CARBON NANOTUBES CHARACTERIZATION AND QUALITY ANALYSIS
USING ARTIFICIAL INTELLIGENCE

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of MOHAMMAD ABDELFATAH AL-KHEDHER, and find it satisfactory and recommend that it be accepted.

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Chair

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Abstract

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Current research aims towards developing new characterization methodologies of nanostructures to estimate and model nanomaterial behavior using artificial intelligence. The proposed methodology in this research utilizes artificial neural networks and image processing techniques to study the structural and mechanical properties of micro- and nano-structures and to develop a quality estimation approach of these materials. For their engineering significance, carbon nanotubes (CNTs) are the main focus of this research. The proposed scalable process will dramatically improve materials design, the use of these materials in nanotechnology and MEMS, and it will facilitate full scale production. In this research project, a new approach based on artificial neural networks modeling was developed to model the aging behavior of an Al-Mg-Si alloy and to distinguish the precipitate morphology at each stage of aging of this microstructure. An image analysis algorithm capable of capturing orientation gradient, nearest neighbor distances, number density, shapes, and size of precipitates was developed. The neural networks model combines the most important precipitate parameters including volume fraction, shape, size and distance between precipitates extracted by the image analysis. It was found that
the model is able to successfully predict the age hardening behavior of AA6022 in both deformed and undeformed conditions. To characterize carbon nanotube samples, we have identified a set of intermediate steps that will lead to a comprehensive, scalable set of procedures for analyzing nanotubes. Image analysis techniques were employed and stereological relations were determined for SEM images of CNT structures; these results were utilized to estimate the morphology of the turf (i.e. CNTs alignment and curvature) using artificial neural networks classifier. This model was also used to investigate the link between Raman spectra of CNTs and the quality of the structure morphology, where strong relations were found for the structural effect on the Raman features. We have also proposed a new methodology to investigate the correlation between indentation resistance of multi-wall carbon nanotube turfs, Raman spectra and the geometrical properties of the turf structure using adaptive neuro-fuzzy phenomenological modeling. This methodology yields a novel approach for modeling at the nanoscale by evaluating the effect of structural morphologies on nanomaterial properties using Raman Spectroscopy. A parametrical study of these features was conducted using artificial intelligence to determine the effectiveness of the involved parameters included in this study.
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Dedication

Expressing my sincere love to my mother, father and my wonderful family, especially my brother Prof. Sharaf, I dedicate this work to them.
CHAPTER ONE

1. INTRODUCTION

Our focus in this study is carbon nanotube structures (CNTs); one of the most frequently mentioned building blocks of nanotechnology with exceptional strength, as well as thermal and chemical stability [1]. The outstanding properties of carbon nanotubes have attracted much attention in recent years not only for their small dimensions, high electrical and thermal conductivities and unique morphologies, but also for their potential applications in different technologies. It is expectations such as these that are currently raising the race to build up techniques of nanotube mass-production in economic quantities. It is therefore important to control the structure of these CNTs if we want to control the properties they exhibit.

In section 1.1 the structure of carbon nanotubes is explained. The synthesis of CNTs is discussed in section 1.2. The modeling aspects of the mechanical behavior of carbon nanotubes are stated in section 1.3. Section 1.4 describes the outline of each chapter of this dissertation.

1.1 Structures of Carbon Nanotube

These unique nanostructures of carbon nanotubes, discovered in 1991 [2], are envisioned as forming from hexagonal sheets of $sp^2$ – hybridized carbon which are folded into seamless tubes and capped by fullerene fragments. These CNTs vary in diameter and chirality and the symmetry of the folding process dictates whether the resulting nanotubes are metallic or semiconducting [3]. Individual CNTs are often self-assembled into bundles held together by van der Waals forces [4] and the resulting bulk mechanical properties are dependent on the overall morphology of the assembly.
Carbon nanotubes grow in two distinct forms, single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). MWCNTs consist of a number of concentric tubes of individual carbon nanotubes that are weakly coupled through van der Waals forces [5]. The spacing between these individual walls is about 0.34 nm. The diameter and number of tubes in MWCNT is dependent on the fabrication process. The samples analyzed in this research are multi-wall carbon nanotubes.

1.2 Synthesis of Carbon Nanotubes

Several techniques have been developed to produce carbon nanotubes in large quantities for large scale applications, such as: arc discharge, laser ablation, high pressure carbon monoxide, and Chemical Vapor Deposition (CVD). The nanotubes used in this research are grown using CVD process. The components required for CVD growth of nanotubes are a catalyst particle and a hot environment of carbon-containing gas. The particle catalyzes the decomposition of the carbon-containing gas, and the carbon dissolves in the catalyst particle, and then builds up the supersaturated carbon as a tube [6].

1.3 Modeling of Carbon Nanotube Properties

It is known that modeling and simulations can help in investigating, analysis and design of nanomaterials. Due to size challenges, analytical models are hard to establish at the nanoscale, while it is expensive to conduct experiments, the need to have an efficient empirical phenomenological model became necessary. Thus, new models capable of incorporating the most important nanostructural parameters are highly desirable.

On the other hand, nanostructures characterization has been studied using several modeling approaches, yet, most of the existing models focus on simplified situations, and these simplified assumptions appear sometimes impractical. Much of the early work
studying the mechanical properties of nanostructures is based on computational methods such as molecular dynamics and \textit{ab initio} models \cite{7, 8}. These models are primarily used to study simple structures, because of the increase in computational resources necessary to model systems comprised of a larger number of atoms. Besides, most of these models assume defect-free nanotubes.

In this research, artificial phenomenological modeling is proposed to analyze micro- and nano-structures by enabling the study of incredibly diverse phenomena which are not as yet accessible to physical modeling. Based on this approach numerous characterization methods can be developed.

\textbf{1.4 Outline of the Current Research}

This dissertation aims to provide a fundamental methodology for modeling the micro- and nano-structural influence on the materials behavior using artificial intelligence techniques. Following are the outline and general objectives of the current research:

a. Chapter 2 demonstrates the experimental techniques that were involved in characterizing aluminum alloys and carbon nanotube structures. These techniques include scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and nanoindentation.

b. In Chapter 3, an artificial neural network model of the microstructural aging behavior of Al-Mg-Si alloy is developed by studying different types of precipitate structures and morphologies in the material.

c. Chapter 4 proposes a quality classifier of carbon nanotube samples based on geometrical appearance of the structure. The morphology of the CNT bundles is extracted using image analysis methods.
d. Chapter 5 investigates the link between Raman spectra of CNTs and the quality of the structure morphologies. Different features of the Raman spectra are correlated to the geometrical properties of the samples at different excitation wavelengths.

e. In Chapter 6 and 7, the mechanical behavior of vertically aligned carbon nanotube structures is analyzed and modeled using the geometrical features of the structure and correlated to the Raman features of the turfs. A parametric study of the influence of these features is described.

f. Chapter 8 summarizes the significance of the current research and our contribution to the problem of quantifying nano-structural properties.

g. Chapter 9 describes the main conclusions of the dissertation.

h. Chapter 10 discusses our suggestions for future work.

1.5 References


CHAPTER TWO

2. CHARACTERIZATION TECHNIQUES

2.1 Introduction

In order to commercialize carbon nanotube technology, advances must be made in production of nanotubes. Besides vital issues involving process scale-up, one of the major obstacles for successful commercialization that has been identified is performing quick and accurate characterization of the properties of a given batch of nanotubes.

Establishing analytical models at the nanoscale to interpret nanomaterials properties is challenging due to the nonuniformity and irregularity in quality of as-grown samples and the lack of an accurate procedure to evaluate structural properties of nanotubes in these samples, therefore, it is important to determine a set of consequential characterization techniques. For a complete understanding of the presented work in this dissertation, a brief review on the involved characterization techniques of micro- and nano-structures is discussed in this chapter.

2.2 Scanning Electron Microscopy

The scanning electron microscope (SEM) generates a beam of electrons in a vacuum with energies normally in the range from a few hundred eV to about 30 keV. Using different types of lenses, the beam is focused and scanned across the surface of sample. The image is produced by collecting different signals that are released by the sample. The most widely used modes are secondary electron (SE) and backscattered electron (BSE) imaging. Secondary electrons, with energies between 0 and 50eV, are used for analyzing the surface topography details. Backscattered electrons represent the other electrons
emitted from the sample; it is sensitive to the magnetic and crystallographic nature of the sample [1].

In this research, electron microscopy is used to reveal the nanostructure of tubes and the morphology of the nanotube assembly. Coupled with image analysis procedures, electron microscopy permits the distribution of tube structures, including the tube diameter, alignment and curvature to be determined. The images are obtained using an ultra-high resolution FEI Sirion 200 field emission scanning electron microscope (FESEM), which is ideal for studying materials at the microscale.

2.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an imaging technique where a beam of electrons is generated, accelerated and transmitted through a specimen through different types of magnetic lenses. The image is formed and magnified using different objective lenses and then directed to either a fluorescent screen or detected by a CCD camera [2].

2.4 Raman Spectroscopy of Carbon Nanotubes

Raman spectroscopy reveals phonon modes and is possibly the most commonly used characterization technique to study carbon materials, because it provides qualitative and quantitative information on the hybridization (spⁿ) state [3], the size of the crystallites [4], and the degree of ordering of the material [5].

The Raman spectroscopy is a light scattering process that reveals structure-dependent vibrational frequencies. Most photons are elastically scattered, this process is called Rayleigh scattering. In Rayleigh scattering, the emitted light has the same wavelength as the absorbed one. Raman Spectrum is a result of the Raman effect, an inelastic scattering of the photons, where the absorbed photon bounces off with a loss of
energy, this lost energy causes molecule vibrations [6]. The energies of the absorbed and emitted photons are different; figure 2.1 shows the energy states for photon scattering.

![Figure 2.1 Energy levels and transitions related to the Raman effect.](image)

The Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule, because the energy gained or lost is related to the vibrational energy spacing. Experimentally, the Stokes shift in a Raman spectrum is observed, because it has higher intensity than the anti-Stokes lines. For a transition to be Raman active there must be a change in polarizability of the molecule. Polarizability is the change of the dipole moment with distance [7].

In aligned crystalline materials, Raman spectra obtained as a function of polarization of the incident and scattered light is particularly useful due to the ability to selective by excite and detect vibrations of a particular symmetry. The resonance Raman effect provides additional detail when the excitation wavelength approaches that of an allowed electronic transition [8].

Particularly in the case of SWCNTs, Raman spectroscopy has been used to distinguish metallic from semiconducting CNTs, to determine tube diameters [9], and to reveal defects.
The power of Raman spectroscopy for analysis of SWCNTs derives from several factors, including the high symmetry of individual NTs which dictates the activity of a limited number of vibrational modes in Raman and infrared spectroscopy. The low-frequency radial breathing mode (RBM) is strongly dependent on the tube diameter. In addition, the presence of an optically allowed band-gap transitions which depend on symmetry and tube diameter results in wavelength-dependent features deriving from the resonance Raman effect. Finally, the presence of second-order scattering, which can depend on the presence of defects, provides additional information [10].

Raman spectroscopy has proven to be an especially powerful tool for determining the structure of CNTs, mostly of the single-walled type. Though fewer fundamental studies of the more complex mutli-wall carbon nanotubes have been reported, their larger diameter and the presence of concentric CNTs may lead to unique properties not possessed by SWCNTs [11].

In the present work, a unique approach is described to expand the power of Raman spectroscopy to the analysis of MWCNT turfs. The Raman measurements in this study are performed using a single monochromator (Acton Spectra-Pro 2300i) and a thermoelectrically cooled CCD detector (Roper Scientific Spec10:256E). The monochromator/detector system can be coupled to any of three laser sources: a large-frame argon ion laser (Coherent Innova 400/15-3), a small frame krypton ion laser (Spectra Physics Beamlock 2060), and a ring dye laser (Coherent 899-01) pumped by the argon ion laser.
2.5 Nanoindentation

Indentation tests became one of the most frequently applied tests of the mechanical properties of materials. A hard tip is forced down into the sample with a defined applied load. After a specified loading and unloading time schedule, the load is removed. The purpose of nanoindentation is to perform indents on very small volumes of materials, where the contact area between the sample and the tip is small [12].

The nanoindentation results are obtained by a Hysitron Triboscope nanomechanical testing system; it is capable of measuring Young’s modulus, hardness, fracture toughness and other mechanical properties via indentation. It is a hybrid of a Hysitron indenter and a Park Autoprobe CP scanning probe microscope (SPM), connected with a signal adapter.

2.6 References


CHAPTER THREE

3. ARTIFICIAL NEURAL NETWORKS MODELING OF THE
MECHANICAL BEHAVIOR OF MICROSTRUCTURES-CASE
STUDY: ALUMINUM ALLOYS

3.1 Introduction

There have been numerous research studies on aluminum alloys in recent years due partially to the increasing demand for the utilization of lighter materials in the automotive industry. The heat treatable 6xxx series, Al-Mg-Si alloys, are of special interest for outer panel applications, where high strength and dent resistance are required, and bumpers, where good strength and shock absorption are needed. In both cases good formability is also an important requirement. However the formability and strength properties often have adverse affect on each other and thus they need to be optimized.

It is well established that the formability and strength in heat treatable aluminum alloys can be optimized by controlling the aging behavior of these alloys. Hence understanding and modeling the aging behavior of these alloys has been an area of intense activity by many researchers. In literature, one can find a range of efforts in modeling the aging behavior including atomistic modeling [1, 2], process modeling [3-6], complex mathematical modeling [7], and micromechanical modeling [8]. However, most of the existing models focus on simplified situations. For instance, in the case of homogeneous precipitation, a single precipitate phase is assumed. For heterogeneous precipitation on structural defects (grain boundary, dislocations), homogeneous precipitation is assumed to be absent. In many systems, these simplifying assumptions
appear somewhat unrealistic: precipitation occurs through a sequence of metastable phases, and heterogeneous and homogeneous precipitations are competing phenomena.

In view of the variety of mechanisms involved, it is hopeless to develop models for such situations at the same level of detail as the academic models. In order to understand and to model these complex situations, one has first to qualitatively characterize the relevant microstructural features and then to use them in predicting the material behavior. In this vein, application of new models capable of incorporating the most important microstructural parameters is highly desirable. The artificial neural network (ANN) modeling has the potential to be used for such purposes. The broad application of ANN models in materials science has been reviewed recently by Bhadeshia [9], and Raabe [10]. Particularly ANN models are useful in studying the materials behavior wherever the complexity of the problem is overwhelming from a fundamental standpoint and where simplification is unrealistic.

This chapter is concerned with application of ANN models to evaluate microstructures behavior, in particular predicting the aging behavior of a relatively simple system, AA6022, which is the base of a whole family of Al-Mg-Si alloys, and has been the material of choice for automotive skin panels. The aging behavior of AA6022 was studied during isothermal heating at 175°C due to its potential industrial application (Paint Bake Process), and was characterized by hardness measurements. The structural evolution during aging treatment was studied by transmission electron microscopy (TEM). To describe the precipitate morphologies during aging treatment, the image analysis algorithm capable of characterizing orientation gradient, nearest neighbor distances, number density, shapes, and size of precipitates was developed. These features
were measured after several image filtering steps to take into account only the precipitate cross sections in the image. The relation between the characterized precipitate parameters and the evolution of material hardness during aging treatment was modeled by the ANN method.

3.2 Artificial Neural Network Approach

Neural network analysis is a system identification technique for assisting the study of phenomena which are not yet amenable to analytical modeling. This method is used widely in process control, process design, alloy design [9] and material characterization [11]. The structure of neural network, data representation, normalization of inputs–outputs and suitable selection of activation functions have a strong influence on the efficiency and performance of the trained neural network [12].

The neural network used in this study consists of three layers, i.e. input $p_i$ (representing the precipitate parameters which will be extracted from TEM images), hidden and output $a_j$ (hardness data) layers; figure 3.1 shows the structure of the used neural network system.
Backpropagation training methodology is used in training the type of neural network used in this chapter. The net input to unit $i$ in layer $k+1$ is:

$$n_{i}^{k+1} = \sum_{j=1}^{l} w_{i,j}^{k+1} a_{j}^{k} + b_{i}^{k+1}$$  \hspace{1cm} (3.1)

The output of unit $i$ will be:

$$a_{i}^{k+1} = f^{k+1}(n_{i}^{k+1})$$  \hspace{1cm} (3.2)

Where $f$ is the activation function of neurons in the $(k+1)$th layer. In order to select the appropriate training parameters, different activation functions were implemented at different number of neurons and epochs. The activation (transfer) functions can be any differentiable transfer function such as linear, hyperbolic tangent sigmoid or log sigmoid. After multiple iterations to minimize the MSE (Mean Square error) of the network
output, hyperbolic tangent sigmoid (Eq. 3.3) and log sigmoid (Eq. 3.4) transfer functions are applied to the hidden and the output layer respectively.

\[
Tansig(n) = \frac{2}{1 + \exp(-2 \cdot n)} - 1
\]  
(3.3)

\[
Logsig(n) = \frac{1}{1 + \exp(-n)}
\]  
(3.4)

The performance index, which shows all the features of this compound system, is chosen as the mean squared error:

\[
V = \frac{1}{2} \sum_{q=1}^{Q} (t_q - a_q^M)^T (t_q - a_q^M) = \frac{1}{2} \sum_{q=1}^{Q} e_q^T e_q
\]  
(3.5)

In Eq. (3.5), \(a_q^M\) is the output of the network corresponding to the \(q\)th input \(p_q\) at layer \(M\), \(t_q\) is the target, and \(e_q = (t_q - a_q^M)\) is the error term. Weight update is performed after the presentation of all training data (batch training). The weight update for the steepest descent algorithm is:

\[
\Delta w_{i,j}^k = -\alpha \frac{\partial V}{\partial w_{i,j}^k}
\]  
(3.6)

\[
\Delta b_i^k = -\alpha \frac{\partial V}{\partial b_i^k}
\]  
(3.7)

where \(\alpha\) is the learning rate, which is chosen to be small enough for the true estimate and also at the same time large enough to accelerate convergence. Effects of changes in the net input of neuron \(i\) in layer \(k\) to the performance index are defined as the sensitivity:

\[
\delta_i^k = \frac{\partial V}{\partial n_i^k}
\]  
(3.8)
The backpropagation algorithm is performed as follows: first, inputs are fed to the network and errors are calculated; second, sensitivities are propagated from the output layer to the first layer; then, weights and biases are updated [13]. This methodology has proven to be extremely useful in modeling and classification problems where properties need to be estimated as a function of a vast array of inputs [14].

The number of neurons and epochs used in the training process are optimized based on MSE to improve the trained network performance. Initially the weights for ANN parameters are assigned randomly. The selection of an appropriate set of training cases and procedure is very important to minimize the estimation error. Generally, there is no standard method to generate a comprehensive priori estimate of a required set of training cases before knowing the outcome and convergence of each training process, thus, several training strategies with different data sets have to be initially applied to validate the algorithm. The training data must contain the knowledge that describes the hardness behavior within a finite domain of input and output. This is needed to allow the trained neural network to generalize the hardness response that is implicitly included in the training data. The trained neural network is then examined, and its response is compared with the full range of trained and untrained (verification) data.

3.3 Experimental Procedure

Aluminum alloy 6022 (AA6022) with the composition of 0.55%Mg-1.10%Si-0.07wt%Cu was initially acquired in thin plate form with a thickness of 3.07 mm. The specimens were solution treated at 550°C for 3 hours with a programmable furnace and then water-quenched to room temperature. To study the precipitate evolution during isothermal aging, the samples were aged at 175°C in a salt bath furnace for various
periods of time. Vickers micro-hardness and TEM studies were performed on the aged samples.

TEM specimens were electro-polished in a solution of 300 ml 69% nitric acid + 700 ml methanol at a temperature of -20°C ± 5°C by using a twin jet electro-polishing unit. TEM investigations were carried out in a Philips TM420 microscope operating at 120KeV. Hardness measurements were conducted with a 500g load. The hardness data were determined from the average of at least four readings from each sample.

3.4 Image Processing

The image processing procedure includes image enhancement and measurement through feature extraction. Image defects which could be caused by the digitization process or by faults in the imaging set-up are corrected using Image Enhancement techniques. Measurement Extraction operations are used to extract useful information from the image. In unprocessed images, the useful data often represents only a small portion of the available range of digital values. Contrast enhancement increases the contrast between precipitates and the backgrounds.

After enhancing the image quality, spatial filtering is used to improve the appearance of an image. Spatial filters are designed to emphasize specific features in an image based on their wavelengths. A wavelength is correlated to the image texture. Coarse textured areas of an image have high wavelengths, while even areas with little variation in tone over several pixels, have low wavelengths.

A Wiener de-noise filter is performed to smooth and reduce the noise in the image; it estimates the local mean \( \mu \) and variance \( \sigma^2 \) in the region of each pixel.
\[
\mu = \frac{1}{NM} \sum_{n_1, n_2 \in \eta} I(n_1, n_2) \\
\sigma^2 = \frac{1}{NM} \sum_{n_1, n_2 \in \eta} I^2(n_1, n_2) - \mu^2
\]

\(\sum\) is the \(N\)-by-\(M\) neighborhood of each pixel in the image \((I)\). To produce the filtered image \((O)\), the Wiener filter is applied for each pixel using:

\[
O(n_1, n_2) = \mu + \frac{\sigma^2}{\varepsilon^2}(I(n_1, n_2) - \mu)
\]

The average of all the local calculated variances is used to replace the unknown noise variance \(\varepsilon^2\) [15].

A two-dimensional Fast Fourier Transform (FFT) is applied (Eq. 3.12) to characterize the image in the frequency domain, which helps in filtering and understanding the image details.

\[
F(m, n) = \sum_{x=1}^{M} \sum_{y=1}^{N} I(x, y) e^{-\frac{2\pi m x}{M}} e^{-\frac{2\pi n y}{N}}
\]

Where \(1 \leq m \leq M\) and \(1 \leq n \leq N\), \((M, N)\) is the image \((I)\) size.

After FFT Transformation, selected wavelengths can be filtered before the image is transformed back to the spatial domain. A low-pass filter is designed to emphasize larger, uniform areas of similar tone and remove the smaller features in an image. High-pass filters do the opposite and are used to sharpen the appearance of fine feature in an image [16].
Due to the imaging and scanning procedure, some images have defects with different sizes. Based on the precipitates statistics, a size filter is designed to clean the image from those defects.

After precipitate detection in the microstructure using the proper image scale, size distribution measurements are performed using pixel span information. The nonuniformity of precipitates distribution in an image is quantified by measuring the nearest neighbor distances (Eq. 3.13). In general, precipitate structures may exist as clustered, random or uniformly spaced. The mean nearest neighbor distance indicates the distribution style, for a clustered structure; the mean nearest neighbor distance is generally smaller than the uniform structure. For a random structure, it forms a random distribution (Poisson, Gaussian…etc), such that the standard deviation is close to zero,

\[ N(x, y) = \min_i \left( \sqrt{(y - y_i)^2 + (x - x_i)^2} \right) \]  

(3.13)

where \((x, y)\) are the coordinates of precipitate centroid, and \(i\) is an index for the surrounding precipitates.

The nearest neighbor information is used to describe the structure anisotropy. Rose plots of precipitates are produced to represent the precipitates preferred directions. In addition to precipitate orientations, the size gradients in \(x\) and \(y\) directions were characterized using average pixel brightness in the \(x\) and \(y\) primary directions [17].

### 3.5 Results

Figure 3.2 shows the age-hardening behavior of the AA6022 during aging at 175°C. The age-hardening behavior of AA6022 follows the classical aging behavior of precipitation hardening alloys. At the beginning the rate of hardening is very slow due to nucleation of
precipitates from supersaturated matrix. After about 40min, the rate of hardening starts to increase significantly due to the growth and change in the degree of coherency between precipitates and aluminum matrix. The hardness reaches a maximum after about 8 hours aging, and afterward over-aging starts due to the formation of large particles which have no coherency with the matrix.

![Graph showing variation of hardness versus time for AA6022 during aging at 175°C.](image)

**Figure 3.2** Variation of hardness versus time for AA6022 during aging at 175°C.

The details of the precipitation sequence in AA6022 have been reported [18]. In this paragraph a brief review of precipitate types is given. Figure 3.3 shows dark field TEM images of precipitate morphologies at 4 different stages of aging. Figure 3.3(a) corresponds to the morphology of the precipitates after 140min aging at 175°C. The small needle-shaped precipitates are distributed in \(<100>_{\text{Al}}\) zone axes, and the diffraction analysis of the microstructure revealed that the precipitates are \(\beta''\) [18]. Figure 3.3(b) shows the morphology of the precipitates in the peak-aged sample. The majority of precipitates is still needle-shaped distributed in \(<100>_{\text{Al}}\) zone axes, and the minority are
lath-shaped oriented with angle less than 11º from <100> aluminum zone axes. The lath-shaped precipitates are a precursor of Q′ phase [19]. Figure 3.3(c) shows the microstructure of the sample in a slightly over-aged (~730 min) condition. In addition to Q′ and β″ precipitates, a few large rod-like precipitates were observed in the microstructure. The elongated dimension of rod-like precipitates is about 100-200 nm which agrees well with the reported size for β′ precipitates [20]. After 5500 min aging the precipitate structure consisted of equilibrium cuboid β [21] phase along with Q′ and β′ precipitates (figure 3.3(d)).

Figure 3.3 TEM dark field images of precipitates after aging at 175ºC for (a) 140min, (b) 500min, (c) 730min and (d) 5500min.
To establish the microstructure-property relationships, the first task is to develop the methodology for extracting precipitation information in the form of numerical data set applicable for further modeling efforts. This can be achieved by performing rigorous image analysis on the TEM images. The filtering procedure discussed in Section 3.4 was performed to enhance the quality of the TEM micrographs. Figure 3.4 shows the morphology of precipitates after filtering series. The contrast of the image has been improved, precipitate structures are more resolved and the background noise is filtered out. Figure 3.4(a) shows a clear filtered image at 140min aging. The noise in figure 3.4(b) is filtered out using FFT pattern, the result is shown in figure 3.5(b). The redundant particles in figure 3.4c are removed using a size-based filter. The image at 5500min aging (figure 3.4(d)) contains background noise which is also cleaned out.
The quality of previously shown images can be further enhanced by using the FFT filtering procedure discussed in Section 3.4. According to this technique a frequency spectrum is correlated to the precipitate size distribution. The insets in figure 3.5 show the FFT pattern of the TEM images given in figure 3.3. Figure 3.5 shows an example for images after cutting off the undesired noise (using a band pass filter) and converting the image from the frequency domain to the spatial domain. The precipitates with higher
brightness have higher wavelength which is represented by darker color according to the frequency spectrum.

Figure 3.5 FFT filtering (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175°C, the inset is the FFT pattern.

In the next step, image analysis was performed on the filtered TEM images to extract the precipitate information. The area fraction distribution of precipitate cross sections is represented in figure 3.6. As can be seen, up to the peak of aging (figures 3.6(a, b)), the mean area of precipitates remains unchanged (~34 nm²). However, the variation of precipitate area is higher at early stages of aging which may be attributed to
the simultaneous nucleation and growth of $\beta^\prime$ precipitates. As we discussed earlier, at 730min the $\beta^\prime$ and lath-shaped precipitates start to transform to $\beta'$ and $Q'$ phases with larger dimensions. This means that slightly after peak-aged condition the mean area of precipitates should increase while the variation of the precipitate’s area should remain unchanged (figure 3.6(c)). In the overaged condition (figure 3.6(d)) the mean area of precipitates is almost double in comparison to the early stages of aging which indicates the growth of precipitates is the dominant mechanism.

Figure 3.6 Precipitates area distribution (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175ºC.
The orientation distribution of precipitates is represented in typical rose plots (figure 3.7). It can be seen that at early stages of aging (figure 3.7(a)) there is no preferred orientation among the precipitates, whereas in the later stages of aging, the majority of precipitates are oriented in specific crystallographic directions (figures 3.7(b,c)). This is in agreement with the precipitate evolution during aging. At age of 140min, the $\beta''$ precipitates form on GP zones which are randomly distributed in aluminum matrix, assuming their precipitation is not affected by the microstructural defects present in the bulk aluminum matrix. However, at later stages of aging the growth of $\beta''$ and its transformation to $\beta'$ and $Q'$ happens in preferred crystallographic orientations.
To extract information related to the distance between precipitates, the nearest neighborhood distance between precipitates was analyzed. Figure 3.8 shows that the distribution of the nearest neighborhood distance varies at different stages of aging. The mean and STD of the distribution were calculated to determine the nature of the
distribution. It was found that the nearest neighborhood distance distributions are close to a random distribution; however, the degree of randomness depends on the aging time. While figure 3.8(a) represents a random distribution of precipitates, the degree of randomness decreases after 500 min aging (figure 3.8(b)). It can be seen that at peak-aging the precipitates have uniform distribution and the mean of nearest neighborhood distance is about 20 nm. After 730 min aging time (figure 3.8(c)) the non-uniformity of distribution increases and it is maximal after 5500 min aging (figure 3.8(d)). The variation of precipitate nearest neighborhood distances agrees well with the precipitate evolution during aging. At early stage of aging, the $\beta''$ precipitates forms in random manner in the bulk aluminum matrix. At later stages of aging the growth of $\beta''$ precipitates and their transformation to $\beta'$ and $Q'$ phase decrease the degree of randomness, which is more pronounced in the overaged condition.
Figure 3.8 Nearest neighbor distance (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175ºC.

Figure 3.9 represents the aspect ratio (major axis to minor axis ratio) variation of precipitate cross sections during aging treatment. It can be seen that while the precipitates are more or less circular (aspect ratio ≈ 1) at early stages of aging (figure 3.9(a)), the aspect ratio starts to deviate from 1 (ellipsoidal precipitates). This behavior is in agreement with the previous precipitate analyses in Al-Mg-Si alloys [22]. At 500min aging, the peak-aged condition, the majority of precipitate are β” with polyhedral cross section along with minor lath-shaped precipitates which explain the tendency of aspect ratio to be larger than 1. It is interesting to note that at 730min, at a slightly overaged
condition, the majority of precipitates show both circular and ellipsoidal cross sections (figure 3.9(c)). According to [22], during overaging the $\beta''$ precipitates transforms to rod-like $\beta'$ and the lath-precipitates transform to $Q'$ precipitates with rectangular-shaped cross section. The formation of rod-liked precipitates explains the presence of a peak for the aspect ratio of close to 1 in figure 3.8(c). At longer time, 5500min, the precipitates close to equilibrium condition [23], $\beta$, Si and Q start to form which are no longer circular in cross section (figure 3.9(d)).

![Major axis to minor axis ratio Distribution](image)

Figure 3.9 Major axis to minor axis ratio (a) 140min, (b) 500min, (c) 730min and (d) 5500min aging time at 175ºC.
3.6 Age-Hardening Model

In this study, a model based on the ANN approach for predicting the aging behavior of AA6022 has been proposed. In Section 3.6.1, experimental data taken from hardness tests was used to train the model. The mean square error (MSE) was minimized by changing the number of neurons and epochs. Once the model was established, in Section 3.6.2, a parametric study was performed to study the influence of precipitate parameters on age-hardening behavior. Then the model predictions for deformed and undeformed structures were studied in Section 3.6.3.

3.6.1 Model Training and Generalization

The extracted precipitate information is divided into two sets as training and test sets. Neural networks are trained by using a set of precipitate characteristics obtained from TEM images discussed earlier. Then, the generalization capacity is examined by extracting the precipitate information from a new set of TEM images (test sets). The training data was not used in test data. Simulations with test data were repeated many times with different weight and bias initializations.

Figure 3.10 shows the hardness response of ANN model after training, and shows that the model outputs are in agreement with experimental hardness measurements. It is interesting to note that, despite the narrow hardness variation for the time interval of 100 to 1000s, the trained ANN model is still able to capture the variation of hardness.
The efficiency of the model can be improved by MSE minimization. This was performed by changing the number of neurons and epochs for the trained network. Figures (3.11, 3.12) show the MSE response of the ANN model as a function of number of neurons and epochs. To minimize MSE; first we executed the training process for certain number of epochs and multiple number of neurons, 25 neurons was seen to give the least MSE almost no matter what the epochs number was (figure 3.11). After that we executed the program at 25 neurons and different number of epochs to optimize the training time and MSE, figure 3.12 shows that applying 300 epochs is sufficient to get the desired performance. Hence, 300 epochs and 25 neurons are used in the final execution.
Figure 3.11 MSE of age-hardening model output versus number of neurons (50 epochs).

Figure 3.12 MSE of age-hardening model output versus number of epochs (25 neurons in the hidden layer).
3.6.2 Parametric Analysis

After establishing the model and minimization of error, a parametric study was performed to better understand the significance of each precipitate parameter on the model response, and to eliminate the redundant parameters. Table 3.1 shows the weight of each input \( w^i \) averaged after several runs of ANN program; the most efficient input has the highest weight value. Among the precipitate parameters, the number of precipitates per unit area, the area of the precipitates, nearest neighborhood distance, and major to minor axes ratio of precipitates were found to strongly affect the accuracy of the model.

Table 3.1 The average influence of inputs on the age-hardening model.

<table>
<thead>
<tr>
<th>Model Inputs ( (p_i) )</th>
<th>Weights ( (w^i) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of particles per unit Area</td>
<td>16.7</td>
</tr>
<tr>
<td>Precipitates Area distribution</td>
<td>9.4</td>
</tr>
<tr>
<td>Nearest Neighborhood distance</td>
<td>6.2</td>
</tr>
<tr>
<td>Ratios of major axis to minor axis</td>
<td>5.3</td>
</tr>
<tr>
<td>Nearest Neighborhood angle</td>
<td>1.1</td>
</tr>
<tr>
<td>Precipitates orientation</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The first three parameters represent volume fraction, size and distance between precipitates. In fact, in the literature, various models based on volume fraction [8], size [24] and distance between precipitates have been reported for age-hardening of aluminum alloys. Therefore the strong dependency of model to these parameters is not surprising and agrees well with previous works.
Among the most effective parameters given in table 1, the ratio of major to minor axis of precipitates or the shape of precipitate cross sections, has been less studied. According to table 1 this shape strongly affects the hardening behavior of the alloy. From materials science point of view, the aspect ratio represents the precipitate types. When this ratio is close to 1, the precipitates are $\beta''$ or $\beta'$ and when this ratio is larger than 1, they are lath-shaped or $Q'$. Depending on whether $Q$-type or $\beta$-type precipitates exist, the $\Theta$ angle required for dislocation to overcome the precipitates in the $\{111\}$ slip planes will be different, which directly affects the hardening behavior (Orowan mechanism). This has been schematically illustrated in figure 3.13. Recent studies by Nie and co-workers [25, 26] highlight the importance of precipitate shape on the hardening behavior of Al-Mg-Si alloys. The information obtained herein supports existing theories and offers a means by which mechanical properties can be determined from a detailed knowledge of the microstructure.
Figure 3.13 (a) The orientation relationship of rod-like precipitates in the unit crystal of aluminum matrix. The precipitates are oriented in <100> direction of aluminum. (b) The interaction of rod-like precipitates with dislocations in {111} plane. (c) The orientation relationship of lath-shaped precipitates in the unit crystal of aluminum matrix. The precipitates are oriented in <100> direction of aluminum. (b) The interaction of lath-shaped precipitates with dislocations in {111} plane. (The shadowed triangle represents the {111} plane.)

3.6.3 Model Prediction

Once the model is established, its accuracy has to be verified by comparing the model predictions versus the experimental results. The term “ANN prediction” is reserved for
ANN response for cases that were not used in the pre-training stages. This is used in order to examine the ANN’s ability to associate and generalize a true physical response that has not been previously “seen.” A good prediction for these cases is the ultimate verification test for the ANN models. These tests have to be applied for input and output response within the domain of training. It should be expected that ANN will produce poor results for data that are outside the training domain.

Multiple runs are used for the training process after ANN calibration to compensate for the initial random assignment of ANN weights and biases. Using multiple runs will guarantee that the random initialization is not affecting the network performance.

*Un-deformed structures*: The model was tested against a new set of experimental microstructure and hardness data taken after 500 mins and 140 mins aging. According to table 3.2, the model is able to predict the hardness with maximum 2% error.

**Table 3.2 Age-hardening model prediction results.**

<table>
<thead>
<tr>
<th>Aging time (mins)</th>
<th>Experimental Vickers hardness</th>
<th>ANN Prediction of Vickers hardness (average of multiple runs)</th>
<th>Percentage Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Un-deformed structures</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>67.4</td>
<td>67.6</td>
<td>0.3</td>
</tr>
<tr>
<td>140</td>
<td>62.4</td>
<td>63.7</td>
<td>2</td>
</tr>
<tr>
<td><strong>Deformed structures</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>56.2</td>
<td>53.1</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Deformed structures: The influence of pre-deformation on the nature of precipitate evolution has been studied by Yassar et al [27, 28]. It is well established that deformation is associated with the production of large number of microstructural defects which in turn govern the nucleation rate and growth rate of precipitates. This can result in changing the nature of precipitation sequence and precipitate characteristics. In addition, the interaction between dislocations and precipitates results in a complex physical problem. It is not perfectly clear that the hardening due to precipitates or dislocations is dominant. Therefore in deformed structures it is very difficult to model or predict the materials behavior.

To investigate the power of the ANN model and its ability to predict the hardening behavior of pre-deformed structures, selected samples were analyzed in deformed condition. This was achieved by deforming the as-quenched samples prior to the aging treatment. Figure 3.14 represented the dark field imaging of precipitates after 30% deformation and aging at 175ºC for 480 mins. Interestingly table 2 shows that the model was able to predict the hardness value in the range of experimental measurements within an acceptable error of 5.5%. This means that regardless of dislocation structures, the precipitate information extracted from figure 3.14 was sufficient to forecast the hardness. In another words, the hardening behavior of AA6022 strongly depends on precipitate characteristics and less to dislocation structure.

The excellent agreement between model predictions and experimental results confirms that ANN modeling can provide a unique opportunity for materials modelers to study the materials behavior in complex structures and to develop more realistic structural based models.
Figure 3.14 TEM dark field images of precipitates in a deformed sample after aging at 175ºC for 480 mins.

### 3.7 Summary and Conclusions

A model based on feed-forward neural networks in simulating hardness behavior of heat treatable 6000 series, Al-Mg-Si alloys is proposed. The data extracted from image processing of TEM images for each aging time is utilized to train the neural network model. The model captures the detail of precipitate evolution by tracking the variation in volume fraction, shape, size and distance between precipitates. It is found that the resulting model is capable of predicting hardness values of deformed and undeformed structures within the range of experimental measurements with maximum 5% error. It was concluded that hardening behavior of AA6022 strongly depends on precipitate characteristics.

These successful results of this study of microstructures motivated our goal in investigating the physical and mechanical properties of nanostructures. In the next chapter, we will apply the methodology of structure classification based on physical
appearance of carbon nanotubes, as a first step for a comprehensive quality evaluation of these materials at the nanoscale.

3.8 References


CHAPTER FOUR

4. QUALITY CLASSIFICATION OF CARBON NANOTUBES VIA ARTIFICIAL NEURAL NETWORKS

4.1 Introduction

The exceptional properties of carbon nanotubes have attracted much attention in recent years as a result of their small dimensions, relatively low density, high strength to weight ratio, high electrical and thermal conductivities and unique morphologies [1-3]. Several techniques have been developed to produce carbon nanotubes in large quantities for large scale applications, such as: arc discharge, laser ablation, high pressure carbon monoxide, and Chemical Vapor Deposition (CVD) [4]. Due to the uncontrolled nucleation of nanotubes and the incapability to direct the growth from and to any desired sites, CNTs lack the uniformity essential for research and industry. A significant factor delaying practical applications has been the incapability to easily quantify the CNT structure morphology in a given sample. Characterization and quantitative analysis of nanotube bulk structure is technically difficult due to the natural trend of the CNTs to form bundles held together by Van der Waals forces [5].

In this chapter, the morphology of CNT turfs was characterized using image processing of SEM images and by applying stereological relations to quantify sample structural properties such as: alignment and curvature. These structural qualities were categorized using Artificial Neural Networks (ANN) classifier.

4.2 Synthesis

The multi-wall carbon nanotube turfs in this study were grown using chemical vapor deposition with an iron catalyst. The catalyst thin film was grown on a (100) silicon
wafer. The resulting smooth thin film has a consistent height of 500 nm, as observed by Atomic Force Microscope (AFM). MWCNTs are grown on wafers placed in a tube furnace with an admixture of H₂ and C₂H₂, at 700°C while maintaining the chamber pressure at 75 Torr [6].

4.3 Image Analysis

Since there are no direct experimental tests available that can easily determine the growth behavior and structural properties of nanoscopic materials; it is our goal to develop a practical procedure to evaluate morphology and physical properties of nanotubes from SEM microscopy [7-10]. Several procedures have been developed to analyze images of different materials using image transformations, development of binary images, algebraic and geometric image manipulations, Fourier analysis and image contrast correction [11, 12]. These techniques have been employed for quantitative characterization [13] and the study of macroscopic behavior [14] of nanoscale materials. These methods could be helpful in the study of carbon nanotube structures [15], but until now the lack of published algorithms to convert CNT microscopic images into numerical quantities has hindered the determination of their structural quality [16].

We have recently introduced image processing techniques to extract morphology of precipitants in aluminum alloys from SEM micrographs [17]. In the present work, we apply these techniques to obtain geometrical information about MWCNT turf structure to characterize curvature, alignment and volume density. SEM images were obtained from our collaborators as described in ref. [6] and subjected to a standard thresholding procedure followed by two-dimensional fast Fourier transform (2D-FFT) analysis and determination of stereological parameters as described below.
The thresholding procedure was optimized for maximum information content by determination of the 2D correlation coefficient (4.1), for the raw and thresholded images as follows:

\[ r = \frac{\sum_{m,n} (A_{mn} - \bar{A})(B_{mn} - B)}{\sqrt{\left(\sum_{m,n} (A_{mn} - \bar{A})^2\right)\left(\sum_{m,n} (B_{mn} - B)^2\right)}} \]

(4.1)

where: \((A, B)\) are the gray-scale matrices of the raw and thresholded images, \((\bar{A}, \bar{B})\) are mean of \(A\) and \(B\), and \((m,n)\) are pixel indices.

Image frequency content was studied using two-dimensional fast Fourier transform (2D-FFT), which helps in filtering and understanding the image details [9, 18]. After FFT Transformation, selected frequencies were filtered out before the image is transformed back to the spatial domain using a low-pass filter to highlight larger, uniform areas of similar tone and remove the smaller components of the image. High-pass filters were used to sharpen the appearance of the fine features in the image. FFT analysis was applied to both thresholded SEM images and to ideal designed images with known values of geometry distribution based on (4.2), (4.3) and (4.4), to interpret the results based on CNTs alignment and curvature properties. As will be shown, FFT statistics indicate the general alignment, curvature, orientation and diameter of MWCNT turfs, but the results do not provide quantitative classification of these properties from image analysis. Thus, we determined stereological parameters of the thresholded images as described in the next section.

Since the micrographs are projection images, stereological relations were applied to extract the geometrical relations between the 3D CNT structure and the images of that
structure. The CNT image was sampled uniformly and randomly with line or plane probes. The sampling is determined by minimizing the variance of the estimated quantity, (4.2), (4.3) and (4.4), to enhance the measurement precision. Events that result from interactions of these probes with the structure were counted. Normalized averages of these measurements were used to calculate the average count for the complete distribution of probes. The area of interfaces in the structure was estimated using line probes sense, while plane probes sense the average tangent diameter of features. The area fraction occupied by CNTs in a single layer of the turf was estimated by $A_{A}$:

$$A_{A} = \sum_{w} \frac{A_{CNT}}{A_{w}}$$  \hspace{1cm} (4.2)

where $A_{w}$ is the area of the sampling window, $w$, and $A_{CNT}$ is the area of CNTs.

The normalized parameter, $L_{A}$ (4.3), is the ratio of the total length of boundaries of all CNTs in the sampling window divided by the area of that window.

$$L_{A} = \sum_{w} \frac{L_{CNT}}{A_{w}}$$  \hspace{1cm} (4.3)

where $L_{CNT}$ is the nanotubes boundary length.

The ratio of the number of intersections counted to the total length of line probe sampled was calculated using $P_{L}$ (4.4) which is known as “line intercept count”.

$$P_{L} = \sum_{\theta} \frac{P}{L_{probe}} = \sum_{\theta} P_{L}(\theta)$$  \hspace{1cm} (4.4)

where $P$ is the number of intersections, $\theta$ is the probe angle, and $L_{probe}$ is the probe length.

Since CNT structures are not isotropic, $P_{L}(\theta)$ varies for different directions of the probe line. A rose polar plot of $P_{L}$ as a function of $\theta$ provides a graphical description of this anisotropy [19].
4.4 Artificial Neural Network Model for CNTs Quality Classification

Artificial Neural Networks, a member of a group of intelligence technologies for data analysis, are considered as simplified mathematical models that work as parallel distributed computing networks.

In this chapter, the frequency analysis of the SEM images and the stereological procedures were used as input to an ANN model to classify nanotube images based on alignment and curvature estimations, which are used to evaluate the sample’s quality. To perform this task, two training methodologies were developed: initially a set of ideal rope images with defined values of curvature and alignment was created and used to train the ANN system. Next, a training subset of CNTs images was manually analyzed to estimate the relative curvature and alignment values. The relative measurements were performed on randomly selected nanotubes in each image. The alignment of nanotubes, \( A \), was measured based on the variance of the relative distances \( d_i \), between equal-length segments, \( s_i \), of any two nanotubes \( (C_1, C_2) \) [20].

\[
A = \frac{1}{M} \sum_{j=1}^{M} \left( \frac{\text{var}(d_j)}{N} \right) = \frac{1}{M} \sum_{j=1}^{M} \left( \frac{1}{N} \sum_{i=1}^{N} (d_i - \bar{d})^2 \right)
\]  

(4.5)

where \( d_i = |C_1(s_i) - C_2(s_i)| \), \( N \) is the total number of segments, and \( M \) is the number of two nanotube combinations.

The curvature measurements were estimated using an arbitrary moving tangent line, which is swept along the nanotube [21]. The curvature, \( k \), at considered segments is defined as the rate of rotation, \( \theta \), of the nanotube tangent as the contact point moves along the segment length, \( s \):

\[
k = \frac{d\theta}{ds}
\]  

(4.6)
The measurements of the alignment and curvature qualities were normalized to the greatest evaluated values of the tested images.

The neural network used in this study is described in ref. [17]. For each image, the 86 input vectors consist of the stereological parameters: $A_A$ (4.2), $L_A$ (4.3) and $P_L$ (4.4) calculated at 12 different angles between $0^\circ$ to $90^\circ$, and the 2D-FFT statistics, i.e. mean, standard deviation and sum for 4 by 6 subdivisions of the FFT pattern (8 by 6 total subdivisions). The output vector is composed of the alignment and curvature quality values. Backpropagation training methodology was used for the training process.

4.5 Results and Discussion

4.5.1 Image Analysis

Figure 4.4 shows a typical scanning electron micrograph of a carbon nanotube sample. The turfs consist of vertically aligned nanotubes with lengths of about 50 µm and diameters between 10 and 15 nm. Representative images were taken in the sidewall planes of the turfs, in which different morphologies of nanotubes were observed. The SEM micrographs were digitized on a 600X500 matrix with 256 gray levels (8 bit per pixel), resulting in a resolution of 2.304 nm per pixel. Ten images per turf were acquired and used for image analysis.

SEM images often contain distortion and noise that needs to be corrected before any further analysis. The filtering procedure discussed previously was performed to enhance the quality of the SEM images. As can be seen in figure 4.4, the contrast between nanotubes and the background is not consistent due to the uneven illumination of the sample by the electron beam. This contrast should be improved, such that CNT
structures are more resolved. The complexity of CNT structures makes it difficult to automate this process using “off-the-shelf” image analysis tools.

![Figure 4.4](image.png)

Figure 4.4 (a) SEM image of MWCNT turf (b) Magnification of (a).

Using SEM images to characterize nanotube samples is associated with a depth-of-field error; this problem was resolved by changing the thresholding level to differentiate the top layer from the background layers. Multiple thresholds were performed on the filtered SEM image, and then the 2D correlation with the untreated image was measured to estimate the optimum threshold which keeps the most important details of the image. In figure 4.5, the threshold of about 85 (gray-scale) was applied as an optimal value.

![Figure 4.5](image.png)

Figure 4.5 Auto-Threshold (a) raw image (b) 2D correlation vs. threshold (c) Thresholded image at 85 (gray-scale).

For the frequency analysis of the micrographs; we used a two-dimensional fast Fourier transform (2D-FFT). The 2D power spectrum, for analysis of the spatial
The frequencies of the images, was obtained from the FFT analysis. The relationship between the FFT patterns and the structure of the nanotubes was further analyzed. The frequency information of each image was fed to an image classifier Neural Network system for quality distinction purposes. FFT statistics (figure 4.6) shows that the frequency content is an indicator of the physical properties of the CNTs. FFT was applied to both real images and ideal images, to understand the significance of these results based on CNTs alignment and curvature properties.

![FFT patterns](image)

Figure 4.6 Different FFT patterns of created ideal images (a-c) and SEM images (d-e). Insets are the thresholded images.
As mentioned earlier, the created database of ideal images was used in training of the ANN system. The distribution of the alignment and curvature properties was programmed to be random, gradual or uniform. The effect of the change in alignment and curvature values of the ideal images on the FFT pattern of the images can be seen clearly in figure 4.6(a-c). The limited number of frequencies along the x-axis in figure 4.6(a) corresponds to the change of pixels intensities along a horizontal section while the change along a vertical section is negligible, this represents the ideal alignment. In the real images, more frequencies in both x-axis and y-axis are required to match the complexity of the nanotubes distribution, but the previous theory is still valid and can be used to quantify the alignment and curvature qualities of the sample.

The basic stereological relations are found to be helpful to extract information for both line and plane sections of CNT images in order to compare different CNT structures and to correlate the geometric properties of the structure with the quality of the sample. In figure 4.7, two SEM micrographs (a1-a2) of two different CNT samples are considered to demonstrate the procedure, where sample (a1) has more aligned and less curvy nanotubes than sample (a2). Using $A_d$, the proportion of a layer of the turf covered by nanotubes was found to be related to the alignment of the tubes, where more aligned nanotubes where found to be more dense than the nonaligned turfs. Figures 4.7(b1, b2) show $A_d$ values for (a1 and a2) images, an average of 0.4 was seen for the nonaligned nanotubes in (a2) where $A_d$ was about 0.48 for aligned nanotubes in (a1). On the other hand, as shown in figures 4.7(c1, c2), the ratio of the total length of CNTs boundaries per unit area, $L_d$, was greater for curvy samples, about $0.048 \text{ nm}^{-1}$, with higher density of kinks and
bending points, while it was 0.039 nm\(^{-1}\) for aligned nanotubes, this is due to the existence of longer nanotubes in curvy samples.

In figures 4.7(d1, d2), the rose plots of the line intercept count, \(P_L(\theta)\), clarifies the anisotropy behavior of the nanotubes. The figure shows the results for 10 different images of the turf, the change of the count distribution as \(\theta\) varies was clearly observed. The main difference was mostly in the vertical probe, where fewer intersections were counted for aligned nanotubes, where the elliptical shape was formed for more complex images, due to a higher number of intersections with the vertical probe.
Figure 4.7 (a) Samples of analyzed SEM images, (b) measurements of $A_A$, (C) $L_A$ and (d) $P_L(\theta)$ for images in (a).

### 4.5.2 CNTs Quality Classification Results

Neural Networks learn by example; therefore, no prior rules need to be identified to construct the network. This was ideal for our problem because it is difficult to describe clearly the physical appearance of nanotubes in a digitized SEM image using parameters
based on gray-scale levels. In addition, ANNs are non-linear systems; they may recognize novel relationships between system variables.

In our work, the ANN structure was designed to be flexible by selecting the network to be tuned by adjusting a few parameters. Two layers were used: one hidden layer, and one output layer. The activation functions, logarithmic sigmoid and hyperbolic tangent sigmoid transfer functions were used throughout the net (figure 4.8). All neurons had a bias weight. The weights were adjusted using the error back-propagation algorithm. The Mean Square Error (MSE) was minimized by changing the number of neurons and epochs of the network. As mentioned earlier, the training data sets include ideal and real images with percentage estimations for both the alignment and curvature qualities.

Figure 4.8 Back propagation activation functions (a) Logarithmic sigmoid (b) Hyperbolic tangent sigmoid.

Figure 4.9 illustrates the results of applying the model on two different micrographs; the aligned nanotubes were found to have a relative alignment and curvature values of about 70% and 20% respectively, while figure 4.9(b) shows averages of about 12% and 63%. The agreement between the classifier results and the set of training images shows that the ANN classifier can recognize different structure types.
Figure 4.9 Model outputs for (a) sample1 and (b) sample2 alignment estimations, (c) sample1 and (d) sample2 curvature estimations. Insets are the SEM images of the analyzed samples.
4.6 Conclusions

In this chapter, we have developed a quantitative technique where SEM micrographs of nanotubes were analyzed using image processing methods to make essential observations and collect fundamental information about CNT morphologies using 2D-FFT analysis and basic stereological relations to distinguish different structures of CNT turfs, these results were further investigated using feed forward neural networks for quality evaluation of nanotube structures. The neural network model for sample classification of CNTs using image analysis shows accurate categorizing results with an acceptable range of approximation relative to measurement inaccuracy. These results will be used in chapter 5 to understand the structure influence on Raman spectroscopy by studying the Raman spectral features and link them to the main structural parameters discussed in this chapter.

4.7 References


[20] Zheng L, Xiaonan L and Chengying G 2005 *Proc. 18th Int. Conf. on Pattern Recognition* (Hong Kong) pp 357-60
CHAPTER FIVE

5. QUALITY EVALUATION OF CARBON NANOTUBE BUNDLES USING RAMAN SPECTRA

5.1 Introduction

Many modeling theories and approaches in macro- and micro-mechanics could still be applicable at the nanoscale, while many others may not, which makes it complicated to study nanoscale structures analytically. Therefore, a comprehensive method connecting analytical, experimental and computational approaches has to be adopted to deal with this multiscale problem to build an efficient empirical and phenomenological model capable of incorporating the most important nanostructural parameters.

The ANN model along with the classifier results in chapter 4 was used to study Raman spectral information and to investigate the relationship between the quality of the turf morphology and the Raman spectrum. This scalable process will facilitate the use of such models to link CNT properties with the growth conditions using Raman spectroscopy analysis and SEM image analysis. The suggested methodology could be used, in in-situ applications, to manipulate the nucleation factors such that the optimum properties of the nanotubes in large quantities can be achieved [1-4].

5.2 Raman Spectral Analysis of CNT Turfs

Features of the Raman spectrum of CNTs include: the radial breathing mode (RBM: between 75 and 300 cm⁻¹), the disorder induced mode (D mode: between 1330-1360 cm⁻¹), the tangential mode (G mode: stretching mode in the graphite plane at about 1580 cm⁻¹). The resonance Raman phenomenon causes the excitation wavelength dependence of Raman intensities for CNTs which have their van Hove singularities in the
valence and conduction bands at the proper position to be in resonance with the incident laser [5]. Using polarization phenomena, the orientation of the tubes can be estimated by studying relative intensities of the Raman spectrum [6]. It is well-known that the frequency of the radial breathing mode is proportional to the inverse of the nanotube diameter [7, 8], thus, the average diameter of carbon nanotubes in a sample can be estimated by measuring the RBM frequency. The dependence of the phonon frequencies on the bond lengths or angles, which is related to strain, can be used to study the mechanical properties of the nanotubes [6]. Though observation of these characteristic Raman peaks determines the presence of CNTs in the sample, a quantitative understanding of the relation between Raman spectra and CNT structure has not yet been achieved, especially for MWCNTs.

Studies have shown that Raman spectra of multi-wall carbon nanotubes are more complex and have more unexplained peaks than those of single-wall nanotubes spectra [7]. It has been proposed that the strength of the D-mode relative to the G-mode is a measure of the amount of disorder in the nanotubes [9, 10]. The goal of the present work is to identify and correlate the Raman features to the other structural characteristics of the nanotubes, so that this information can be used for quality evaluation purposes of CNTs samples [8, 11].

5.3 Quantitative Analysis of Raman Spectrum

To accurately quantify features embedded in a Raman spectrum, various approaches using numerical data processing have been applied for noise–signal ratio reduction in Raman spectroscopy; however, having a non-uniform distribution of the noise required using more comprehensive filtering tools.
In order to achieve a good overall signal-to-noise ratio, Wavelet de-noising analysis was implemented to produce a smoothed Raman signal without losing any peaks information included in the spectrum [12]. Wavelet Transform (WT) method has been used for suppressing non-correlated noise and background signals in the Raman spectra.

The discrete wavelet transform of a Raman signal \( Raman(f) \), where \( f \) is relative wavenumbers, can be written as [13]:

\[
W_{\text{Raman}}(j,k) = \{ Raman(f), \psi_{j,k}(f) \} = 2^{-j/2} \int_{-\infty}^{\infty} Raman(f) \psi_{j,k}(f) df
\]  

(5.1)

where \((j,k) \in \mathbb{Z}, \) and the discrete wavelet basis (known as “mother wavelet”) is defined as:

\[
\psi_{j,k}(f) = 2^{-j/2} \psi(2^{-j} f - k)
\]  

(5.2)

The Raman spectrum \( Raman(f) \), for a set of given discrete orthonormal basis \( \psi_{j,k}(f) \), is decomposed as:

\[
Raman(f) = \sum_{j,k \in \mathbb{Z}} \{ Raman(f), \psi_{j,k}(f) \} \psi_{j,k}(f)
\]  

(5.3)

Using the discrete fast approach, proposed by Mallat [14], where the discrete signal \( Raman(f) \) is assumed to be described by \( \{ C_0 \} \), and \( \psi_{j,k}(f) \) can be described by a group of discrete filters \( H=\{h_l\}, l \in \mathbb{Z} \) and \( G=\{g_l\} \), then \( C_0 \) can be decomposed as:

\[
C^j_k = \sum_{n=-\infty}^{\infty} h_{n-2k} C^{j-l}_n
\]  

(5.4)

\[
D^j_k = \sum_{n=-\infty}^{\infty} g_{n-2k} C^{j-l}_n
\]  

(5.5)

where \( j \) is the decomposition scale, the low frequency and high frequency parts of the signal are described by \( C^j \) and \( D^j \) respectively. After decomposition, the algorithm
maintains the same data point number as the original signal. Therefore, the de-noised result was obtained by simply selecting a component with lower frequency from the decomposed components ($C_j$).

Raman peaks were found using local maxima search algorithm. Lorentzian fitting for these peaks was used to quantify the spectrum features, where the intensity, the line centroid position and the half-width at half-maximum (HWHM) of Lorentzian components were considered for modeling purposes. These were expressed as a function of excitation wavelength $\lambda$. All of these peaks information were used later to study the quality of CNTs turf.

5.4 Artificial Neural Network Model for Raman Spectrum Identification

ANN is a very powerful technique to illustrate the physical interpretation of morphological characteristics through recognition of the patterns and relationships in data fed to the adaptive system. Literature in materials science shows that ANN applications are rapidly growing as a system identification technique for assisting the study of phenomena which are not yet amenable to analytical modeling. The broad application of ANN models in materials science has been reviewed recently by Bhadeshia [15], and Raabe [16]. In particular, ANN models are useful in studying the materials behavior wherever the complexity of the problem is overwhelming from a fundamental standpoint and where simplification is unrealistic [17]. This methodology has been used extensively in process control, process design, alloy design [15], and interpretation of the indentation load–displacement curves which are difficult to formulate and solve using analytical methods due to material and geometric nonlinearities as well as complex contact
interactions [18-20]. An ANN model has been used to differentiate between SWCNT samples of different diameters on the basis of their Raman G-band [21].

Using an ANN model, the results of morphology recognition in chapter 4 were employed to identify relations between Raman spectral information and structural characteristics of CNTs. The input set to this system was represented by the inputs of the quality classifying system discussed in chapter 4; with one additional input parameter, the Raman excitation wavelength. As the goal of this model is to provide a better understanding of the morphology influence on a Raman signal, the output vector included the information extracted from Raman spectra.

5.5 Results and Discussion

5.5.1 Raman Spectral Analysis

Raman spectra of the 18 MWCNT samples were measured at room temperature in ambient air with the intact turfs on the silicon wafer substrates upon which they were synthesized. The Raman spectra were excited at 488 nm and 514 nm with an argon ion laser and at 531 and 568 nm with a krypton ion laser. Incident power at the sample was 50 mW. The excitation light was focused onto the sample with a cylindrical lens, and the emitted light was focused on the entrance slit of a single monochromator (Acton Spectra-Pro 2300i) after passing through a holographic notch filter (Kaiser Optical) to reject the elastically scattered light. The dispersed light was detected using a thermoelectrically cooled CCD (Roper Scientific; Spec 10, 256E). The spectra were not corrected for the spectrometer response. Each CNT spectrum was normalized to the intensity of the Si Raman line at 522 cm$^{-1}$ by translating the sample so that the laser was exciting the bare Si substrate. The standard deviation of the measurement error of the peak shift of the Si-
Raman line as derived was less than 0.5 cm\(^{-1}\), while the full range of the peak shift for different samples at different excitation wavelengths of the silicon Raman line was found to be ± 1.5 cm\(^{-1}\).

Raman spectra were measured using the same samples studied by SEM. Areas of a few square microns were sampled in Raman, therefore, the collected data was related to the average properties of the CNTs in the corresponding volume. It was found that Raman spectra don’t change significantly if the laser is scanned over multiple spots on the same CNT turf. Figure 5.1 shows multiple Raman spectra of 488 nm and 530.9 nm excitation lasers taken from two different samples.

![Figure 5.1 Raman Spectra of two different CNT samples taken at two excitation wavelengths: 488.0 and 530.9 nm. The shown range is: 600-3400 cm\(^{-1}\).](image)

Figure 5.1 Raman Spectra of two different CNT samples taken at two excitation wavelengths: 488.0 and 530.9 nm. The shown range is: 600-3400 cm\(^{-1}\).
In this study, the strong Raman first-order bands: D (1340-1360 cm\(^{-1}\)) and G (1584-1594 cm\(^{-1}\)), and the second-order bands: 2D (2695-2720 cm\(^{-1}\)) and D+G (2935-2955 cm\(^{-1}\)) were studied in order to investigate the influence of structure on these peaks using the ANN model, the 12 output vectors of the model include the intensity, width and position of these bands.

Wavelet de-noising was performed on two regions of interest: first order region from 1100 cm\(^{-1}\)- 1800 cm\(^{-1}\) and the second order region from 2500 cm\(^{-1}\)- 3100 cm\(^{-1}\). The discrete wavelets transform (DWT) decomposition and the inverse DWT (IDWT) techniques were implemented to filter out the noise. As shown in figure 5.2, the Raman signal from 2500 cm\(^{-1}\)- 3100 cm\(^{-1}\) was decomposed into eight subsets (D\(^1\)-D\(^8\)) with different amplitudes with D\(^8\) as the lowest frequency. Neglecting the high frequency components which have the lowest amplitude (D\(^1\)-D\(^3\) in figure 5.2) and some background noises in some spectra, the Raman signal was assembled and the non-correlated noise signals were eliminated.

Figure 5.2 (a) Raw portion of Raman signal (b) DWT and IDWT data processing (c) filtered Raman signal.
Raman features were analyzed by a Lorentzian fit of the spectra after subtracting a constant base line from each peak, figure 5.3 shows the fitting of the 2D band. These features contain (for each recognized peak): intensity, peak position and HWHM. It was observed that MWCNTs Raman peaks generally show asymmetric characteristic line shape possibly because of the diameter distribution.

Figure 5.3 Lorentzian fitting of 2D band at 2718 cm⁻¹.

5.5.2 Quality Evaluation Using Raman Spectra

As seen earlier, SEM images showed different types of bending nanotube structures. During the growth process, for small local strain, the nanotubes are expected to have elliptical deformation of the cross-sections, this is not visible in the SEM micrographs. On the other hand, buckling of CNTs takes place as the stored strain goes beyond a critical limit. This quantifiable structure change result in some differences in electronic transition energies [22], which state the conditions for resonant Raman scattering in
CNTs. The ANN model was implemented to investigate the influence of the structural variations on Raman spectra of the CNT turfs.

To achieve a better characterization of features distribution in the sample, Raman spectra measurements were performed using various excitation wavelengths. For the implemented supervised learning method, the 72 collected spectra were arbitrarily divided into two batches: the “Training” group includes 56 spectra which were used for the training process, where 16 spectra were used as “Testing” group.

Figure 5.4 shows the neural network testing results for the influence of the resonance phenomenon on D and 2D frequencies. It shows a precise estimation of the presented linear relation, where a red shift of about 20 cm\(^{-1}\) was observed in the D band (figure 5.4 (a)) as the excitation wavelength varies from 488.0 nm to 568.2 nm, while figure 5.4 (b) shows shifts down of about 24 cm\(^{-1}\) in the 2D band when the excitation wavelength changes from 488.0 nm to 530.9 nm. These shifts are explained in the literature by the double resonance process [23]. Figure 5.4 (c) shows evidently the significance of the excitation energy input on the ANN frequency modeling of the D peak. It clearly verifies that the other geometrical inputs have an insignificant effect on the D band shift.
Figure 5.4 Effect of excitation wavelength on (a) D, (b) 2D peak positions, (c) Inputs weights map for modeling of the D band where inputs (1-24), (25-48) and (49-72) are mean, standard deviation and sum of FFT subdivisions respectively; (73), (74), and (75-86) are $A_A$, $L_A$ and $P_L$ respectively; (87) is the excitation wavelength. SN: sample number.

ANN model proved the dependence of other Raman features on the structural changes of CNT turfs. This reliance is due to the changes in the vibrational force constants which consecutively determine the vibrational energies.

It was found that an increment in length per area, $L_A$, or line intercept count, $P_L$, results in a significant broadening of Raman peaks. The model testing results of the G band HWHM are shown in figure 5.5, it shows broadening of about 16 cm$^{-1}$ of the G band with the change of $L_A$ from 0.0358 to 0.0442 nm$^{-1}$ (figure 5.5(a)) and $P_L$ from 0.0268 to 0.033 nm$^{-1}$ (figure 5.5(b)). The broadening of Raman peaks in curvy and nonaligned bulk nanotube samples, where CNTs are twisted together and the bonding interaction within the bundles is maximized, is possibly due to exciting the nanotubes
with different vibration frequencies because of defects or nanotubes interactions in the sample caused by the structural variations associated with the alignment disorder.
Figure 5.5 ANN results for the effect of structural properties (a) $L_A$ (b) $P_L$ on the HWHM of G line.

The correlation between Raman features and stereological parameters were studied at fixed wavelengths to eliminate the influence of resonance phenomena. Noticeable shifts of about $2 \text{ cm}^{-1}$ and $4 \text{ cm}^{-1}$ of the D and 2D Raman peaks respectively are shown in figure 5.6 for the excitation wavelength 488.0 nm. The ANN model proposes that the blue shift in the D and 2D bands could be a result of the network constrains represented in terms of $P_L$ and $L_A$, due to the surrounding nanotube bundles which cause a weak inter-tubule interactions through Van der Waals forces.
Figure 5.6 Neural network results of the D line (a) Upshift in D band as a function of $P_L$,
(b) Upshift in 2D band as a function of $L_d$. 
Figure 5.7 ANN modeling of the Raman intensity ratio: $I_D/I_{D+G}$ in terms of (a) $P_L$, (b) $L_A$. 
Using the ANN model, the intensity ratio $I_D/I_{D+G}$ (figure 5.7) at the 488.0 nm excitation wavelength was roughly found to be linearly proportional to the disorder in the alignment and curvature of the nanotube bundles represented in terms of $L_A$ and $P_L$. This ratio changes from 0.3-0.57 as $P_L$ varies from 0.029-0.042 nm$^{-1}$ and $L_A$ from about 0.038-0.055 nm$^{-1}$. This is due to the fact that D band is activated in the first-order scattering process of $sp^2$ carbons by the presence of structure defects, a result of curvy and nonaligned nanotubes, which lower the crystalline symmetry. This linearity was not observed at other wavelengths, perhaps due to the resonance phenomenon. This behavior will be further investigated in future work.

5.6 Conclusions

After having the quality of nanotube structures estimated in chapter 4, those features were mapped to different Raman spectral patterns using the ANN model. The resonance effect was observed and Raman features were related to the nanotube structural qualities. We established the validity of relating the physical appearance of CNT turfs to Raman Features using ANN models as an efficient quality evaluation tool of these turfs. In chapter 6, we will utilize these results to study the effect of the CNT structural changes on the mechanical behavior of the turf and to extract a general approach to link the quality of these nanotubes to their mechanical properties.

5.7 References


CHAPTER SIX

6. ADAPTIVE NEURO-FUZZY MODELING OF MECHANICAL BEHAVIOR OF VERTICALLY ALIGNED CARBON NANOTUBE TURFS

6.1 Introduction

The exceptional structural and mechanical properties of carbon nanotubes (CNTs) [1-3] have opened the way over the last decade for their promising use in novel applications in material science, especially their potential use as reinforcement for composite materials. Individual CNTs are often self-assembled into bundles held together by van der Waals forces [4] and the resulting bulk mechanical properties are dependent on the overall morphology of the assembly [5].

In [6], we studied the structural impact of MWCNT turfs on Raman spectra using image analysis of SEM micrographs. We showed the dependence of Raman spectral features on MWCNT structure and expected that the mechanical properties of CNTs turfs are related to the nanotube geometries which dictate the observed vibrational frequencies in Raman spectra.

In the present work, we propose a comprehensive approach to investigate and model the correlation between the relative mechanical stiffness of MWCNTs turfs measured using nanoindentation with Raman spectral data and turf morphology (i.e. curvature and alignment) characterized by stereological measurements, through the use of Adaptive Neuro-Fuzzy inference systems (ANFIS).
6.2 Experimental Procedures

6.2.1 Raman Spectral Analysis for Stiffness Analysis

Several studies observed an upshift of the 2D Raman peak, an overtone of the D peak, of samples under compressive stresses [7-10]. However, few other features of the Raman spectrum have been investigated to study the mechanical behavior of CNTs and their composites. In this work, we propose novel relations between Raman features and the stiffness analysis of vertically aligned carbon nanotube (VACNT) turfs.

6.2.2 Nanoindentation of CNT Turfs

The mechanical properties of MWCNT turfs are of both fundamental and practical interest to applications at the macro- and micro-scale such as MEMS. Nanoindentation tests are used to measure the stiffness of VACNT turfs and their resistance to penetration [11].

Figure 6.1(a) shows a typical indentation load \((P)\)-depth \((h)\) curve for a nanoindentation experiment on VACNT turf, from Ref. 10. Multiple indents on three different samples were obtained using a Berkovich diamond tip with an effective tip radius of 1.79 µm. Samples were quasi-statically indented with maximum load of 200 µN. The hysteresis in the curve is due to energy absorption by the turf, while the pull-off force is caused by the adhesion between the tip and the turf. The return of the curve to the original point shows that the deformation is elastic at these loads and depths [12]. Multiple stiffness measurements are made in each location using the continuous stiffness method, which is achieved by adding a sinusoidal modulation to the loading schedule.
Figure 6.1 A typical nanoindentation test on VACNT turf, (a) the load-depth curve with the sinusoidal oscillation at the peak load (b) the indentation results as a function of time.
In general, though the load-depth curve may depend on the location where the indentor penetrates into the VACNT turf, the data used in this study showed good repeatability at different locations on the turf. Due to depth dependent elasticity of the turf, the load-depth curve will be considered for modeling purposes. The measured elastic unloading stiffness is correlated to the structure geometrical properties and Raman features.

6.2.3 Geometrical Properties of CNT Turfs

Other groups have studied the effect of CNT curvature in nanotube-reinforced polymer composites [13] and nanotube sheets [14] and their results have suggested that reducing the waviness of nanotubes would improve Young’s moduli in these materials. However, these results are not verified yet for as-grown VACNT turfs. Only a few existing models of mechanical properties of VACNT [11, 15] have included the diameter, length and the areal density of CNTs.

Since there are no direct experimental tests available that can easily determine the structural properties of nanoscopic materials, electron microscopy has become essential to the study of CNTs, as it directly reveals the nanostructure of individual tubes and the morphology of the nanotube assembly. Using different image processing techniques [16-21], quantitative characterization of geometrical features [22, 23] and the study of macroscopic behavior of VACNT turfs has become achievable.

In chapter 4, we have introduced image processing techniques to extract morphological information of VACNT turfs from SEM micrographs to characterize curvature, alignment and volume density [6, 24].
To study the structural influence on the indentation tests of VACNT turfs, stereological relations were applied to extract the geometrical relations between the 3D CNT assembly and the 2D images of the turf structure. The stereological properties of thresholded SEM images were summarized by three parameters: $A_A$, defined as the area fraction occupied by CNTs in a single layer of the turf, $L_A$, the total length of the CNTs boundaries divided by the area of the sampled window, and $P_L$, the ratio of the number of probe-tube intersections per unit probe length summed over a discrete number of angles between the probe line and the horizontal direction. To study the anisotropy of the turf structure, the average and standard deviation (STD) of $P_L$ are calculated for the discrete number of probe angles [25]. $P_L$ and $L_A$ are normalized to $A_A$ values.

### 6.3 Adaptive Neuro-Fuzzy Inference Systems for Modeling of Nanoindentation and Raman Spectroscopy Data

To date, empirical modeling of mechanical measurements of nanotubes has been typically done by approximating the CNTs to be elastic structures. These approaches do not take in consideration morphology distinctiveness or growth defects in the structure. To have a better understanding of mechanical behavior of MWCNT turfs, an ANFIS phenomenological model is employed to estimate and predict the mechanical properties of VACNT turfs based on Raman spectral features, morphological information, and nanoindentation tests. ANFIS models are recognized for their capability of modeling nonlinear properties of materials [26] and identifying complex patterns of Raman spectra [27].

A Neuro-fuzzy system is a hybrid system combining fuzzy logic and neural networks. The fuzzy inference process is implemented as a generalized neural network,
which is then adjusted by a combination of least squares estimation and backpropagation algorithm [28]. The fuzzy rules and the range of the membership functions are optimized to minimize the output error between the output of the fuzzy model and the input data. Figure 6.2 shows the architecture of the implemented five-layer ANFIS system of Sugeno type [29].

Figure 6.2 Architecture of the Adaptive-Neuro-Fuzzy phenomenological model.

The first layer is the input layer, the 18-input vectors \((x_1-x_{18})\) are shown in figure 6.2. The corresponding output of input \(x_j\) at node \((i)\) in layer \((1)\) is \(O_{ij}^1\). Layer 1 contains \(k\) nodes for every input, which correspond to bell membership functions (BMF) , \(\mu\), according to:

\[
O_{ij}^1 = \mu_{A_{ij}}(x_j) \quad ; \quad i=1,2,\ldots,k , \ j=1,2,\ldots,18 \quad (6.1)
\]

Here, \(A_{ij}\) are fuzzy sets describing the input, while \(\mu_{A_{ij}}(x_j)\) is the degree of membership of a variable \(x_j\) into the fuzzy set \(A_{ij}\). To calculate the firing strength of \(m^{th}\) rule (total n rules) in layer 2, \(w_m\), the rule output is equal to the product of incoming inputs from layer 1:
\[ O^2_m = w_m = \prod_{i=1}^{n} \mu_{A_i}(x_j) \quad ; \quad i, j \text{ are defined in } m^{th} \text{ rule} \quad (6.2) \]

The process continues to layer 3, the \( m^{th} \) node computes the ratio of the \( m^{th} \) rule’s firing strength to the sum of firing strength (normalization):

\[ O^3_m = \bar{w}_m = \frac{w_m}{\sum_{m=1}^{n} w_m} \quad (6.3) \]

Layer 4: Each node in this layer represents a rule; it has adaptive nodes with corresponding functions:

\[ O^4_m = \bar{w}_m \times f_m \quad (6.4) \]

where \( f_i \) is a crisp variable of \( m^{th} \) rule to describe the output.

The last layer 5 has a single node, which computes the output (indentation loads) as the summation of layer 4 outputs:

\[ O^5_i = \sum_{m=1}^{n} \bar{w}_m \times f_m \quad (6.5) \]

The implemented learning algorithms involve unsupervised learning of the BMF (i.e. centers and widths) followed by unsupervised learning of the rules (calculation of rules and updates), and error back propagation for optimization of the membership functions (The output and the error are fed back to layer 2). Different data sets were used to validate the accuracy of the model.

6.4 Results and Discussion

6.4.1 Stereological Parameters

Figure 6.3 shows sample images of the analyzed VACNT turfs. The stereological parameters of these images are summarized in table 6.1.
It can be seen that sample (A) has less curvy and more aligned nanotubes than the other samples. As found in table 6.1, the VACNT turf in (A) was found to have a greater $A_A$ than the nonaligned turfs. $A_A$ values varied from 38% for the nonaligned nanotubes in (C) to about 49.5% for the aligned nanotubes in (A). On the other hand, the ratio of the total length of CNTs boundaries per unit area, $L_A$, was greater for the curvy and nonaligned nanotubes in (C), about 0.1018 nm$^{-1}$, due to higher density of kinks, bending points and longer nanotubes, while it was about 0.091 nm$^{-1}$ for the aligned sample.
Lower averages of number of intersections with the line probe were counted for the aligned nanotubes in (A); the average $P_L$ was about 0.0677 nm$^{-1}$. The aligned and curvy nanotubes in (B) caused the average $P_L$ to be greater than (A) and closer to (C). The greatest values are found for the nonaligned turf in (C), demonstrating the waviness and nonalignment of CNTs in (C) turf structure. These results were helpful to compare different CNT structures and to correlate the geometric properties of the structure with the quality of the sample.

Table 6.1 Stereological parameters extracted for VACNT samples shown in figure 6.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_A$ (%)</th>
<th>$L_A$ (nm$^{-1}$)</th>
<th>$P_L$ (nm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>49.46</td>
<td>0.09099</td>
<td>0.067657</td>
</tr>
<tr>
<td>B</td>
<td>43.17</td>
<td>0.09547</td>
<td>0.075256</td>
</tr>
<tr>
<td>C</td>
<td>38.09</td>
<td>0.10179</td>
<td>0.077208</td>
</tr>
</tbody>
</table>

6.4.2 The Relation between Elastic Unloading Stiffness Analysis and Stereological Parameters

One model of the mechanical behavior of nanotube sheets has suggested that reduced waviness of nanotube matrix would enhance the Young’s modulus [14]. Other studies reported that the alignment of nanotubes represents a major difficulty in understanding the uniaxial compression tests of CNTs [30].

The elastic unloading stiffness, $S = dP/dh$, is an important measured feature from the indentation load ($P$)-depth ($h$) curve and defined as the slope of the upper portion of the unloading curve [31]. To have a better understanding of the structural influence of
VACNTs on the mechanical behavior of these turfs, stiffness measurements are correlated to the structural parameters $A_A$, $L_A$ and $P_L$.

Figure 6.4 shows clearly the correlation between stiffness measurements and the structural parameters. Figure 6.4(a) illustrates that a larger area fraction would enhance the stiffness of the turf, it shows that increasing $A_A$ by about 10% can improve the stiffness by the order of 2.5. Although a greater volume density can be achieved experimentally, increasing the area fraction could affect the alignment and average curvature in the structure, which, as shown in figure 6.4(b, c), will decrease the measured stiffness.
Figure 6.4 Elastic unloading stiffness as a function of the stereological parameters: (a) $A_A$, (b) $L_A$ and (c) $P_L$. $L_A$, $P_L$ are normalized to $A_A$. 
6.4.3 The Relation between Elastic Unloading Stiffness Analysis and Raman Features

The measured features of Raman bands can give an indication of the mechanical properties of carbon nanotubes [8]. Upshift of the 2D band was reported in several studies on nanotube-reinforced composites under compression forces [9] as an indicator of the stress transfer from the composite to the nanotubes and therefore reinforcement of the structure [7].

This dependence of Raman features of CNTs on structural geometries [6] is a result of the corresponding differences in electronic transition energies [32]. Kinks and bending points due to the nonaligned growth of as-produced CNTs is associated with stored amount of strain in the turf, which states the conditions for resonant Raman scattering in CNTs. Figure 6.5(a, b) illustrates the shifts of the D (about 2 cm\(^{-1}\)) and 2D (about 2.5 cm\(^{-1}\)) bands toward higher wavenumbers, this shift is possibly due to the shortening of the C–C bonds and therefore exciting the nanotubes with different vibration frequencies because of defects or nanotubes interactions in the sample caused by the structural variations associated with the alignment disorder.
Figure 6.5 Elastic unloading stiffness as a function of the Raman features: (a) D, (b) 2D peak positions, and intensity ratios of (c) D (d) D+G using 488.0 nm excitation wavelength.
The increments in the intensity ratios of D, D+G peaks in figure 6.5 (c, d) can be explained by the results of figure 6.4(a), where samples with higher volume density have more intense peaks.

6.4.4 Adaptive Neuro-Fuzzy System for Modeling of Nanoindentation and Raman Spectroscopy Data

Using the measurements of Raman spectra and stereological parameters, an adaptive neuro-fuzzy inference system is proposed to model the indentation resistance (load-depth) curve measured by nanoindentation tests on VACNT turfs. The inputs of the model are shown in figure 6.2. One third of the load-depth data was used in the validation process of the model. Figure 6.6 shows the model load outputs for both training and validation data sets. The validation outputs follows the same trend of that for the training data set, which proves the reliance of the model.
The load-depth curve are shown in figures 6.7 and 6.8 for samples A, B and C. The loading and unloading curves were easier to model than the holding or the adhesion related part of the load-depth curve. Our interest is to model the load-depth curve where the stiffness can be measured accurately, which is achieved as seen for the upper unloading portion of the $P-h$ curve. The slope for the used data and the modeled one is identical and thus the model was able to extract the relation between the used inputs and the measured indentation loads.
Figure 6.7 ANFIS output for the load-depth training curve: (a) Sample A, (b) Sample B and (c) Sample C.
As seen in figure 6.9 (a, b), the error measurements of the indentation load shows a consistent behavior for both training and validation data sets. This is important to enhance the model generalization for more accurate estimation of the modeled values. It is found that the maximum error occurs at the peak load and the adhesion-related portion of the load-depth curve.
Figure 6.9 Error signal in (a) training and (b) validation ANFIS outputs.
Figure 6.10 shows the root mean square error (RMSE) for the load output for both the training and checking data set using 150 epochs. It can be seen that the checking error follows the training one, which proves the reliability of the model. As the epochs reach about 125 epochs the error reaches its steady state for both error curves.

![Figure 6.10 RMSE of nanoindentation model output versus number of epochs.](image)

The developed ANFIS model has proven the dependence of indentation resistance on the structural differences of CNT turfs and Raman features. This nonlinear reliance on Raman spectra is due to the changes in the vibrational force constants in different turf geometries, which consecutively determine the vibrational energies.
The proposed model highlights the geometrical features of VACNT turfs and the spectral information as important factors that may ultimately be employed to evaluate and enhance their future applications.

6.5 Conclusions

In this work, we suggest that significant enhancements in the mechanical behavior of VACNT turfs can be achieved by improving the alignment and curvature properties of the structure. These properties were characterized using basic stereological parameters extracted from SEM images. It has been demonstrated that Raman spectroscopy can be used to characterize these structural features, especially the D and 2D bands. The proposed neuro-fuzzy model of nanoindentation tests on VACNTs together with the measured spectral and geometrical properties of CNTs provided a relatively simple approach for evaluating the resistance of the turf to indentation loads and measuring the stiffness of nanotube structures. The reliability of this model suggests the potential use of this method as a quality control tool in mass production. The ANN model is employed to perform a parametric study of the influence of Raman features and stereological parameters on the measured indentation load. Chapter 7 will further explore the relative affect of the parameters involved in this study on the mechanical behavior of the turf structures.

6.6 References


CHAPTER SEVEN

7. PARAMETRIC STUDY OF THE MECHANICAL BEHAVIOR OF VERTICALLY ALIGNED CARBON NANOTUBE TURFS USING RAMAN SPECTROSCOPY AND STEREOLOGICAL MEASUREMENTS

7.1 Introduction

Studying the structural properties of VACNTs is of great importance to ensure better mechanical properties for the nanotube assembly and their use in composites [1]. However, the influence of the geometrical properties of nanotube matrices on the effective mechanical properties of VACNT turfs is not clear yet [2, 3].

In this chapter, the ANN model is used to study the influence of the Raman spectra and the stereological analysis on the indentation resistance.

7.2 ANN System for Parametrical Study of Structural and Spectral Influence on the Measured Indentation Loads

The ANN model in section 3.2 is used to analyze the Raman spectral data and the stereological parameters and their relative influence on the indentation load. The inputs to this system are: Depth, \( A_d \), \( L_d \), Mean of \( P_t(\theta) \), Standard deviation of \( P_t(\theta) \) and Raman Features: position, intensity, HWHM of [D, G, 2D, D+G bands].

7.3 Results and Discussion

The ANN model has 10 neurons and ran for 1000 epochs, the results of the validation data set are shown in figure 7.1. It is noticed that the ANN model results are more
accurate than ANFIS results. It should be noticed that the ANN model had 1000 epochs while the ANIFS had only 150 epochs due to memory limitations.

Figure 7.1 Validation outputs of ANN indentation load model as function of indentation time.

Figures 7.2 (a, b, c) show accurate modeling of the load-depth curve for all regions of the curve, because ANN tries to obtain the best fit of the data with the available inputs, while ANFIS tries to cluster the data and find the best rules governing the inputs’ influence to the output, which require more data points than ANN.
Figure (a) shows a graph with the load (mN) on the y-axis and indentation depth (nm) on the x-axis. The graph includes data points labeled 'Validation Data A' and 'ANN Output.'

Figure (b) contains a similar graph, with load (mN) on the y-axis and indentation depth (nm) on the x-axis. It also includes data points labeled 'Validation Data B' and 'ANN Output.'
The summary of the Raman features’ and stereological parameters’ influence on the indentation resistance is shown in figure 7.3. Since the indentation stiffness is depth dependent, it was found that the depth input has the highest relative influence of about 3.9. The stereological inputs had the second highest influence, which agrees with the results in figure 6.4. The Raman D peak (inputs 6) has the greatest relative influence to the other peaks; this supports the results in figure 6.5. The Raman intensity ratio and HWHM of peak D+G (inputs 12) was discussed in figure 6.5(d) where the shown linearity of the stiffness as function of this parameter is proven by the strong relative influence shown in figure 7.3.
Figure 7.3 The average influence of ANN inputs on the indentation load.


### 7.4 Conclusions

In this chapter a parametrical study of the main parameters discussed in this work was conducted to explore their relative influence on the measured indentation load. The depth was found to be an important parameter to estimate the measured load. While the stereological parameters which characterize the geometrical properties of the turf had a strong affect on the change in the indention stiffness. The D, 2D and D+G peak were found to be very useful tools to estimate the differences in the indentation loads.
7.5 References


CHAPTER EIGHT

8. CONTRIBUTION OF THIS WORK

At the moment this work is quite challenging because detailed models of nanotubes behavior are not well developed. Another major obstacle for this area of research that has been recognized is performing quick and precise characterization of the CNTs properties.

As discussed earlier, practical methods for deterministic synthesis of carbon nanostructures have not been developed, however, it has been well established that the quality of CNTs produced can be controlled by adjusting the environment of growth [1-3]. Since there are no direct experimental tests available that could be performed easily on nanoscopic specimens to determine their growth behavior and structural properties; it is important to have a practical procedure to evaluate the basic information about the nanotubes morphology and physical properties.

Besides, lack of published algorithms to convert microscopy images into numerical data made it more difficult to provide an absolute value of CNTs quality [4]. In order to understand and model these complex situations, one has first to qualitatively characterize the relevant nanostructural features and then use them in predicting the material behavior, thus, application of new models capable of incorporating the most important nanostructural parameters is extremely valuable.

In this dissertation, we approached the solution to this problem by establishing a procedure to analyze different CNT samples, investigate the correlation between Raman spectra and the nanostructure, and model the mechanical properties of these structures. This method was validated by studying the morphological influence of the precipitations on the mechanical behavior of the microstructure of Al-alloys.
The contribution of this work to CNTs characterization can be summarized as:

1) Developing an automated process for filtering and thresholding the SEM image, and enhancing the signal-to-noise ratio in Raman spectra using Wavelets de-nosing techniques.

2) Extracting the morphology of nanostructures using image processing techniques of SEM images, stereological relations and curvature and alignment measurements.

3) Designing a neural networks classifier to distinguish different nanotube structures based on their geometrical properties.

4) Performing a comprehensive Raman spectroscopy investigation of the characterized CNT specimens using multiple excitation wavelengths.

5) Defining the relationship between the experimental spectroscopic analysis and the morphology of the structure using ANN models.

6) Investigating the nanoindentation resistance to measure and correlate the unloading stiffness with the stereological parameters and Raman features.

This methodology will be of interest to the engineering community by extending the application of Raman spectroscopy to quality control in more complex and heterogeneous systems. The phenomenological approach discussed in this work is proposed to solve modeling problems for other complex structures. From the physical chemistry point of view, the application of ANN to analysis of structural properties and vibrational spectra of complex systems will be useful to guide the development of theoretical approaches for the determination of morphological properties of such structures.
8.1 References


CHAPTER NINE

9. CONCLUSIONS

In this dissertation, the specific aim was to develop a rapid nondestructive quality evaluation protocol that will be able to predict mechanical and structural properties of micro- and nano-structures. In the first step, we developed a new approach for modeling the age-hardening behavior of Al-Mg-Si alloys that utilizes artificial neural networks models to connect key microstructural parameters for realistic precipitate morphologies with the age-hardening response. A systematic combination of hardness measurements, transmission electron microscopy, image analysis and the ANN method was used to correlate the key precipitate parameters with the age-hardening response. The aging behavior of AA6022 during isothermal heating was characterized by hardness measurements and the structural evolution was studied by TEM. To distinguish the precipitate morphology at each stage of aging, an image analysis algorithm capable of capturing orientation gradient, nearest neighbor distances, number density, shapes, and size of precipitates was developed. A parametric study was performed to identify the significance of each precipitate parameter, and then the most important parameters were used to train the ANN model. The model combines the most important precipitate parameters including volume fraction, shape, size and distance between precipitates. It was found that the model is able to successfully predict the age hardening behavior of AA6022 in both deformed and undeformed conditions.

To analyze carbon nanotube structures, we proposed a new methodology starts with image enhancement of SEM micrographs. Image analysis techniques were employed and stereological relations were determined for SEM images of CNT
structures; these results were utilized to estimate the morphology of the turf (i.e. CNTs alignment and curvature) using artificial neural networks classifier. FFT statistics were found to be a good indicator for the alignment, curvature, orientation, and thickness properties of CNTs.

Another important goal of this research was to uncover fundamental relations for the dependence of MWCNT Raman spectra on structure and morphology. Wavelet denoising analysis was implemented to filter Raman signal without losing any peaks information embedded in the spectrum. The ANN modeling of Raman features revealed the dependence of Raman frequencies, bandwidths, and intensities on stereological properties. The effect of the excitation wavelength on Raman features was studied.

Finally, we proposed a new methodology to investigate the correlation between indentation resistance of multi-wall carbon nanotube turfs, Raman spectra and the geometrical properties of the turf structure using adaptive neuro-fuzzy phenomenological modeling. The ability of Raman spectral data, stereological parameters and ANN modeling to predict the observed indentation properties was investigated and the significance of these parameters was determined.
CHAPTER TEN

10. SUGGESTIONS FOR FUTURE WORK

The methodologies discussed in this dissertation yield a novel approach for quantitative characterization and modeling at the nanoscale. The proposed method can be used to characterize the effect of nanostructural morphologies on the nanomaterial behavior, and to identify mechanisms for property enhancement through material design. This will help in building up new techniques for nanomaterial production in economic quantities which will improve number of engineering application especially electronic systems and MEMS.

In addition, this methodology will improve in-situ applications, which proved that the growth rate, structure and morphology of the grown carbon nanotubes depend upon nucleation environment [1-4]. Section 10.1 explains the suggested system for in-situ application.

10.1 In-Situ Identification System of CNTs Growth Through the Use of Microscopy and Spectroscopy Analysis

The as-grown material typically contains a mixture of SWCNTs, MWCNTs, amorphous carbon and catalyst of metal particles, and the ratio of the components varies and depends on growth conditions. Therefore, the major challenge is to have control over the nanotubes structure during the growth process. In figure 10.1, we propose a methodology to control the quality of produced CNTs using a control algorithm that involves growth conditions and ANFIS analysis of optimal CNTs. Beside realizing the results of our research in this dissertation, understanding the correlation between CNT growth aspects
and its properties is the other key factor to develop quality control methods for controlled synthesis and assembly of carbon nanotubes.

Figure 10.1 In-situ quality control system of CNTs growth using microscopy and spectroscopy analysis

The proposed system can manipulate the growth conditions based on predicted properties of CNTs using the ANFIS model described in this research which employs the spectroscopy and microscopy analysis as a feedback signal. This methodology will result in a big step forward in large scale production of CNTs with breakthroughs in bringing the cost of high quality composition to reasonable levels for structural applications.

10.2 References

APPENDIX A: MATLAB Code of the ANN Model

% Artificial Neural Network with MATLAB
% Neural Network system, backpropagation learning for n input with one
% Hidden layer and n-outputs, sigmoid function
%---------------------- -------------
clear;
clec;
% defining inputs and outputs
x1=-10:.5:9.5;
x2=-5:.25:4.75;

for i=1:40
    if mod(i,2)==1
        ytrain((i+1)/2)=x1(i)+5*x2(i)^2;
xtr1((i+1)/2)=x1(i);
xtr2((i+1)/2)=x2(i);
    else
        ytesting(i/2)=x1(i)+5*x2(i)^2;
xte1(i/2)=x1(i);
xte2(i/2)=x2(i);
    end
end

plot(ytrain,'r')
hold on
plot(ytesting,'b')
hold off

% normalizing
[xtrn1,aa,bb]=premnmx(xtr1);
xtrn2,cc,dd]=premnmx(xtr2);
[ytrn1,ee,ff]=premnmx(ytrain);
% to make it work with sigmoidal we will make the rang 0-1
Inpt=[(xtrn1+1)/2;(xtrn2+1)/2];
ytemp=(yntrain+1)/2;
desiredOutpt=ytemp';
inpsize=size(Inpt);
outsize=size(desiredOutpt);
nratio=input('Enter the ratio of neurons in the hidden layer to number of inputs, recommended 5 ==>     ');
Eta=input('Enter Eta Value, ex. Eta = 0.5   ===>     ');

% number of neurons in the Hidden Layer
for moh=1:10
    neurons=nratio*inpsize(1);
% random initial Weight values for V & W & T
V = randn(inpsize(1), neurons);
W = randn(neurons, outsize(1));

% Create Threshold for each Layers: Hidden & Output
TB = randn(neurons, 1);
TC = randn(outsize(1), 1);

% loop for a number of epochs = 1000
for epochs = 1:100*moh

% ForwardPath
% Calculation of the output for each neuron in the Hidden Layer
sumtemp = 0;
for i = 1:inpsize(2)
  for j = 1:neurons
    for k = 1:inpsize(1)
      sumtemp = sumtemp + V(k, j)*Inpt(k, i);
    end
    x = sumtemp + TB(j, 1);
    b(j, i) = 1/(1 + exp(-x));
    sumtemp = 0;
  end
end

% Calculation of the output for each neuron in the Output Layer
sumtemp = 0;
for i = 1:outsize(2)
  for j = 1:outsize(1)
    for k = 1:neurons
      sumtemp = sumtemp + W(k, j)*b(k, i);
    end
    x = sumtemp + TC(j, 1);
    C(i, j) = 1/(1 + exp(-x));
    sumtemp = 0;
  end
end

% Calculation of the errorsquare for the Output Layer
for i = 1:outsize(2)
  for j = 1:outsize(1)
    errorsquare(i, j) = 0.5*(desiredOutpt(i, j) - C(i, j))^2;
  end
end

% Calculation of the Weight & Threshold updates
%
%Calculation of the Delta Values
%Output Layer
for i=1:outsize(2)
    for j=1:outsize(1)
        DB(i,j)=(desiredOutput(i,j)-C(i,j))*(1-C(i,j))*C(i,j);
    end
end
%the Hidden Layer
sumtemp=0;
for i=1:inpsize(2)
    for j=1:neurons
        for k=1:outsize(1)
            sumtemp=sumtemp+W(j,k)*DB(i,k);
        end
        DC(j,i)=b(j,i)*(1-b(j,i))*sumtemp;
        sumtemp=0;
    end
end
%--------
%Calculation of the update
%Calculation for the update in V (Between the Input & Hidden Layers)
for i=1:inpsize(1)
    for j=1:inpsize(2)
        for k=1:neurons
            DV(k,j,i)=Eta*DC(k,j)*Inpt(i,j);
        end
    end
end
%Calculation for the update in W (Between the Hidden & Output Layers)
for i=1:outsize(1)
    for j=1:outsize(2)
        for k=1:neurons
            DW(k,j,i)=Eta*b(k,j)*DB(j,i);
        end
    end
end
%Calculation for the update in T (For both Hidden & Output Layers)
for i=1:inpsize(2)
    for j=1:neurons
        DTB(j,i)=Eta*DC(j,i);
    end
end
for i=1:outsize(2)
    for j=1:outsize(1)
        DTC(i,j)=Eta*DB(i,j);
    end
end
end
%---------------------------------
%Calculation of the total weights & threshold for each neuron in the
Hidden and Output Layers
%Calculation of the total V's (between the Input & Hidden Layers)
for i=1:inpsize(1)
temp=DV(:,:,i);
for j=1:neurons
    sumV(j,i)=sum(temp(j,1:inpsize(2)));
end
end
%Calculation of the total W's (between the Hidden & Output Layers)
for i=1:outsize(1)
temp=DW(:,:,i);
for j=1:neurons
    sumW(j,i)=sum(temp(j,1:outsize(2)));
end
end
%Calculation of the total T's (for the Hidden Layer)
sumtemp=0;
for i=1:neurons
    for j=1:inpsize(2)
        sumtemp=sumtemp+DTB(i,j);
    end
    sumTB(i,1)=sumtemp;
    sumtemp=0;
end
%Calculation of the total T's (for the Output Layer)
sumtemp=0;
for i=1:outsize(1)
    for j=1:outsize(2)
        sumtemp=sumtemp+DTC(j,i);
    end
    sumTC(i)=sumtemp;
    sumtemp=0;
end
%---------------------------------
%Calculation of the Updates
%For V's
Vnew=V'+sumV;

%For W's
Wnew=W+sumW;

%For TB's
TBnew=TB+sumTB;

%For TC’s
TCnew=TC+sumTC;

%%%%%%%%%%%%%%%%%%

V=Vnew';
W=Wnew;
TB=TBnew;
TC=TCnew;
%%%%%%%%%%%%%%%%%%

end

%%%%%%%%%%%%%%%%%%
ytrain;
[realoutput]= postmnmx(2*C-1,min(ytrain),max(ytrain))';%return to normal scale

%%%%%%%%%%%%%%%%%%

%TESTING

[xten1,aa,bb]=premnmx(xte1);
[xten2,cc,dd]=premnmx(xte2);
[yntesting,ee,ff]=premnmx(ytesting);
%to make it work with sigmoidal we will make the rang 0-1
Inpte=[(xten1+1)/2;(xten2+1)/2];
ytempe=(yntesting+1)/2;
desiredOutpte=ytempe';
inpsiz=size(Inpte);
outsiz=size(desiredOutpte');
%Calculation of the output for each neuron in the Hidden Layer
sumtempe=0;
for i=1:inpsiz(2)
    for j=1:neurons
        for k=1:inpsiz(1)
            sumtempe=sumtempe+V(k,j)*Inpte(k,i);
        end
        x=sumtempe+TB(j,1);
        b(j,i)=1/(1+exp(-x));
        sumtempe=0;
    end
end
%Calculation of the output for each neuron in the Output Layer
sumtempe=0;
for i=1:outsiz(2)
    for j=1:outsiz(1)
        for k=1:neurons

sumtempe=sumtempe+W(k,j)*b(k,i);
end
x=sumtempe+TC(j,1);
C(i,j)=1/(1+exp(-x));
sumtempe=0;
end
end
%Calculation of the errorsquare for the Output Layer
for i=1:outsiz(2)
    for j=1:outsiz(1)
        errorsquar(i,j)=(desiredOutpte(i,j)-C(i,j))^2;
    end
end
errorsum(moh)=sum(errorsquar);
ytesting
[realoutput]=postmnmx(2*C-1,min(ytesting),max(ytesting))%return to normal scale
end
figure
plot(100:100:100*moh,errorsum);
title('Square Error Vs. No. of epochs');
xlabel('No. epochs');
ylabel('Square Error');
APPENDIX B: MATLAB Code of Image and Stereological Analysis

% Image divisions for FFT in x and y
jmax=4;
imax=6;
scale=500/217; % pixel/nanometer scale =217pixel/500nm for all
% Ideal=0; % 1 if ideal images are used, 0 if real
% Real=1;

all={'A','C','Mone','Mgrad','T','Mrand','O','SN80','SN81','SN83','SN86','SN87','SN88','SN89','SN92'}; % for A alignment’s C curvature, samples: sn80,sn83
numy=[10,10,10,10,5,10,17,10,10,10,10,10,10,10]; %number of images

for tro=8:length(all) %
tro
char=all{tro};
num=numy(tro); % number of images

for Pict=1:num

if (tro <=7) % for real images
imorg=imread(['CNTIDEAL\',char,'\',char,num2str(Pict),'.tif']);
im=255*im2double(imorg);
cd('C:\Documents and Settings\Administrator\Desktop \Programs \matlab \Fun01_FFTandthshold_corr\threshold'); %location of thresholding file
[emage cor S2]=thrsh_vs_correlation(im);
cd('C:\Documents and Settings\Administrator\Desktop\Programs\matlab\Fun01_FFTandthshold_corr');

else % for ideal images
imorg=imread(['CNTSEM\',char,'\',char,num2str(Pict),'.tif']);
figure, imshow(imorg)

imt=imresize(imorg,[540 600],bicubic);
im=im2double(im);
se = strel('disk',10);
Itop = imtophat(imt, se);
Ibot = imbothat(imt, se);
imo = imsubtract(imadd(Itop, imt), Ibot);
figure, imshow(imo), title('original + top-hat - bottom-hat');
im = imadjust(imo,[0.05 0.6],[1]);
figure, imshow(im), title('Adjust intensity 0.05-0.6');

%threshold
cd('C:\Documents and Settings\Administrator\Desktop\Programs\matlab\Fun01_FFTandthreshold_corr\threshold');
[emage cor S2]=thrsh_vs_correlation(im);
cd('C:\Documents and Settings\Administrator\Desktop\Programs\matlab\Fun01_FFTandthreshold_corr');

%size analysis

cd('C:\Documents and Settings\Administrator \Desktop \Programs\matlab\Fun01_FFTandthreshold_corr\Fun_Size Analysis');
input_image=im2bw(emage);% Important backgroung should be black and binary
threshold_island_size = [1000,500000000];
output_binary_image = island_threshold(input_image,threshold_island_size);
figure,imshow(output_binary_image);
title('Deletes all islands smaller than 1000 square pixels ');
emage=output_binary_image;
cd('C:\Documents and Settings \Administrator\Desktop\Programs\matlab\Fun01_FFTandthreshold_corr');
end

fftIM=fftshift(fft2(im));
Freq = log(abs(fftIM));
maxFreq=max(max(Freq));
minFreq=min(min(Freq));
maxFreq=max([maxFreq,abs(minFreq)]);
% FreqNorm = (Freq-minFreq)./(maxFreq-minFreq);
FreqNorm = Freq./maxFreq;

Phas=angle(fftIM)*180/pi;
maxPhas=max(max(Phas));
minPhas=min(min(Phas));
maxPhasp=max([maxPhas,abs(minPhas)]);
% PhasNorm = (Phas-minPhas)./(maxPhas-minPhas);
PhasNorm = Phas./maxPhasp;

figure
imshow(FreqNorm)
colormap(jet)
colorbar
title('Frequency Map Norm')
saveas(gcf,['figures\','char,\',char,num2str(Pict),'\',char,'F freq.tif'], 'tif')

figure
imshow(PhasNorm)
colormap(jet)
colorbar
title('Phase Map Norm')

meanFreq=mean2(Freq);
stdFreq=std2(Freq);
meanPhas=mean2(Phas);
stdPhas=std2(Phas);
meanFreqNorm=mean2(FreqNorm);
stdFreqNorm=std2(FreqNorm);
meanPhasNorm=mean2(PhasNorm);
stdPhasNorm=std2(PhasNorm);
meanimage=mean2(im);
stdimage=std2(im);

im=image;
% Area fraction
resx=size(im,2);
resy=size(im,1);
count=0;
wind=[];
Aa=[];
Area_f=[];
for window=40:5:80
    count=count+1;
    for w=1:40
        wincx=round((resx-window)*rand(1)+window/2); % random selection for the window center x y
        wincy=round((resy-window)*rand(1)+window/2);

        if wincx==window/2
            wincx=wincx+1;
        end
        if wincy==window/2
            wincy=wincy+1;
        end
        Ast=im(wincy-window/2:wincy+window/2,wincx-window/2:wincx+window/2);

        Aa(w)=sum(sum(Ast))/((window+1)*(window+1));
    end
    Area_f(count)=sum(Aa)/w;
    wind(count)=(window+1)^2;
end

Aavg(Pict)=mean(Area_f);
\[ A_{\text{min}} = \min(Area_f); \]
\[ A_{\text{max}} = \max(Area_f); \]
\[ R_{\text{avg}} = A_{\text{max}} - A_{\text{min}}; \]
\[ \text{STD}_{\text{avg}} = \text{std}(Area_f); \]
\[ \text{UCL}_{\text{avg}} = A_{\text{avg}}(\text{Pict}) + 3 \times \text{STD}_{\text{avg}}; \]
\[ \text{LCL}_{\text{avg}} = A_{\text{avg}}(\text{Pict}) - 3 \times \text{STD}_{\text{avg}}; \]
\[ \text{Var}_{\text{avg}} = \text{var}(Area_f); \]

\begin{verbatim}
figure
plot(wind, Aavg(Pict)*ones(length(wind),1),'r')
hold on
stem(wind, Area_f,'fill','-.')
title('A_A distr.')
xlabel('Window size (pixels)')
ylabel('A_A fraction')
axis([min(wind) max(wind) 0.9*\text{Amin} 1.1*\text{Amax}])
saveas(gcf,['figures\',char('\text{Pict}\',char(num2str(Pict)),'AA.tiff'] , 'tiff')

% 'LA line fraction per unit area'
imdedge = edge(im,'canny');
resx=size(im,2);
resy=size(im,1);
count=0;
La=[];
Line_f=[];
wind1=[];
for \text{window}=40:5:80
  count=count+1;
  for w=1:40
    wincx=round((resx-window)*rand(1)+window/2);%random selection
    wincy=round((resy-window)*rand(1)+window/2);
    if wincx==window/2
      wincx=wincx+1;
    end
    if wincy==window/2
      wincy=wincy+1;
    end
    L=imdedge(wincy-window/2:wincy+window/2,wincx-window/2:wincx+window/2);
    La(w)=sum(sum(L))/((window+1)*(window+1));
  end
  Line_f(count)=sum(La)/w;
end
\end{verbatim}
wind1(count) = (window+1)^2;
end

Lavg(Pict)=mean(Line_f);
Lmin=min(Line_f);
Lmax=max(Line_f);
Ravg=Lmax-Lmin;
STDavg=std(Line_f);
UCLavg=Lavg(Pict)+3*STDavg;
LCLavg=Lavg(Pict)-3*STDavg;
Varavg=var(Line_f);

figure
plot(wind1,Lavg(Pict)*ones(length(wind1),1),'r')
hold on
stem(wind1,Line_f,'fill','-.')
title('L_A distr.')
xlabel('Window size (pixels)')
ylabel('L_A fraction')
axis([min(wind1) max(wind1) 0.9*Lmin 1.1*Lmax])
saveas(gcf,['figures\',char,'\',char,num2str(Pict),'LA.tiff'], 'tiff')

% PL line fraction per unit area
Point_f=[];
thetangle=[];
imagesize=size(imedge');
slopcount=1;
theta=0;
Img=ones(imagesize(2),imagesize(1));
slope=tan(theta*pi/180);
for shift=-5000:round(50+abs(slope)*50):2000
    Img=Img&Drawline(imagesize,slope,shift);
end
Img=~Img;
for rota=0:10:90; %change back to 7
    J = imrotate(Img,rota,'bilinear','crop');
    LineLength=sum(sum(J))/3;
    Imfinal=imedge&J;
    [labeled,numObjects] = bwdlabel(Imfinal,8); % Label components.
    Pa=numObjects/LineLength;
figure
imshow(J);
axis on;
figure
imshow(imedge);
axis on;
figure
imshow(Imfinal);
colormap(gray)
axis on;
box on;
set(gca,'XTick',[])
set(gca,'YTick',[])
axis([0 imagesize(1) 0 imagesize(2)])
Point_f(slopcount)=Pa;
thetangle(slopcount)= rota;
slopcount=slopcount+1;
end

PLavg=Point_f;
Point_fC=flipr(Point_f);
Point_fp(Pict,:)=[Point_f,Point_fC,Point_f,Point_fC];
slop=[thetangle, thetangle+90,thetangle+180,thetangle+270];
Pavg=mean(Point_fp(Pict,:));
Pmin=min(Point_fp(Pict,:));
Pmax=max(Point_fp(Pict,:));
Ravg=Pmax-Pmin;
STDavg=std(Point_fp(Pict,:));
UCLavg=Pavg+3*STDavg;
LCLavg=Pavg-3*STDavg;
Varavg=var(Point_fp(Pict,:));
figure
plot(slop,Pavg*ones(length(slop),1),r',slop,Pmax*ones(length(slop),1),r-
',slop,Pmin*ones(length(slop),1),r-.')
hold on
stem(slop,Point_fp(Pict,:),'fill','-.')
title('P_L distr.')
xlabel('slope (Degrees)')
ylabel('P_L fraction')
axis([min(slop) max(slop) 0.9*Pmin 1.1*Pmax])
figure
polar(slop*pi/180,Point_fp(Pict,:)/scale)
saveas(gcf,['figures',char,'\',char,num2str(Pict),'PL.tiff'], 'tiff')

S2=S2(:,1:300);%Autocorrelation of the filtered image
S2(500,1:300)=S2(499,1:300);
FreqNorm=FreqNorm(:,1:300); % norm freq from FFT
PhasNorm = PhasNorm(:,1:300);

fg = round(sqrt(300*200/(imax*jmax)));
ser = 1;
for j=0:(jmax-1)
  for i=0:(imax-1)
    FreqNormavg(ser) = mean2(FreqNorm(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100));
    FreqNormsum(ser) = sum(sum(FreqNorm(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100)));
    PhasNormavg(ser) = mean2(PhasNorm(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100));
    PhasNormstd(ser) = std2(PhasNorm(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100));
    FreqNormstd(ser) = std2(FreqNorm(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100));
    S2avg(ser) = mean2(S2(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100));
    S2std(ser) = std2(S2(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100));
    S2sum(ser) = sum(sum(S2(fg*i+101:fg*(i+1)+100,fg*j+101:fg*(j+1)+100)));
    ser = ser + 1;
  end
end

imageprop = [S2avg, S2std, FreqNormavg, FreqNormstd, PhasNormavg, PhasNormstd, Aavg(Pict), Lavg(Pict), PLavg, FreqNormsum, S2sum];

if (tro <= 7)
  save(['CNTIDEAL\', char, '\', char, num2str(Pict), 'prop.mat'], 'imageprop')
else
  save(['CNTSEM\', char, '\', char, num2str(Pict), 'prop.mat'], 'imageprop')
end

clear Area_f Aa wind Line_f wind1 La Point_f thetangle slopcount S2avg S2std S2sum FreqNormavg FreqNormstd PhasNormavg PhasNormstd Aavg(Pict), Lavg(Pict), PLavg, FreqNormsum, S2sum
close all
cle
figure
stem(Aavg.'fill', '-.')
title('A_A distr.')
xlabel('Image number per sample')
ylabel('A_A fraction')
axis([0 1+length(Aavg) 0 1])
% axis([0 1+length(Aavg) 0.9*min(Aavg) 1.1*max(Aavg)])
saveas(gcf,['figures\',char,'\',char,'AA.tiff'], 'tiff')

figure
stem(Aavg,'fill','-.')
title('A_A distr.')
xlabel('Image number per sample')
ylabel('A_A fraction')
axis([0 1+length(Aavg) 0.9*min(Aavg) 1.1*max(Aavg)])
saveas(gcf,['figures\',char,'\',char,'AA2.tiff'], 'tiff')

figure
stem(Lavg/scale,'fill','-.')
title('L_A distr.')
xlabel('Image number per sample')
ylabel('L_A fraction (nm/nm^2)')
axis([0 1+length(Lavg) 0.03 0.07])
% axis([0 1+length(Lavg) 0.9*min(Lavg) 1.1*max(Lavg)])
saveas(gcf,['figures\',char,'\',char,'LA.tiff'], 'tiff')

figure
stem(Lavg/scale,'fill','-.')
title('L_A distr.')
xlabel('Image number per sample')
ylabel('L_A fraction (nm/nm^2)')
axis([0 1+length(Lavg) 0.9*min(Lavg/scale) 1.1*max(Lavg/scale)])
saveas(gcf,['figures\',char,'\',char,'LA2.tiff'], 'tiff')

h = polar([0 2*pi], [0 max(max(Point_fp/scale))]);
delete(h)
for r=size(Point_fp,1):-1:1
    hold on
    polar(slop*pi/180,Point_fp(r,:)/scale,'--')
    title('P_L distr.')
    xlabel('slope (Degrees)')
    saveas(gcf,['figures\',char,'\',char,'PL.tiff'], 'tiff')
end
close all
clear Aavg PLavg Lavg Point_f Point_fp end