Physical and Mechanical Characteriz owires Influence of

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Abstract

Magnetic 1-D nanostructures have received great interest due to their various applications including high-density magnetic storage, sensors, drug delivery, and NEMS/MEMS systems. Among different 1-D nanostructures, magnetic nickel (Ni) nanowires with their ferromagnetic properties are of interest in such applications due to their lower cost, and they can be consistently synthesized via electrodeposition. While physical properties are influenced by processing parameters during electrodeposition of Ni nanowires, understanding of their influence on the mechanical properties is still not available. This is primarily due to the following challenges: tediousness involved in experimental techniques for mechanical characterization at nanoscale; sophisticated and careful experimentation required to be performed with advanced microscopy systems (SEM, AFM); robust nanoscale manipulators needed to place a single nanowire within the device; and difficulty in correctly loading and obtaining data for stress-strain within high powered microscopy environments. All of these factors pose significant challenges, limiting the current state of the art in mechanical characterization to its infancy, with wide differences in characterization curves and reported properties in this field.

The present research and dissertation focuses on: 1. Experimental synthesis of electrodeposited Ni nanowires at different current densities and external magnetic fields, 2. Physical properties characterization of the synthesized nanowires to understand their morphology, structural and crystallographic properties, 3. Mechanical properties characterization of synthesized Ni nanowires through careful experiments within scanning electron microscope (SEM) based on uni-axial MEMS tensile loading device, 4. Data analysis to understand the process, physical and mechanical property interrelationship and to obtain insights on tensile deformation and failure modes observed in the Ni nanowires studied. Key research insights from

the present experimental research include: Electrodeposition method consistently synthesizes high purity Ni nanowires (98% and higher based on energy dispersive spectroscopy (EDS)) with a significant improvement in surface morphology when magnetic field is present during synthesis; X-ray diffraction (XRD) characterization and analysis indicate that electric current density has significant influence on the crystal orientation of Ni nanowire, while a decrease in crystal size was noticed with increased magnetic field intensity for same current densities. Carefully studied uni-axial tensile characterization using MEMS tensile loading device indicates an increase in elastic tensile modulus when the magnetic field is present during electrodeposition and consistent observation of three different variants of ductile failure modes. Results and discussions of tensile stress-strain mechanical characteristics of Ni nanowires and their failure modes provide key research findings that are not currently available in the literature to our knowledge. The present research contributes to the experimental understanding of tensile deformation of Ni nanowires, as well as developing and presenting a robust experimental methodology for future extension to other metallic nanowires. Research findings clearly illustrate a need for three-dimensional high fidelity experimental tools and relevant computational modeling for a full understanding and insight on deformation and failure mechanisms involved at nanoscale.

CHAPTER 1

Introduction

One-dimensional (1-D) nanostructures have received enormous attention due to their distinctive and fascinating chemical, electronics and mechanical properties. They have become the focus of intensive research owing to their unique applications in the field of catalysis, photography, electronics, photonics, information storage, optoelectronics, energy storage, drug delivery, biological labeling, imaging, and sensing, etc. Due to tremendous potential of these nanostructures, a number of methods with varied processing parameters have been studied and shown to be successful to synthesize 1-D nanostructures of various sizes, morphology and composition that have resulted in exciting and fundamentally different configurations. Of the various methods, template-assisted electrodeposition is the most popular method for synthesizing metallic nanowires with controlled diameters and higher yields in a cost effective way. However, the properties of synthesized nanowires are significantly influenced by the synthesis parameters, namely, solution pH, temperature, agitation speed, additives, magnetic field and current density used during electrodeposition.

While the influence of synthesis parameters during electrodeposition on physical properties of metallic nanowires has been extensively investigated, understanding of their influence on the mechanical properties is extremely limited. This is primarily due to the fact that experimental techniques for mechanical characterization at nanoscale are tedious, and require sophisticated and careful experimentation to be performed with high powered microscopy systems (SEM, AFM). Also, special nanoscale devices and techniques are needed for nanowires manipulation during characterization which involves: placing a single nanowire within the device; correctly loading it for the intended deformation testing; and obtaining the data for loaddeflection during deformation - all within the high powered microscopy environments. All these pose significant challenges for a successful experimentation. For instance, separation of single nanowire from bundles of nanowires and mounting it on a customized nanoscale testing device is an exhaustive task; and requires careful in-situ microscopy experimentation techniques and skills. Due to these difficulties, to date, mechanical characterization of metallic nanowires is a scarcely investigated field. Various techniques at different levels of fidelity, resolution, and induced errors have been attempted by material science, nanomaterials, and nanomechanics researchers. However, the state-of-the-art and standardized techniques in mechanical characterization of 1-D nanostructures are still at its infancy. All these factors result in wide differences in characterization curves and reported properties of nanowires.

Among different 1-D nanostructures used in various applications, magnetic nickel (Ni) nanowires are of special interest due to their potential applications in areas such as high density data storage, in biological applications upon functionalization, and magnetic sensors. To date, several synthesis and characterization methods have been developed and employed to synthesize and characterize these Ni nanowires; with most of the work focused primarily on processing parameters. Specifically, for Ni nanowires synthesized using template-assisted electrodeposition technique, effect of electrodeposition process parameters, viz, solution pH, bath temperatures, current density, and additives on the growth and morphology of the Ni nanowires have been investigated to some extent. Most attempts focused on studying and improving magnetic properties of these Ni nanowires by applying external magnetic field during electrodeposition, and by optimizing the process parameters. However, the influence of external magnetic field and current density during electrodeposition, and their combined effect on the physical and mechanical properties have not yet been reported in the literature.

Both engineered and biological materials have been shown to have process-structure-property correlation at various scales. While some of these material structure and morphological effects are homogenized at larger engineering material scales, small changes in the material structures play an important role at lower length scales. Since the nature of the 1-D nanostructures is to exhibit different behaviors at different conditions (environmental and synthesis), it is important to study the behavior of these Ni nanowires starting from their synthesis; using well refined characterization techniques to understand fully the material structure, morphology characteristics and associated influencing synthesis parameters on the formed nanostructure and its properties. Similarly, as the current research in experimental mechanical characterization of 1-D nanostructures is still limited, there is a tremendous need for careful experimental studies to develop a good scientific and engineering understanding of the influence of processing parameters during nanomaterial synthesis.

The present research addresses these factors and focuses on the analysis and understanding of the physical and mechanical properties of electrodeposited 1-D Ni nanowires that are synthesized at different current densities and external magnetic field intensities. In particular, present research involves:

1. Experimental synthesis of electrodeposited Ni nanowires in the diameter range of 200-300 nm at varying current densities and external magnetic fields.
2. Physical characterization of synthesized nanowires to understand their morphology, growth length, crystal orientation and crystal size.
3. Mechanical characterization of synthesized Ni nanowires at different processing conditions through careful in-situ SEM experimentation using a MEMS uni-axial tensile loading device (Device Courtesy: Dr. Yong Zhu group at NCSU, Raleigh).

1.1 Motivation

In the last few years, 1-D nanostructures, especially nanowires have gained tremendous interest in the field of nanotechnology. This is due to their unique and exceptional properties at lower length scales. Since the discovery of various theories and findings on remarkable properties of materials at lower length scales, numerous techniques have been explored and demonstrated to be practical and successful in synthesizing nanowires with fascinating behavior and enhanced desirable properties.

Recent experimental observations have shown that the properties of nanowires are strongly influenced by processing methods and synthesis parameters employed. Of the various methods cited in literature (Xia et al., 2003); electrodeposition is shown to be a viable and effective method for Ni nanowires (Samykano et al., 2015). In template-assisted electrodeposition method, process parameters such as solution pH, temperature, agitation condition, template material, additive, and current density are found to determine the properties of the nanowires synthesized. Additionally, as Ni is one of the four ferromagnetic elements which have ferromagnetic properties - application of magnetic field is found to influence its properties. Literature cites extensive work on the influence of magnetic field on the magnetic properties of electrodeposited Ni nanowires. However, limited work to date has focused on understanding physical and mechanical property changes associated with application of external magnetic field, and variation in current density during electrodeposition. Present research focuses on such understanding; striving to develop a potential correlation between processing, physical, and mechanical properties through careful experimental design, experimentation, and analysis.

The motivation for understanding process-physical-mechanical property correlation of electrodeposited Ni nanowires further stems from recent experimental studies that have shown that nanowires prepared by chemical methods are polycrystalline in nature, in which the crystal boundaries will play a significant role on its mechanical properties (Tian et al., 2010). However, due to the complications and challenges associated with mechanical testing at nanoscale, very little attention has been given to experimentally characterize polycrystalline nanowires, and mechanical properties of the polycrystalline nanowires are still not very well understood (Tian et al., 2010). From a nanotechnology applications perspective, such understanding of structural-mechanical properties are very critical to avoid mechanical failure due to incidental forces in nano-devices (Varghese et al., 2008).

1.2 Research Objectives

The specific research objectives, experimental and analysis studies in the current work based on outlined research focus and advancing the present state of art are presented next.

i. **Electrodeposition synthesis of Ni nanowires.**

- Employ a template assisted electrodeposition technique for synthesis of Ni nanowires.
- Determine optimal synthesis parameter (current density) for growth of Ni nanowires.
- Design, develop, and modify the template assisted electrodeposition method to facilitate application of external magnetic field during synthesis.
- Develop a processing condition matrix consisting of three electrical current density and external magnetic field for Ni nanowire synthesis.

- Synthesis of Ni nanowires under different electrical current density and external magnetic field.

ii. **Physical property characterization and analysis.**

- Morphology, structural and crystallographic characterization of synthesized Ni nanowires using:
    - Scanning electron microscope (SEM).
    - Energy dispersive spectroscopy (EDS).
    - X-Ray diffraction (XRD).
- Analyze experimental data obtained to study and understand the influence of electric current density and external magnetic field on physical properties of synthesized Ni nanowires and their variations due to modifications in processing conditions.

iii. **Mechanical property characterization of single nanowires.**

Electrodeposition method results in multitude of Ni nanowires formed during synthesis for each of the processing parameters used. Current research focuses on mechanical characterization of a single nanowire using a uni-axial MEMS tensile loading device within a SEM environment. This requires careful manipulation and mounting microscopy techniques. Experimental mechanical characterization within SEM environment thus focused on:

- Develop suitable manipulation techniques within SEM for placement of a single Ni nanowire on the MEMS device and mounting the ends.
- Careful loading and imaging of the tensile deformation of Ni nanowire placed in the MEMS device.

- Develop and analyze the stress-strain curve from uni-axial tensile deformation of the Ni nanowires synthesized at different processing conditions at different current densities and external magnetic fields.
- Study the mechanical behavior and determine the associated properties of these nanowires and study the observed tensile deformation progression and failure.

iv. **Process-structure-property interrelationship of electrodeposited Ni nanowires.**

- Study and analyze the physical and mechanical characterization experimental data obtained to understand the interrelationship between the crystallographic features and associated mechanical stress-strain behavior, deformation and failure.

1.3 Challenges with Experimental Mechanical Characterization of a Single Nanowire

While methods for mechanical characterization at engineering scale are well established and routinely performed, performing or studying the mechanical properties of individual nanowires are still very intricate, as well as limited in the state of the art due its size at the present time, and can be expected to continue to remain so. Advances in various areas are required to ensure repeatability in test methods, reliable measurements and overall fidelity of the data obtained from mechanical characterization. Currently, on a practical side, even performing few tests for property measurements and mechanical characterization at nanoscale can take up to months compared to mechanical testing at engineering/macro scale due to various difficulties such as sample preparation, equipment compatibility among several others. The challenges faced during mechanical characterization of single Ni nanowires in the present work are:

i. Nanowire separation: Nanowires produced after synthesis by electrodeposition are normally in the form of clusters or bundles. They tend to agglomerate or bundle together due to forces acting between surfaces or due to processing technique itself. This causes a difficulty to separate an individual nanowire from the cluster of the nanowires for characterization. Hence, it is desirable to develop a process which could disperse the synthesized nanowire and can ease the manipulation or isolation of a single nanowire. Figure 1.1 shows a SEM image of Ni nanowires as synthesized, indicating a bundle or cluster of nanowires formed.

ii. Nanowire alignment: Alignment of the nanowire for uni-axial loading employing the MEMS device considered in the present work is very crucial. Even a slight misalignment of the nanowire axis and loading direction may result in an undesirable bending moment. This bending moment will result in non-uniform stress across the specimen cross section, which causes inconsistency between the actual and recorded stress. Finally such misalignment can also lead to premature specimen failure (Ganesh et al., 2005).

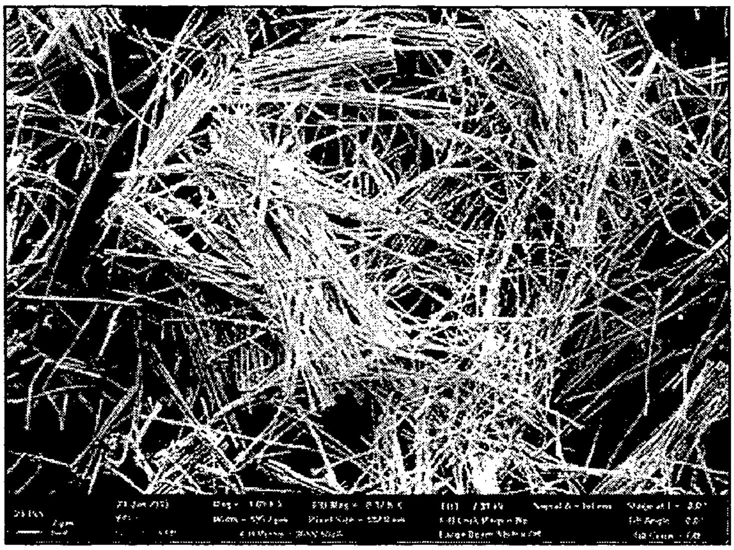

Figure 1.1. Synthesized Ni nanowires

iii. Nano-manipulation: Both large moving range and a very small step movement are required for nano-manipulation when testing is performed within an SEM environment. The large moving range is required for transferring the nanowire from the substrate to the

MEMS device, while small approaching step movements are required to approach the tip to the MEMS platform. Since the micro-manipulator used in this study had a slightly large step movement, it posed additional risk during approaching step of the tip to the MEMS platform. Thus, to overcome this problem, the manipulator was kept at specific or fixed distance, and the MEMS platform was moved to approach the tip. These are in contrast to the conventional method where the tip generally approaches the MEMS platform.

iv. Manipulator tip: Manipulator tips have a very small diameter and are made from tungsten with a low resonance frequency. Thus, these tips are very susceptible to vibration during manipulation. To overcome this problem, a short tip is preferred and possibly with a slightly larger support diameter without compromising the tip edge diameter. Special care and detailed attention has to be taken to avoid any crashing during manipulation. Such a crash can destroy not only the tip but also the MEMS device.

v. Scanning electron microscope (SEM) imaging: Conventional SEM has a two-dimensional (2-D) imaging system since it is equipped only with a single beam source. Thus the images developed are actually a projection view of the nanowire or material sample from the top. The nanowire or material sample may seem to look parallel to the substrate, even when the stage is tilted by a small angle. But in reality, the material sample or nanowire might have a large tilted angle. This poses problems for correct placement of a single nanowire on the MEMS device. When the nanowire is brought closer for placement on the MEMS platform, one side of the wire could appear touching the nanowire, while the other end would not be in contact. Thus, after fixing one end of the nanowire by electron beam induced deposition (EBID), the other end is made to

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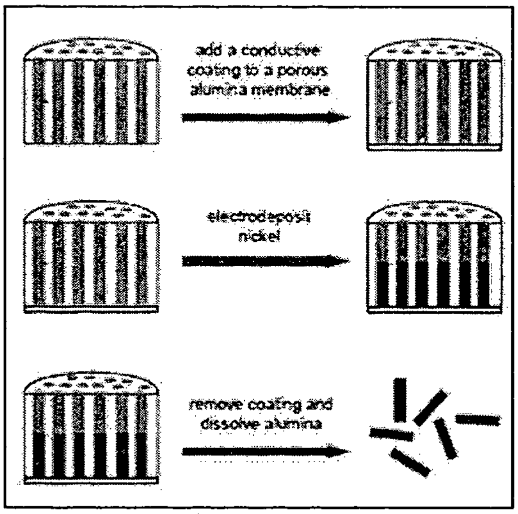
CHAPTER 3

Synthesis and Physical Properties Characterization

.1 Synthesis of Ni Nanowires

Figure 3.1 illustrates the mechanism of template-assisted electrodeposition method; the eps involved starting from template preparation to formation of freestanding nanowires. In the resent work, 1-D Ni nanowire arrays were prepared by electrodeposition of Ni ions into the ores of Anopore® alumina oxide (AAO) template with an average pore diameter of 200 nm Whatman, Germany). The alumina template was thoroughly cleaned with deionized water and ried prior to use. A film of aluminum with approximate thickness of about 1 μm was deposited n one side of the template (using Kurt J. Lesker, PVD 75) to serve as the working electrode.



igure 3.1. Schematic of template-assisted electrodeposition of nanowires

This was followed by the electrochemical deposition of Ni into the template using a ickel-sulfamate ($NiSO_4$) based electrodeposition bath containing a commercially available pre-repared solution (SN-10). Prior to electrochemical deposition, a special holder was fabricated sing 3D printing technology so as to enable precise control of the distance and alignment of electrode, template and magnetic field direction. Figure 3.2 shows the image of the holder fabricated with span distance of 20 mm.

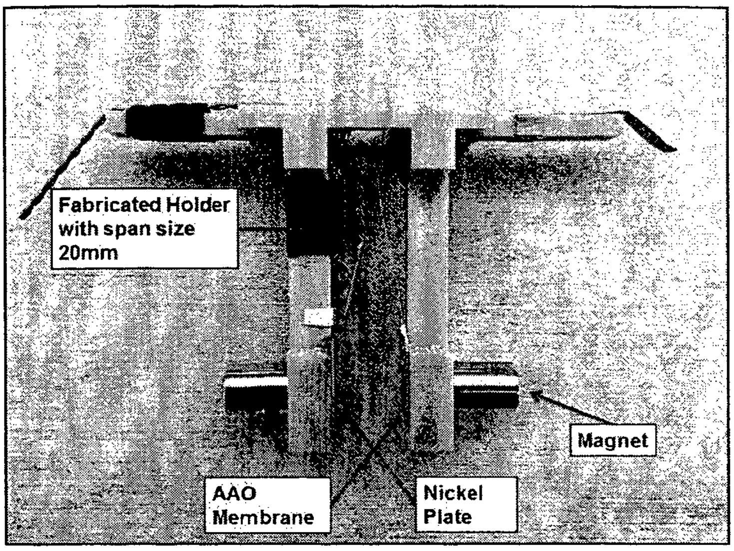
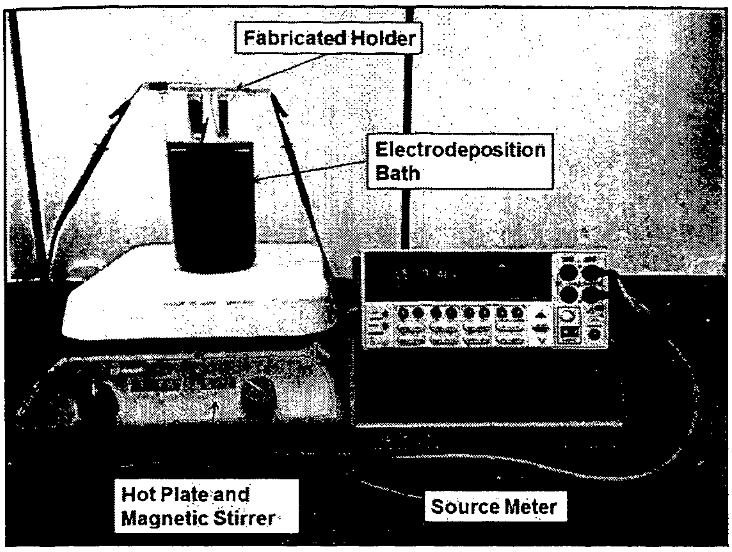


Figure 3.2. 3D printer fabricated sample holder

The holder is then placed in the electrochemical bath for electrodeposition as shown in Figure 3.3. Next, the nanowire synthesis is performed either with or without magnetic field. For nanowire synthesis with magnetic field, known magnetic field intensity was placed close to the template and electrode (with magnetic field aligned parallel to nanowire growth). As the stoichiometry of the Ni nanowires are significantly affected by solution pH, agitation conditions, temperature, external magnetic field, solution additives and deposition time, all these process parameters were maintained to be consistent during the electrodeposition process except for the external magnetic field and current density.

Table 3.1 lists the deposition parameters used in the present work. All synthesis was done for 1 hour of deposition at a temperature of about 35 °C. After the electrodeposition process, the templates were cleaned with deionized water prior to dissolution in sodium hydroxide (NaOH) lution to obtain freestanding Ni nanowires. NaOH solution was later replaced with methanol

lution.



igure 3.3. Electrodeposition set-up for Ni nanowire synthesis

able 3.1

eposition process parameters used for synthesis

Parameters	Values	Units
Magnetic field	0, 3817 and 5758	Gauss
Current density	3, 5 and 7	$mA.cm^{-2}$
Temperature	35	°C
Solution pH	4.2 - 4.8	n/a
Agitation	100	rpm
Time	60	minutes