7) does not appear to depend to any extent upon the degree of crystal refinement. In other words, processing in
nanocrystalline form, in and of itself, does not appear to be the reason why the mechanical property data analyzed herein does not correlate well with either Equation (1-5) or (1-7).

5.3.3 Hardness to Strength Ratio as a Function of Gauge Volume

As discussed in Chapter 4, a satisfactory description of the overall intrinsic microstructure-dependent tensile response of nanomaterials has been hampered by confusion in the literature surrounding the effect of sample geometry on the shape of the stress-strain curve. Both Dalla Torre et al. [22] and Fan et al. [23] observed a significant drop in ultimate tensile strength with increasing sample size, for instance. This behaviour was rationalized as a manifestation of the “weak link concept” of probabilistic fracture mechanics [24] whereby a larger sample will exhibit a greater likelihood of possessing a dangerous critical defect within the gauge volume during tensile testing. Given this context, the impact of tensile gauge volume on the hardness-strength ratios was examined, and the results are presented in Figure 5-6. In Figure 5-6(a), it is evident that there exists no clear correlation between $H_{V}/\sigma_{Y}$ and tensile gauge volume for this relatively large sample set that encompasses a very broad range of gauge volumes (2.5 to 535 mm$^3$). Hence, it can be concluded that the breakdown of Equation (1-5) for electrodeposited nanomaterials cannot be attributed solely to sample size effects.

Similarly, the experimentally recorded $H_{V}/\sigma_{UTS}$ data is presented as a function of tensile test specimen gauge volume in Figure 5-6(b). In this case, the breadth of the $H_{V}/\sigma_{UTS}$ data does diminish with increasing gauge volume. However, as mentioned earlier, most of the specimens corresponding to the smaller gauge volume data points in Figure 5-6 were cut from very thin foils. As discussed in Chapter 4, thin tensile samples possess a general tendency to fracture early
on in the tensile test and this represents a potentially significant source of error in the
determination of the intrinsic tensile properties of the material. These samples aside, no
meaningful size effect trend to help explain the observed deviation from Equation (1-7) was
derived from Figure 5-6(b).

Figure 5-6 The ratio of hardness to (a) yield strength, and (b) ultimate tensile strength as a
function of grain size, as measured by XRD line broadening.
5.3.4 Relationship of Hardness to Ultimate Tensile Strength

In order to reveal how hardness correlates to ultimate tensile strength for the materials examined in the present study, it is first instructive to summarize the conclusions drawn by Tabor concerning the proportionality between indentation hardness and ultimate tensile strength for the Ni, Fe, Cu and Al-based materials employed in his seminal work on the topic [25]:

1) To a first approximation, the ratio of the hardness to the ultimate tensile strength is independent of the metal under consideration: it depends primarily upon the degree of work hardening of the metal i.e. on the work hardening exponent \( n \) or the Meyer hardness [25] coefficient \( m \), where \( m = n + 2 \);

2) For strain hardening materials, the following expression can be used to describe the hardness-strength relationship [26]:

\[
\sigma_{UTS} = \frac{H_v}{2.9} \left[ 1 - (m - 2) \right] \left[ \frac{12.5(m - 2)}{1 - (m - 2)} \right]^{(m-2)}
\]  

(5-1)

where \( m = n + 2 \).

In order to illustrate the magnitude of the strain hardening effect on \( \frac{H_v}{\sigma_{UTS}} \), Equation (5-1) has been plotted in Figure 5-7 and it can be readily observed that the \( \frac{H_v}{\sigma_{UTS}} \) ratio lies in the range of 2.9 to 3.3 within the domain of \( n \leq 0.20 \) that is applicable to the electrodeposited nanomaterials considered here. In other words, based upon Tabor’s study of strain hardening metals, one would expect \( H_v = 3 \cdot \sigma_{UTS} \) to hold reasonably true for the electrodeposited materials analyzed in the present study owing to the fact that their strain hardening exponents are less than or equal to
Hardness-Strength Relationships

a value of 0.20. However, as was demonstrated in Figure 5-4, this was not the case for many of the specimens tested.

![Graph showing the influence of the material strain hardening exponent on hardness-to-strength ratios](image)

**Figure 5-7** The influence of the material strain hardening exponent $n$ on the calculated ratios of hardness to ultimate tensile strength (using the model of Tabor [25]; Equation (5-1)) and hardness to yield strength (using the models of Cahoon et al. [30] (Equation (5-2)) and Gao [28] (Equation (5-3))).

In light of the fact that electrodeposited nanocrystalline materials display work hardening behaviour and conventional Vickers microhardness indentations generally involve substantial, albeit non-uniform, plastic material deformation with a “representative” level of strain that is commonly estimated to be equivalent to approximately 8% tensile strain [25], it is reasonable to presume that achievable material tensile ductility could potentially impact the validity of Equation (1-7). In order to explore this effect, $H_V/\sigma_{UTS}$ has been plotted as a function of tensile elongation to failure, $\varepsilon_f$, in Figure 5-8(a). It can be seen that the more brittle nanomaterials exhibit $H_V/\sigma_{UTS}$ ratios in the range of 4-8, while with increasing elongation this value approaches 3. This behaviour suggests that, for those specimens exhibiting elevated $H_V/\sigma_{UTS}$ ratios, tensile sample fracture before the onset of necking instability at peak tensile load has occurred and the
observed deviation from Equation (1-7) is more pronounced for the more brittle materials as compared to those ductile enough to undergo a considerable amount of discernible strain hardening behaviour before a true $\sigma_{UTS}$ is reached. In other words, the closer the material comes to failing by tensile necking instability, the more reliable Equation (1-7) becomes.

![Graph](image)

**Figure 5-8** The ratio of hardness to ultimate tensile strength as a function of tensile elongation for (a) all specimens analyzed, and (b) only specimens displaying a distinct necking instability failure mode.
In order to substantiate this hypothesis, a careful examination was made of stress-strain curves, and a subset originating from tensile specimens that clearly demonstrated plastic deformation beyond the distinct onset of necking instability was selected. The $H_V/\sigma_{UTS}$ ratios for these samples are presented in Figure 5-8(b) and it can be seen that none deviate significantly from Equation (1-7). In addition, the fact that these samples encompass a broad range of $\varepsilon_f$ from 6% to greater than 15% reinforces the importance of deformation until necking instability as opposed to total achievable elongation to failure per se. It can therefore be concluded that the $H_V = 3\cdot\sigma_{UTS}$ (Equation (1-7)) expression is indeed a reliable predictor of the relationship between hardness and strength for electrodeposited nanocrystalline materials, provided the material is ductile enough to sustain tensile deformation before reaching $\sigma_{UTS}$.

### 5.3.5 Relationship of Hardness to Yield Strength

The relationship between hardness and yield strength was analyzed in a similar fashion in order to rationalize the marked deviation of Figure 5-3 data from Equation (1-5). Again, it is instructive to reiterate the conclusions drawn from previous studies on conventional coarse-grained metals concerning the relationship between indentation hardness and tensile yield strength that can be briefly summarized as follows:

1) hardness is an increasing function of yield strength, and for ideally plastic materials ($n = 0$), hardness is a linear function with a proportionality constant of ~2.8-3.0 [27];

2) for strain hardening materials ($n > 0$), the indentation process itself induces an increase in the measured yield or flow stress response [25];
3) in such instances \((n > 0)\), it has been found that work hardening has a stronger influence on the force required to move the indenter for materials that exhibit a smaller elastic strain capacity (small yield strength/elastic modulus ratio) than for materials that are more resistant to the onset of plastic flow (high \(\sigma_y/E\) ratio) \[28\];

4) thus, for so-called “elastic strain-hardening plastic” materials \((n > 0)\), hardness is a multiple function of \(\sigma_y, n,\) and \(E\). The implication for the practical application of hardness-yield strength relationships is that, for a given set of material elastic constants, there are multiple values of \(\sigma_y\) and \(n\) that can produce the same hardness value \[29\].

To illustrate the impact of material strain hardening capability on \(H/V/\sigma_Y\), two previously derived models constructed using completely different strategies were examined. Specifically, the model of Cahoon \textit{et al.} \[30\], which was derived in an empirical fashion and verified experimentally, was examined alongside the more recent model of Gao \[28\], which was derived theoretically by approximating the hardness indentation as a quasi-static expansion of an internally pressurized spherical shell of an elastic strain-hardening plastic material. In the first case, the proportionality constant of Equation (1-5) was calculated for a theoretical conventional coarse-grained polycrystalline metal using the following relationship that was derived by Cahoon \textit{et al.} \[30\]:

\[
\sigma_y = \frac{H_Y}{3}(0.1)^{m-2}
\]  

(5-2)

where the Meyer hardness coefficient \(m = n + 2\). In their derivation, the authors built upon the empirical framework of Tabor \[25\] and then fitted their expression with reasonable accuracy to experimental data for a number of alloy systems \[30\]. It is readily apparent from Figure 5-7, in which this simple empirical expression has been depicted schematically, that the material strain-
Hardness-Strength Relationships

hardening exponent exerts a strong influence on the hardness-yield strength ratio, with $H_v/\sigma_Y$ ranging from a value of 3 at $n = 0$ to nearly 6 when $n = 0.3$.

Owing primarily to the emergence of nanoindentation as a widely accepted material characterization method, the nature of the interaction between indentation hardness and other mechanical properties of solids has received increased scrutiny in recent years and the second model evaluated here is based on one such study. Specifically, Gao [28] addressed the tendency for expanding cavity models (ECM’s) of indentation to break down when applied to materials that strain harden by developing a modified ECM to describe the indentation deformation response of elastic strain-hardening plastic materials. He then used his theoretical framework to formulate the following hardness-yield strength relationship for conical/pyramidal indenters:

$$\frac{H}{\sigma_Y} = \frac{2}{3} \left[ 1 + \frac{3}{4} \left( \frac{1}{3 \sigma_Y \cot \alpha} \right)^n + \frac{1}{n} \left( \frac{1}{3 \sigma_Y \cot \alpha} \right)^n - 1 \right]$$

(5-3)

where $\alpha$ is the indenter half-angle ($68^\circ$ for a Vickers diamond indenter). Inspection of this expression reveals that, for a constant indenter geometry, the proportionality constant between $H_v$ and $\sigma_Y$ is controlled by the indented material characteristics described by $n, E$ and $\sigma_Y$ itself. In a fashion similar to Equation (5-2), this theoretical expression has also been plotted as a function of the material strain-hardening exponent, $n$, in Figure 5-7 and using two values of $\sigma_Y/E$ (0.004 and 0.009) that encompass the majority of the experimentally recorded tensile data used in the current analysis. Again, it is readily apparent that the magnitude of $H_v/\sigma_Y$ is strongly dependent upon the strain-hardening exponent and that this effect is stronger at smaller values of $\sigma_Y/E$. 
Equations (5-2) and (5-3) were then used to generate material yield strength estimates on the basis of experimentally recorded values of $H_V$, $n$, and $E$ for the same samples shown in Figure 5-8(b), i.e. the subset of samples that clearly showed necking instability, and the results are compared to those recorded from tensile testing in Figure 5-9. Upon comparison of the strength values estimated using the two models to those derived using Equation (1-5), it can be concluded that accounting for the influence of strain hardening on the hardness-yield strength relationship is critical if values that approximate those derived from tensile testing are to be expected. It is also evident from Figure 5-9 that the models of both Cahoon et al. and Gao can be used to approximate the yield strength of electrodeposited nanomaterials with reasonable accuracy for some of the samples, while stronger deviation from experimental data exists for others. It is probable that the origin of any deviation of the calculated $\sigma_Y$ values from those recorded in tensile testing is linked to nanomaterial deviation from simple power law hardening behaviour. Both models use power law hardening as a basic starting assumption, i.e. that the magnitude of $n$ accurately depicts the strain hardening characteristics of the specimen in question. In other words, as illustrated in Figure 5-7, both models are quite sensitive to the magnitude of $n$ and their ability to accurately predict material yield strength on the basis of indentation data is therefore strongly dependent upon the level of congruence in the magnitude of the strain hardening exponent $n$ and the actual strain hardening behaviour of the material.
5.3.6 Mechanical Property Data on Similar Materials from Other Sources

In order to assess the validity of the conclusions drawn from this data analysis, previously published mechanical property test data recorded using electrodeposited nanocrystalline material processed by laboratories other than our own was evaluated in a similar fashion. Ebrahimi et al. [2] presented hardness and tensile data taken from a number of electrodeposited pure Ni samples and the results for two typical samples with cathode to free surface cross-sectional grain size gradients from 206 to 97nm and 56 to 38nm, respectively, are presented in Table 5-2. It can be seen that the breakdown of Equation (1-5) is consistent with our own observations as discussed earlier. In addition, Equation (1-7) appears to be a fairly accurate approximation of the hardness-strength relationship for the samples produced and tested by Ebrahimi’s group. In a second study on pure nanocrystalline Ni using much finer-grained material, Dalla Torre et al. [22]
presented data that also corroborate this trend. In other words, the electrodeposited nanocrystalline Ni mechanical property data they reported confirm that a hardness-strength proportionality constant of 3 can only be used with confidence when the post-work hardened stress value i.e. the $\sigma_{UTS}$ is employed in the expression. In a third study, Giga et al. synthesized a range of Ni-W (13-20 at%) alloys, also via electrodeposition [31]. The specimens examined were all exceptionally fine-grained (5-20nm) and brittle (no $\varepsilon_f$ values were provided, but from the published curves it did not appear that any of the samples surpassed 1% tensile strain). Similar to our own observations on brittle deposits, the $H_V/\sigma_{UTS}$ ratio was found to be exceptionally high, ranging between 5.7 and 8.5. Overall, these three independent studies substantiate the important roles that material ductility and proper consideration of strain hardening behaviour play in the legitimacy of the hardness-strength relationships, and helps reinforce the view that caution should be paid whenever they are employed to describe the mechanical response of nanomaterials.

Table 5-2 Data from other sources.

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<th>Ref</th>
<th>Material</th>
<th>Sample</th>
<th>grain size (nm)</th>
<th>Gauge volume (mm$^3$)</th>
<th>$\varepsilon_f$ (%)</th>
<th>$H_V$ (GPa)</th>
<th>$\sigma_Y$ (MPa)</th>
<th>$\sigma_{UTS}$ (MPa)</th>
<th>$H_V/\sigma_Y$</th>
<th>$H_V/\sigma_{UTS}$</th>
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<td>4.3</td>
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<td></td>
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<td>3.7</td>
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<td>1091</td>
<td>4.4</td>
<td>3.4</td>
</tr>
<tr>
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<td>0.086</td>
<td>4 (pl)</td>
<td>6.0</td>
<td>1600</td>
<td>2040</td>
<td>3.8</td>
<td>2.9</td>
</tr>
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<td></td>
<td></td>
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<td>0.086</td>
<td>2.6 (pl)</td>
<td>5.5</td>
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<td>1820</td>
<td>3.9</td>
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5.4 Summary and Conclusions

1) Tensile and hardness data from 198 electrodeposited nanocrystalline Ni- and Co-based specimens of varying shape, composition, microstructure and quality were analyzed in order to reveal whether any of the established hardness-strength relationships in frequent use for conventional coarse-grained materials can be applied to this class of materials and, if so, to elucidate those circumstances under which they might be applied accurately.

2) The majority of the electrodeposited nanomaterials analyzed followed the $H_V = 3\cdot\sigma_{UTS}$ relationship. However, the most brittle specimens tended to diverge from the expected trend and, in some cases, did so quite significantly. Specifically, for brittle electrodeposited nanocrystalline materials, the experimentally measured $H_V/\sigma_{UTS}$ ratio ranged from ~4-8 and approached 3 with increasing tensile elongation. It was concluded that the $H_V = 3\cdot\sigma_{UTS}$ expression is a reliable predictor of the relationship between hardness and strength for electrodeposited nanocrystalline materials, provided the material is ductile enough to sustain tensile deformation until the onset of necking instability.

3) As it pertains to the nanomaterial $H_V/\sigma_Y$ ratio, the capacity of the material to exhibit strain hardening behaviour (as described in the present analysis by the magnitude of the strain hardening exponent $n$) appears to dictate the magnitude of the proportionality constant between hardness and yield strength. This is consistent with experimental observations and previously developed empirical and theoretical modeling of conventional coarse-grained metal systems. The widely used relationship $H_V = 3\cdot\sigma_Y$ was found to be inapplicable to this class of materials owing to the fact that they do not deform in an “ideally plastic” manner and instead exhibit
plastic deformation that is characteristic of strain hardening behaviour. This finding has important practical implications since the application of this commonly used expression results in potentially significant over-estimations of the intrinsic yield strength of electrodeposited nanocrystalline materials.

5.5 References

Hardness-Strength Relationships

Chapter 6
Conclusions

Conclusion #1
A great deal of work has been devoted to the study of nanocrystalline materials and their mechanical properties. However, some of the most important mechanical properties, such as achievable ductility and elastic modulus, are known to be highly sensitive to the presence of processing artifacts. This study demonstrated that electroformed specimens substantially reduced in defects such as hydrogen pitting, chemical contamination, and particulate contamination could be reproducibly synthesized through adoption of specific strategies such as steady state chemical control, fine particulate filtering, and improved feedstock chemical quality.

Conclusion #2
An inability in past studies to produce bulk quantities of nanocrystalline materials has prevented tensile testing according to standardized test protocols such as ASTM E8. Consequently, the persistent use of non-standardized miniature specimen geometries has resulted in considerable confusion concerning the intrinsic mechanical properties of nanocrystalline materials. It was found that processing artifact reduction and electrodeposit internal stress control in large 40L electroforming tanks enabled the systematic production of artifact-reduced 152mm x 152 mm plates of 1mm thickness and beyond. As a result, nanocrystalline materials could be tensile tested in conformance with ASTM E8. This had not been possible prior to this study.
Conclusions

Conclusion #3
Because the linear extension that may be sustained by a typical mechanical test specimen loaded in tension is not a deterministic material-specific property but instead reflects a distribution (size and orientation) of flaws present in the material in addition to the intrinsic material ductility and specimen size and shape dependencies, a thorough analysis of nanocrystalline material ductility required a statistically significant set of specimens. To this end, 161 specimens were tensile tested as part of this study. This large number of samples enabled a statistical evaluation of achievable ductility by Weibull distributional analysis.

Conclusion #4
The primary material “quality” criterion used throughout this work was achievable tensile elongation-to-fracture of multiple samples cut from each individual plate produced. It was found that the impact of electroforming process control on both the absolute value and variability of achievable tensile elongation was strong. In particular, high variability in tensile strain-to-failure was seen in samples cut from plates where more defects originating from the process were thought to have formed in the electrodeposit. On the other hand, samples originating from a more strictly controlled electroforming process were not only more ductile overall, but were more consistent from a sample-to-sample tensile strain-to-failure perspective.

Conclusion #5
The effect of specimen thickness on achievable tensile elongation was studied via fractography and Weibull distributional analysis of plastic strain-to-failure data of tensile specimens taken from a set of pure nanocrystalline Ni plates of varying thickness between 0.025 and 2.5mm. As
Conclusions

compared to the 0.8-1.25mm thickness range, much less predictability was observed in the
tensile ductility of either extremely thin monolithic plates of electrodeposited nanocrystalline Ni
where the fracture mode was highly sensitive to the presence of surface flaws. Similarly, less
predictability was observed in the tensile ductility of extremely thick (greater than approximately
2mm) samples where the presence of critical ductility controlling volume flaws during lengthy
electroforming runs may have become significantly more problematic.

Conclusion #6

The observed dependency of nanocrystalline Ni tensile ductility on sample thickness was
compared to that of a previous study performed using common engineering metallic materials
encompassing a broad range of mechanical properties. All samples of large cross-sectional
gauge area followed Unwin’s equation. However, it was found that, regardless of the material
studied, Unwin’s equation has a tendency to break down for smaller samples exhibiting a $A^{1/2}/L$
value below approximately 0.04 mm/mm as the neck development becomes increasingly
geometry/surface-flaw sensitive with decreasing thickness.

Conclusion #7

Tensile necking elongation in electrodeposited nanocrystalline materials obeys similar
processing quality and geometrical dependencies as in conventional engineering metals.

Conclusion #8

Unlike conventional engineering metals, intrinsic ductility (as measured by maximum uniform
plastic strain) was unexpectedly observed to be independent of microstructure over the grain size
Conclusions

range 10-80nm. This indicated that the underlying physical processes of grain boundary-mediated damage development are strain-oriented phenomena that can be best defined by a critical plastic strain regardless of the strength of the material as a whole.

**Conclusion #9**

The “paradox” between extremely low values of macroscopic elongation-to-fracture in tension and microscopic ductile fracture surfaces in nanocrystalline materials is mainly a mechanics (geometry) effect.

**Conclusion #10**

The prediction of ductility and/or toughness properties using thin samples can be risky and it is better to carry out mechanical testing on the scale and in the loading mode intended for component application than to extrapolate based upon material availability. This sensitivity of tensile elongation to specimen geometry is one of the main reasons why ductility remains a subjective property of a material.

**Conclusion #11**

Despite the widespread use of hardness testing of nanocrystalline materials as a proxy for strength testing, there was a persistent lack of clarity as to which hardness-tensile strength relationships could be reliably applied prior to this study. Data from a large number of 196 samples was evaluated. It was found that the majority of electrodeposited nanomaterials analyzed followed the $H_V = 3 \cdot \sigma_{UTS}$ relationship. However, samples that exhibited little tensile plasticity tended to diverge from the expected trend and, in some cases, did so quite significantly.
Conclusions

It was concluded that the $H_V = 3 \cdot \sigma_{UTS}$ expression is a reliable predictor of the relationship between hardness and strength for electrodeposited nanocrystalline materials, provided the material is ductile enough to sustain tensile deformation until the onset of necking instability.

Conclusion #12

As it pertains to the nanomaterial $H_V/\sigma_Y$ ratio, the capacity of the material to exhibit strain hardening behaviour appears to dictate the magnitude of the proportionality constant between hardness and yield strength. This is consistent with experimental observations and previously developed empirical and theoretical modeling of conventional coarse-grained metal systems. The widely used relationship $H_V = 3 \cdot \sigma_Y$ was found to be inapplicable to this class of materials owing to the fact that they do not deform in an “ideally plastic” manner and instead exhibit plastic deformation that is characteristic of strain hardening behaviour. This finding has important practical implications since the application of this commonly used expression results in potentially significant over-estimations of the intrinsic yield strength of electrodeposited nanocrystalline materials.
Chapter 7
Recommendations for Future Work

Recommendation #1

While significant advancements in the synthesis of bulk quantities of artifact-free nanocrystalline materials by electrodeposition have been made as part of this study, there is room for further improvement. In particular, there exists a need for even more processing artifact removal. This could conceivably be accomplished through a combination of ultrafine (<1µm pore size) filtering and further solution flow pattern optimization to ensure the complete absence of solid matter in the catholyte. In addition, the identification of a method to quantify the co-deposited anode particulate content would greatly assist in the development of a ductility-particulate concentration relationship for this material class, similar to that presented in Figure 1-16.

Recommendation #2

Another primary objective of this study was to explore the intrinsic ductility of electrodeposited nanocrystalline materials. While tensile testing in conformance with ASTM E8 is the most broadly accepted methodology to do so, there are other techniques that should be considered. Most notably, fracture toughness is another important measure of material ductility.

The plane strain fracture toughness, $K_{lc}$, of a metallic material refers to the crack-extension resistance under conditions of crack-tip plane strain in Mode I cracking and involves increasing-force tests of fatigue precracked specimens. In other words, the test provides information on the
intrinsic damage tolerance / sensitivity to pre-existing cracks in the material, as described by the $K_{lc}$ term, which is a geometry-independent property of the material. The procedure to measure $K_{lc}$ is provided in ASTM E399-09 [1]. In order to measure a trustworthy $K_{lc}$ value, the specimen thickness must be sufficiently large for plane strain loading conditions to be achieved. The following criterion is used to determine the minimum required sample thickness:

$$t \geq 2.5 \left( \frac{K_{lc}}{\sigma_Y} \right)^2$$

Equation (7-1) has been plotted in Figure 7-1 for materials varying between 800 and 1400 MPa yield strength. It may be appreciated that weaker (lower $\sigma_Y$) and tougher (higher $K_{lc}$) require thicker samples to achieve plane strain loading conditions.

**Figure 7-1:** Minimum specimen thickness required for trustworthy measurement of the plane strain fracture toughness, $K_{lc}$, of a material as per Equation (7-1).
Recommendations for Future Work

There have been relatively few attempts to measure $K_{IC}$ in nanocrystalline materials. One study by Hanlon *et al.* on electrodeposited nanocrystalline Ni indicated that the plane *stress* fracture toughness value for this material was $25 \text{ MPa} \cdot \text{m}^{-1/2}$[2]. Application of Equation (7-1) with $25 \text{ MPa} \cdot \text{m}^{-1/2}$ as the plane *strain* fracture toughness value and 1000 MPa as the material yield strength reveals that a minimum specimen thickness of 1.56 mm would be required to achieve plane strain deformation and thereby measure a trustworthy $K_{IC}$ value for that material.

As an aside to the present study, a very thick (~5 mm) plate of electrodeposited nanocrystalline Ni-15wt%Fe (~1300 MPa yield strength) was prepared and subjected to testing in conformance with ASTM E399-09. Part of the ASTM E399-09 standard specification is a protocol for testing for plane strain deformation and it was found that a condition of plane strain loading was *not* achieved for the 5mm-thick Ni-Fe sample. In other words, the 5mm specimen thickness of this particular material was insufficient to record a trustworthy $K_{IC}$ value. Application of Equation (7-1) with the aforementioned 5mm thickness and 1300 MPa yield strength values reveals that the plane strain fracture toughness value of this material was therefore at least 58.1 MPa·m$^{-1/2}$. Future work directed towards the measurement of a plane strain fracture toughness value for an electrodeposited nanocrystalline material would be enabled by the development of a synthesis method to produce plates in excess of 5mm thickness.

**Recommendation #3**

The engineering stress-strain data presented in this report indicate the presence of strain hardening behaviour in electrodeposited nanocrystalline materials. Given the small grain size, traditional mechanisms of intracrystalline dislocation interaction are unlikely in nanocrystalline
Recommendations for Future Work

materials. The underlying mechanistic nature of the observed strain hardening behaviour requires further study.

References


Appendix A
Plastic Deformation Mechanisms in Nanocrystalline Materials: An Overview

A.1 Introduction

The nano-scale plastic deformation mechanisms that underpin the Figure 1-6 variation of strength/hardness as a function of grain size have been quite difficult to observe and measure directly. Therefore, the field has adopted a three-fold strategy to reveal the underlying mechanisms, namely:

1. Improved techniques for compiling direct experimental evidence;
2. Computer simulations; and
3. Development of analytical theoretical models

The common goal has been to study nanomaterial plasticity using these fundamentally dissimilar methods, and then aggregate the individual findings in the interest of answering the central question behind them all, namely, “How do nanocrystalline materials deform?”

A.2 Experimental Observations

As mentioned in Section 1.3.2, while TEM represents a powerful tool to study deformation mechanisms in metallic materials, there have been difficulties in extending the technique for direct observation of nanomaterial plasticity, due most notably to grain overlap [1], practical difficulties in loading these high strength materials while simultaneously observing dynamic plasticity in situ in the TEM, and concerns over thin foil surface effects [2]. Most early TEM
studies did not observe dislocations and theoretical speculations suggested that they might not exist because of large image forces that would pull them into the boundaries along with difficulty in activating traditional dislocation sources such as the Frank-Read source. However, subsequent work by Milligan et al. [1] and Ke et al. [3] solved the grain overlap problem by restricting study to thin sputtered films. At grain sizes below 25nm, no dislocations were observed. Signs of significant plasticity were nevertheless noted and attributed to diffusion assisted grain boundary deformation processes. Larger grains showed significant dislocation activity.

In 2001, Youngdahl et al. [4] used the emerging capability of TEM video to record in situ deformation of inert gas condensed nanocrystalline Cu. They reported dislocation activity down to 30nm in grain size but encountered grain overlap problems below that size. In 2003, Kumar et al. [5] carried out video TEM of 30nm grain size electrodeposited nanocrystalline Ni that was mechanically loaded in situ. Evidence of extensive dislocation activity was observed and it appeared as though dislocations were emitted from grain boundaries. However, this could not account for the high levels of plasticity imparted to the specimen. Voids were also observed along grain boundaries. It was therefore concluded that the observed deformation accommodation could be attributed to a combination of dislocation-based plasticity and nucleation and growth of voids.

In 2004, Shan et al. used dark-field video TEM to study the deformation of plasma deposited nanocrystalline Ni, this time with a smaller average grain size of 10nm [6]. They concluded that grain boundary diffusion-controlled grain rotation and agglomeration were the predominant
mechanisms by which plastic flow was accommodated in their specimens. Similar conclusions were also drawn by Jin et al. [7] who made direct in situ TEM observations of grain boundary migration, grain rotation and grain coalescence in ultrafine-grained Al under the influence of externally applied indentation.

More recently, in 2008, Wang et al. carried out in situ tensile deformation of 20nm grain size electrodeposited nanocrystalline Ni in the TEM [8] and also observed grain rotation and neighbouring grain rotation/growth under the influence of tensile loading. A schematic representation of the deformation mechanism proposed by the authors as a result of their TEM observations is included in Figure A-1. Based upon their direct observations, it was concluded that deformation-induced grain boundary sliding leading to grain rotation and, ultimately, grain coalescence/growth are active plastic deformation mechanisms in electrodeposited nanocrystalline Ni [8]. Once again, however, such TEM observations of grain rotation are somewhat controversial because the TEM foils are very thin and may not represent bulk nanocrystalline materials [2].
Figure A-1 Proposed deformation mechanism of electrodeposited nanocrystalline Ni of 20nm grain size based upon the results of *in situ* TEM tensile testing. Grain boundary sliding transforms into crystal lattice rotation in neighboring grains. a) Before plastic deformation, the materials possessed high angle grain boundaries; b) shear of two nano-sized grains 1 and 2 by gliding grain boundary dislocations, and subsequent occurrence of the crystal lattice rotation in the neighboring nanocrystalline grain 3 by climbing GB dislocations; c) multiple grain rotations leading to grain agglomeration; d) a large grain formed with sub-boundaries (highlighted by dotted lines) due to incomplete grain coalescence [8].

In addition to TEM, *in situ* XRD of mechanically loaded 26nm electrodeposited nanocrystalline Ni specimens has been performed by Budrovic *et al.* [9]. They observed diffraction peak broadening but no grain refinement upon mechanical loading, and therefore attributed the peak broadening to inhomogeneous strain in the sample. Moreover, this broadening was reversible in that the peak width returned to its original shape when the sample was unloaded. The authors attributed this recoverable peak broadening to a deformation mechanism that increases the inhomogeneous strain during loading, but this inhomogeneous strain is recovered upon unloading, consistent with no residual dislocation network being accumulated. This observation is consistent with TEM results on nanocrystalline Ni wherein deformed samples did not exhibit non-recoverable dislocation accumulation in the grain interiors.
Appendix A

Tensile deformation with in situ XRD of electrodeposited nanocrystalline Ni-Fe was also carried out by Fan et al. in 2006 [10]. XRD microstrain, which the authors asserted is related to the dislocation density of the materials, did not change after plastic deformation in the uniformly deforming section of the tensile specimen. This result indicated that the nanocrystalline Ni–Fe alloy, if deformed uniformly, does not exhibit dislocation accumulation, an observation that agreed with the results obtained by Budrovic et al. [9]. However, the XRD measurements also indicated that dislocation motion appears to become more active in the post-uniform or localized necking regime of tensile deformation, coincident with strong crystallographic texture development, grain rotation and a slight increase in the microstrain of the sample. In particular, the observed increase in XRD microstrain was attributed to dislocation accumulation, which the authors argued was possible due to the formation of larger crystals resulting from deformation-induced grain coarsening in the necking region as compared with the relatively small grain sizes in the uniformly deforming region of the specimen. Indeed, post-mortem TEM on the specimens indicated that the average grain size of the material in the gauge section of the tensile tested specimen had increased from 23 nm in the as-deposited state to 73 nm in the deformed condition as a result of stress-induced grain coarsening.

These in situ TEM and XRD observations of nanocrystalline material deformation demonstrate that grain boundary sliding and grain rotation may play a significant role in the deformation of nanocrystalline materials, and that sufficiently high levels of plastic deformation can lead to deformation-induced grain growth. Moreover, these observations of plasticity in nanocrystalline materials point towards a transition from conventional lattice dislocation slip to deformation
mediated by grain boundaries with decreasing grain size, with the transition to grain boundary-mechanism dominated plasticity taking place at roughly 10-30nm.

A.3 Computer Simulations and Theoretical Models

Over the past 10 years, a significant contribution to the understanding of the deformation mechanisms operative in nanocrystalline materials has come from computer simulations, most notably molecular dynamics [11,12]. Using this tool, the plasticity of nanostructured materials has been simulated through calculation of the interatomic interaction potential functions of both lattice and interfacial atoms and how they are affected by externally applied loading. Figure A-2 contains an image of a computer generated nanocrystalline Ni sample with a mean grain size of 12 nm synthesized using a molecular dynamics construction [13]. The color code used is based on local crystallinity: grey for atoms with an fcc neighbourhood, red for atoms with an hcp neighbourhood, green for non-12 coordinated and blue for other-12 coordinated atoms. The molecular dynamics approach accounts for crystal lattice anharmonicity and highly inhomogeneous internal stresses in deformed atomic structures. However, the technique is limited to unrealistically high strain rates on the order of $10^7 \text{s}^{-1}$. Also, most simulations are restricted to monatomic solids and therefore cannot account for the presence of second phases or impurities.

Nevertheless, molecular dynamics simulations of plastic deformation of nanocrystalline materials may provide important information on possible structural transformations occurring in these materials. For example, in 2002, twinning in deformed nanocrystalline Al was predicted
Appendix A

by molecular dynamics simulations [14] and was confirmed by experiment the following year [15]. Prior to that time, twinning deformation had, to a large extent, been dismissed in high stacking fault materials such as Al and so the observation was quite significant.

![Computer generated nanocrystalline Ni sample with a mean grain size of 12 nm synthesized using the Voronoi construction](image)

**Figure A-2** Computer generated nanocrystalline Ni sample with a mean grain size of 12 nm synthesized using the Voronoi construction [13].

In 2004, Schiotz performed molecular dynamics simulations of plastic deformation of nanocrystalline Cu with grain sizes between 5 and 50nm [16]. Dislocations were generated at grain boundaries, propagated across the grain interiors, and were absorbed at the opposite grain boundaries. In doing so, semi-circular dislocation configurations were seen to emerge from grain boundaries and dislocation pile-ups were observed for the sample with a 50nm grain size. Similarly, Figure A-3 shows the results of another molecular dynamics simulation study, this time for nanocrystalline Al with a grain size of 12nm [13]. It may seen that a leading partial dislocation nucleates from a grain boundary (Figure A-3(a)), a trailing partial follows (Figure A-3(b)), the dislocation travels through the grain (Figure A-3(c)), and is finally absorbed by the opposite grain boundary (Figure A-3(d)).
Figure A-3 The dislocation mechanism suggested by molecular dynamics for f.c.c. metals: a leading partial is nucleated (a), and a trailing partial follows (b), the dislocation travelling through the grain (c), being finally absorbed in opposite GBs (d) [13].

Using molecular dynamics simulations, Van Swygenhoven *et al.* have reported that perfect and partial lattice dislocation emission from grain boundaries can be interpreted as accommodation processes for grain boundary sliding events [11,16-21]. Grain boundary sliding refers to the relative shear of neighbouring grains that is localized in the boundaries between the grains and is a well-known deformation mechanism in materials that exhibit superplastic behaviour [22]. Simulations by Yamakov [23] have also indicated the existence of grain boundary sliding in nanocrystalline materials. See Figure A-4 for a simple schematic of grain boundary sliding along steps and facets of a boundary in a bi-crystal. It may be appreciated that the grain boundary sliding may be accommodated elastically (Figure A-4(c)), by diffusional accommodation (Figure A-4(d)), by lattice slip within the crystals (Figure A-4(e)), or by local
migration of grain boundaries (Figure A-4(e)). In addition, grain boundary sliding deformation may be accommodated by triple junction migration, free volume movement within grain boundaries, and grain rotation [24].

![Figure A-4](image)

**Figure A-4** Grain boundary sliding along a bi-crystal boundary with steps and facets. (a) Initial state. (b) Non-accommodated grain boundary sliding results in the formation of regions (grey) where neighbouring grains interpenetrate and regions (white) where voids are formed. (c) Elastic accommodation. (d) Diffusional accommodation. (e) Lattice slip accommodation. (f) Accommodating local migration of grain boundaries [24].

In addition to molecular dynamics simulations, analytical models that support the contribution of grain boundary sliding to the plastic deformation of nanocrystalline materials have been developed. Hahn and co-workers presented a model to describe plastic deformation in nanocrystalline materials based upon grain boundary sliding at mesoscopic glide planes [25]. A
schematic diagram illustrating nanomaterial grain boundary sliding at planar interfaces formed by grain boundary migration is shown in Figure A-5. The authors employed experimental data of decreasing hardness with decreasing grain size i.e. the inverse Hall-Petch effect to substantiate their plastic deformation model.

Figure A-5 2D schematic of a grain arrangement in a (A) nano- and (B) polycrystalline material. A mesoscopic planar interface can be formed by grain boundary migration. Atoms located in the darker regions have to be re-arranged in the process of grain boundary sliding [25].

Following on the aforementioned molecular dynamics simulations indicating partial dislocation motion in nanocrystalline materials, Asaro and Suresh considered the emission of a leading partial dislocation followed by its trailing partial dislocation from a triple junction serving as a stress concentrator due to grain boundary sliding in nanocrystalline materials [26]. In their model, the sliding of a grain boundary facet behaves as a small crack, with the possibility of the trailing partial dislocation being emitted at higher levels of stress intensity at the crack tip. Asaro and Suresh also considered the emission of a leading partial dislocation followed by its trailing partial dislocation from a pre-existent grain boundary dislocation [26]. In this fashion, they calculated the shear stress values characterizing the emission process along with various geometric parameters for the partial dislocations, including a model with criteria for emission
from the grain boundary. However, as pointed out later by Van Swygenhoven [13], partial dislocation emission is only one component of the complete mechanism by which plastic flow may be carried in nanocrystalline materials, and that propagation and absorption of the aforementioned dislocations must be properly considered as well. In other words, the nucleation of a partial dislocation must be considered as a separate process from its propagation within the grain. Indeed, partials are often observed to nucleate but not propagate, remaining for a while as extrinsic grain boundary dislocation segments that perform a number of attempts to propagate [13]. The interaction of a propagating dislocation with a grain boundary therefore appears to be very dependent on the structure of that grain boundary.

Moreover, due to the intense interaction between the grain boundary and the dislocations, the grain boundary structure is continuously changing, which in some cases also results in grain boundary migration and associated coarsening of a grain at the expense of its neighboring grain [13], as depicted in Figure A-4(f). Consequently, while the specific mechanisms of dislocation emission from grain boundaries have received focused attention over the past 10 years, the continuously changing structure of the nanomaterial grain boundary and how it influences the motion of the dislocations with which it interacts (including pinning and de-pinning) has made the task of accurately simulating such events extremely challenging. In other words, it is not yet possible to understand the complex dynamic process of grain boundary sliding by analytical modeling as the process is associated with the evolution, annihilation, and mutual interaction of various defect structures in the process [27]. Nevertheless, the analytical modeling framework to describe grain boundary sliding and its concomitant accommodation processes as carriers of plastic flow in nanocrystalline materials remains in development [e.g. 28-32]
In the case of nanocrystalline materials deforming by grain boundary sliding, emission of partial and perfect dislocations from grain boundaries has been suggested as accommodation processes for the grain boundary sliding mechanism [33-35] and as described earlier, these dislocations are thought to traverse the grain interior and become annihilated in the opposite boundary. However, these processes have also been associated with deformation twinning in nanocrystalline materials because certain regularly arranged groups of partial dislocations are capable of effectively carrying twin deformation [e.g. 2]. In other words, regularly arranged groups of partial dislocations emitted from grain boundaries can cause twin deformation in nanocrystalline materials [24]. This mechanism is demonstrated schematically in Figure A6. Zhu et al. [2] have provided a comprehensive review of deformation twinning in nanocrystalline materials. In addition to twin deformation by partial dislocations emitted from a grain boundary, they also review other possible mechanisms by which deformation twins may carry plastic flow in nanocrystalline materials, including overlapping of stacking fault ribbons, grain boundary splitting and migration, sequential twinning, partial multiplication at twin boundaries, and the dislocation rebound mechanism [2].

Figure A-6 Twin deformation conducted by regularly arranged partial dislocations emitted from a grain boundary [24].
Thus, computer simulation and theoretical modeling indicate that the emission of lattice dislocations from grain boundaries, grain boundary sliding and twin deformation represent important plastic deformation mechanisms in nanocrystalline materials. However, there are other deformation mechanisms that could conceivably contribute to plastic flow within the nanocrystalline grain size regime. The common characteristic of all these theoretical models is the identification of the deformation mechanisms inherent to grain boundaries and their description of the competition between these mechanisms and the conventional lattice dislocation slip [24].

The earliest models [e.g. 36,37] suggested that diffusional-based grain boundary (Coble) creep is predominant in nanocrystalline materials deformed at room temperature owing to the high volume fraction of non-lattice interfacial atoms present in the material. A general illustration of the nature of diffusional creep is provided in Figure A-7.

**Figure A-7** Schematic representation of diffusional creep. Self-diffusion should result in plastic flow if matter is carried from boundaries subject to compressive stress (vertical boundaries) over to boundaries under a tensile stress (horizontal boundaries) [38].
Coble creep occurs via dilatation-stress-driven transport of grain boundary vacancies along grain boundaries from regions where tensile stresses exist towards compressed regions [24] and is governed by the following relationship:

$$\frac{d\varepsilon}{dt} = 14\pi\Omega D_{gb} \delta \sigma t^{-3} / k_B T$$

(A-1)

where $D_{gb}$ is the grain boundary diffusion coefficient, $\delta$ is the grain boundary width, $\Omega$ is the vacancy volume, $\sigma$ is the flow stress, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $d$ is the grain size. Similarly, lattice (Nabarro-Herring) and triple junction creep mechanisms may be active in nanocrystalline materials. In the case of Nabarro-Herring creep, plastic deformation occurs by diffusive matter transport through the individual grains rather than along the grain boundaries (Coble) of a stressed polycrystal and is governed by the following relationship:

$$\frac{d\varepsilon}{dt} = 14\Omega D_l \sigma t^{-2} / k_B T$$

(A-2)

where $D_l$ is the lattice diffusion coefficient. Triple junction diffusional creep resembles Coble creep. In the case of triple junction diffusional creep, triple-junction lines or “tubes” characterized by higher effective diffusion coefficients [e.g. 39] form a continuous network distributed throughout the volume of a nanocrystalline material. When a mechanical load is applied to the specimen, atoms and vacancies are driven along the continuous network of triple junctions [24]. Of note is the grain size sensitivity of bulk (Nabarro-Herring) and grain boundary (Coble) diffusional creep characterized by the grain size exponents $d^{-2}$ and $d^{-3}$, respectively. Moreover, it has been suggested that triple junction creep exhibits a $d^{-4}$ dependency on grain size [24]. Based upon the grain size dependence of these diffusion-based mechanisms along with experimental creep measurements on electrodeposited nanocrystalline Ni, Wang et al. were able
Appendix A

to develop an Ashby-style deformation map to describe the predominant deformation mechanisms in nanocrystalline materials, see Figure A-8. It may be appreciated from Figure A-8 that the interfacial (e.g. grain boundary (Coble)) diffusional creep mechanisms play an important role [40] and are thought to become dominant at the very finest grain sizes below approximately 10nm [24].

![Deformation map for pure Ni showing the effect of grain refinement from 32µm to 10nm (finer solid lines) [40].](image)

**Figure A-8** A deformation map for pure Ni showing the effect of grain refinement from 32µm to 10nm (finer solid lines) [40].

Grain rotation has also been proposed as a potentially important plastic deformation mechanism in nanocrystalline materials, especially in combination with other mechanisms such as grain boundary sliding as described earlier. Grain rotation in a polycrystalline solid is depicted in Figure A-9. Theoretical analyses of the grain rotation mechanism [e.g. 41] reveal that grain rotations in nanocrystalline materials are likely controlled by grain boundary diffusional accommodation, as shown in Figure A-9(d). In addition, grain rotation in nanocrystalline materials indicates that crystal lattice orientations in the grains of a nanocrystalline specimen
move to minimize the grain boundary energy, depending on the boundary misorientation parameters [24]. As described earlier, the TEM observations of Wang et al. [8] indicated a grain rotation and coalescence mechanism. Hence, in these circumstances, plastic deformation in nanocrystalline materials essentially changes the structure of the grain boundaries themselves. In this context, the connections between imposed plastic deformation in nanocrystalline materials and the resultant changes in grain boundary structures due to the aforementioned grain boundary diffusion, emission and absorption of lattice dislocation at grain boundaries, grain boundary sliding, and grain rotation are currently a matter of intense debate and could potentially be greatly assisted by the development of an analytical technique to measure grain boundary structure in nanocrystalline materials, similar to the Orientation Imaging Microscopy capability available for such study in coarse-grained materials.

Figure A-9  Grain rotation in a polycrystalline solid. (a) Initial state. (b) Non-accommodated grain rotation results in the formation of small regions (black regions near boundaries of rotated grain) where neighbouring grains interpenetrate and small regions (white regions near boundaries of rotated grain) where voids are formed. (c) Accommodation by bulk diffusion. (d) Accommodation by grain boundary diffusion [24].
Appendix A

In conclusion, at the smallest grain sizes (~10nm), there are numerous possible grain boundary-mediated mechanisms that could contribute to plastic flow in nanocrystalline materials, including grain boundary sliding, grain boundary / triple junction diffusional creep, and grain rotation. Furthermore, there exist numerous theoretical models to support the presence of these mechanisms, and while the discussion of which ones predominate and why is still a matter of intense study [e.g. 28,42-45], the overall consensus is that grain boundary processes such as these are indeed dominant below approximately 10nm [46]. Moreover, it may be possible that many or all of the aforementioned deformation mechanisms are operative to some extent in nanostructured metals of the finest grain sizes below ~10nm [31]. Finally, the absence of traditional intracrystalline dislocation activity in lieu of such grain boundary-mediated deformation mechanisms in such materials likely also underpins the “inverse Hall-Petch” effect illustrated in Figure 1-6.

In the “intermediate” nanocrystalline grain size range above approximately 10nm and below 100nm, the role of dislocations is still being studied, but it is likely that there exists competition between conventional lattice dislocation slip and diffusional deformation, with the relative contributions of these deformation modes being dependent upon the distribution of grain sizes. This competition is illustrated schematically in Figure A-10(a). In addition, given that crystalline materials exhibit a distribution of grain sizes, it is likely that in a given nanocrystalline material, the larger grains may exhibit dislocation slip while the smallest crystals plastically deform by grain boundary-mediated mechanisms as discussed earlier [24]. This is illustrated schematically in Figure A-10(b). How these dislocations are generated, propagated,
interact with each other (if at all) and become annihilated (if at all) is currently being debated [e.g. 13,33,48-58].

Nevertheless, the current thinking is that the basic carriers of plastic flow in materials in the 10-30nm grain size range are partial lattice dislocations generated by dislocation sources located at grain boundaries. Since these mobile lattice dislocations are partial, their movement may be accompanied by the formation of stacking faults and deformation twins. In the 30-100nm grain size range, plastic flow carried by perfect lattice dislocations generated and annihilated at grain boundaries may predominate, although again our understanding of the specific mechanisms is still developing.

Figure A-10 Competition between deformation mechanisms in nanocrystalline materials (schematically). (a) Framework for the grain size dependence of dislocation activity and grain boundary-mediated contributions to nanocrystalline materials, after [47] (b) Lattice dislocation slip and diffusional deformation modes occur in large grains (with dislocation signs) and small (shaded) grains, respectively [24].
A.4 References


Appendix A


Appendix A