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I am submitting herewith a dissertation written by Li Li entitled “Deformation Study of Nanocrystalline Ni-Fe Alloy using Synchrotron Diffraction.” I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Materials Science and Engineering.

Peter K. Liaw, Major Professor

We have read this dissertation
and recommend its acceptance:

Hahn Choo

James R. Morris

John D. Landes

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the
Graduate Council

(Original signatures are on file with official student records)

DEFORMATION STUDY OF NANOCRYSTALLINE NI-FE ALLOY USING
SYNCHROTON DIFFRACTION

A Dissertation Presented for the

Doctor of Philosophy

Degree

The University of Tennessee

Li Li

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ABSTRACT

This dissertation addresses two critical issues in the deformation of nc metals and alloys: (1) A stress-induced genuine grain growth after the plastic deformation rather than just a change of the grain shape; (2) A systematically quantitative study of microstructural evolution during the plastic deformation.

These two critical issues point to the deformation of nc materials with the average-grain sizes within the range of 10 to 50 nm, which is the most interesting and controversial region in the current time. The current study provides a systematic and detailed microstructural evolution for this region, which is definitely beneficial for the investigation of the deformation mechanism in this region, especially for the simulation.

The main experimental and data-analysis methods employed in this research are synchrotron high-energy X-ray diffraction, X-ray line profile analysis, and texture analysis. The combination of these methods is beneficial to the accurate microstructural interpretation of the bulk materials.

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CHAPTER 1: INTRODUCTION

Nanostructured materials are first introduced by Granqvist and Buhrman [1] in the form of “ultra-fine” metal particles and described in detail by Gleiter [2] in 1989. Nanocrystalline (nc) materials are referred to those with an average grain size less than 100 nm. Because their grain sizes come down to nanoscale – 10^{-9} meter, nanomaterials exhibit a wide variety of fascinating mechanical, magnetic, optical, and superconducting properties, which cannot be achieved in their counterparts, coarse-grained materials. Therefore, nanomaterials become the most potential and exciting candidates in many fields for revolutionizing traditional-material designs. For example, nanostructured materials can meet the recent need for the miniaturization of magnetic-recording devices and electromagnetic MEMS and NEMS (micro/nano electromechanical systems) devices. In addition, in the past 20 years, nc metals and alloys attract dramatically increasing attentions because of their promising structural properties, such as the ultra-high strength and superior wear resistance. In this dissertation, the emphasis will be focused on the plastic-deformation study of nc metals and alloys.

The deformation behaviors of nanocrystalline metals and alloys have been the subjects of considerable research after the prediction of the crossover from the Hall-Petch effect to the inverse Hall-Petch effect in the nano region, which indicates the existence of the hardest material [3-4]. It is well known that the yield strengths or hardnesses of metals and alloys follow the Hall-Petch relation with the grain sizes decreasing down to the ultrafine crystalline (ufc) region (>100 nm). In this microcrystalline (mc) and ufc region, the relationships between mechanical behaviors and microstructures have been

developed very well based on dislocation mechanisms. The plastic deformation is mainly carried by dislocations – line defects of the regular crystal lattice – within the individual grains. Dislocations can move through the crystal grains and can interact with each other [5]. When they meet grain boundaries (GBs), GBs often hinder the transmission of dislocations, creating dislocation pile-ups at the boundaries and thereby making the material harder to deform [6]. Here, strengthening is due to the dislocation pile-ups at the grain boundaries. With further grain refinement, when the grain sizes are reduced to nanoscale, there is a large fraction of atoms sitting at the grain boundaries and these atoms are in a non-equilibrium state. The grain-boundary (GB) activities become active, and the dislocation activities within grains may become difficult and even cease, i.e., the dislocation-based theory established in the coarse-grained and ultrafine-grained materials may not persist in nanocrystalline materials any more. For example, for the relatively larger grains of 50 - 100 nm, the deformations are mostly dominated by the dislocation/partial dislocation slips following the normal Hall-Petch effect [7], but the Hall-Petch slope in this region is smaller than that in coarse and ultrafine-grained materials. For the extremely small grains like those below 5 or 10 nm, the materials become weaker and softer with the grain-size decrease [8-10], known as the inverse Hall-Petch effect. Grain-boundary-mediated processes constitute the dominant deformation modes in this stage. However, for the intermediate region, nc materials with average grains of 10 - 50 nm, whether dislocation/partial dislocation or GBs has a dominant role in the deformation is still a question of debate till now. The deformation behaviors in this region are rather material-dependent. My research will be focused on the study of nc materials in this region.

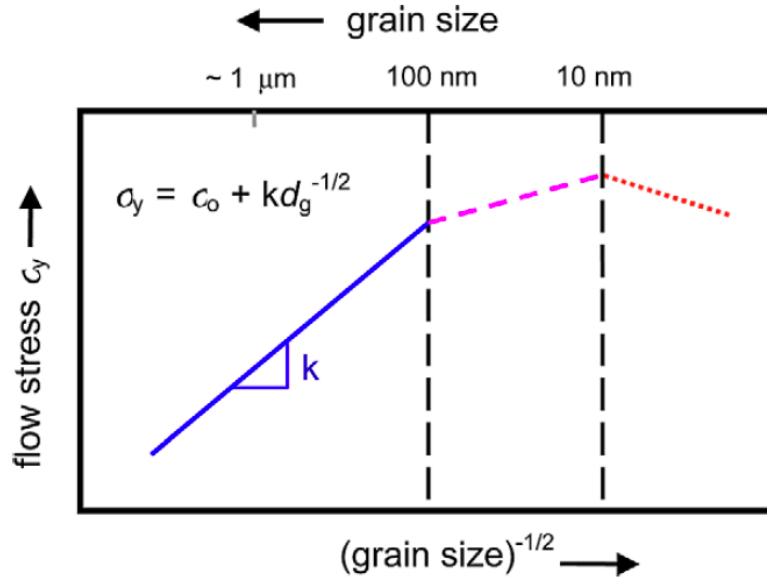


Figure 1-1. A schematic representation of the variation of yield stress as a function of grain size in mc, ufc, and nc metals and alloys [11].

Figure 1-1 shows a schematic representation of the variation of yield stress as a function of grain size in mc, ufc and nc metals and alloys based on the literature work [11].

Another concurrent phenomenon observed in nc metals and alloys during the plastic deformations is grain growth. Grain growth was initially observed from the indentation experiments in an inert-gas-condensed (IGC) nc Cu [12] and Al fabricated by the evaporation method [13]. Later, investigators from different research groups reported the grain growths in different nc metals and alloys deformed under various deformation situations: nc Ni-Fe [14], nc Co [15], and nc Al [16] deformed under uniaxial tensions; nc Ni-Fe alloy under uniaxial quasi-static and dynamic compressions [17-18], nc Ni under high-pressure torsion (HPT) [19], etc. *In-situ* Transmission Electron Microscopy (TEM)

under tensile deformations [20-21] and molecular-dynamics (MD) simulations [21-23] suggested that grain coarsening during plastic deformation is due to two direct mechanisms: GB migration and grain-rotation-induced grain coalescence. Here, GB sliding and GB diffusion are taken as the intermediate processes during the plastic deformation. These two mechanisms can be coupled strongly or weakly leading dramatic or moderate grain growth, respectively (see Chapter 4 as an example). Thus, the observed grain growth can complicate the interpretation of the deformation mechanisms in the nc metals and alloys.

Extensive studies have been made to explore the microstructures and microscopic-deformation mechanisms in nc metals and alloys. Most of them are based on either computer simulations or TEM observations. Two main deformation mechanisms have been suggested. One is GB-mediated processes (e.g. GB sliding [8]/GB migration[21]/GB diffusion [20], grain rotation [20, 22-24], and grain growth as mentioned above). For example, as stated in [8], where most of the plastic deformation is due to a large number of small “sliding” events of atomic plane at the grain boundaries, with only a minor part being caused by dislocation activity in the grains, the softening that we see at small grain sizes is therefore due to the large fraction of atoms at grain boundaries. The complete processes of individual grain rotation and neighboring grain rotation/growth have been observed in the nc Ni and Cu [24-25], respectively. The nc materials possessing high-angle GBs change to low-angle GBs after the deformations. With plastic deformation, a relative shear between grains along their boundaries will be conducted by gliding grain-boundary dislocations (GBDs), whereas the crystal lattice or plane orientation in the neighboring grains will subsequently occur by climbing GBDs,

which results from the splitting of gliding GBD at triple junction into two climbing GBDs. GB sliding transforming into crystal lattice rotation in neighboring grain is suggested as the deformation mechanisms in the nc materials. And the in-situ dynamic TEM observations of nc Ni films with an average grain size of about 10 nm [20, 22-23] clearly show that the GB-mediated processes have become a prominent deformation mode, where the enlarged agglomerates do not result simply from electron irradiation plus stress, but rather from stress-induced deformation. GB and triple junction (TJ) non-equilibrium state plays a crucial role in the extent of plastic deformation [26]. The other deformation mechanism is dislocation/twinning-based plasticity [27-34]. The emission of lattice dislocations from GBs or partials from GBDs has been suggested to be nucleated and absorbed in the GB with the very small temporal and spatial dimensions in the nanocrystalline regime. With conventional dislocation theory in mind, three possible inter-grain deformation mechanisms are assumed: the first by means of partial dislocations that extend across the entire grain creating stacking fault defects; the second by means of full dislocations: a leading and a trailing partial on the same slip plane leaving no dislocation debris; and the third by means of mechanical twinning: a leading and twinning partial on two adjacent planes nucleating a two-layer micro-twin which is taken as the precursor for deformation twinning. Most computer simulations have been performed on face-centered-cubic (fcc) metals. Large-scale MD simulations have provided evidence for a transition with decreasing grain size from intergranular plastic deformation based on grain-boundary accommodation to a mixture of intergranular and intragranular processes where the grain boundary acts as a source of imperfect or partial dislocations [8, 35-37]. Figure 1-2 presents a typical work predicting the deformation

map to elucidate the transition from a dislocation-based to a GB-based deformation mechanism in nanocrystalline fcc metals [37]. The map is expressed in reduced units of the stress (σ/σ_∞) and inverse grain size (r_0/d). The parameters σ_∞ and r_0 are functions of the stacking-fault energy (SFE) and the elastic properties of the material. r and d is the partial dislocation separation and the average grain size, respectively.

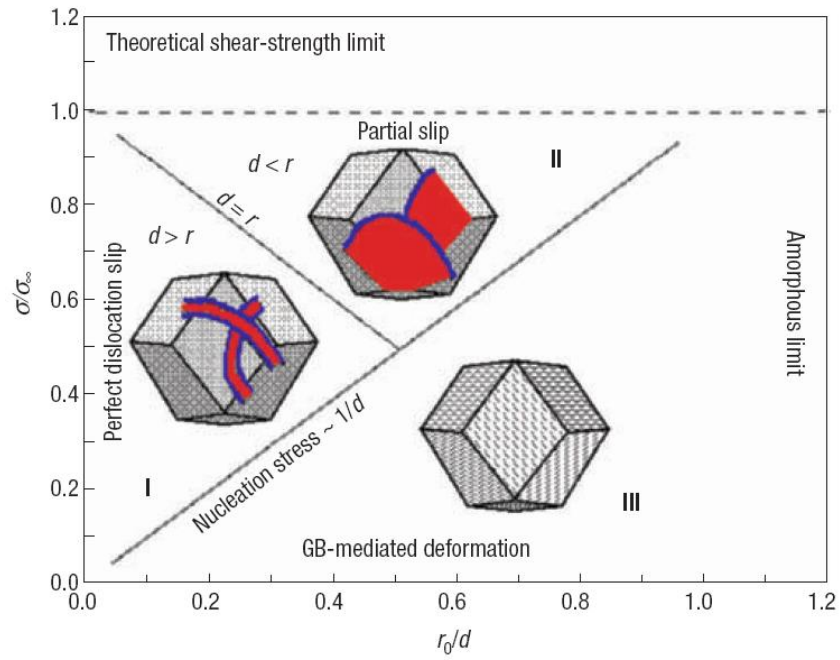


Figure 1-2. Proposed deformation-mechanism map incorporating the role of the stacking fault energy in the deformation behavior [37].

In region I, characteristic of a large grain size (d) and/or a high-SFE (small r) metal, slip deformation prevails as the grains are larger than partial dislocation separation, r , and complete, extended dislocations nucleated from the GBs can propagate across the grains. In region II, characteristic of a small grain size and/or a low SFE (large r) metal, only incomplete dislocations can be nucleated; the grains are therefore transected by stacking faults that inhibit dislocation propagation, thus giving rise to strain hardening. Region III characterizes the very small grain-size or low-stress regime in which no dislocations are present at any stress, and the deformation is therefore controlled by GB-mediated processes. These GB-mediated processes, i.e., GB sliding/migration/diffusion, grain rotation, and sometimes the combination of these processes, may result in the inverse Hall-Petch behavior.

However, because of their nanosecond time scale, MD simulations can only capture the start of the deformation and thus exclude certain time-dependent processes [38]. The simulation should be taken as a tool to understand the current results and guidance to our future work rather than taking the results from the simulations directly as what really happens during the deformations. And also, Derlet et al. [39] has investigated the influence of two parallel free surfaces in the deformation mechanisms of model nanocrystalline fcc materials and predicted that the extent of the surface's influence is of the order of the grain size in nc samples with thin-film thickness comparable with that used in the experiment. The TEM studies, either *in-situ* or *ex-situ*, were applied in two-dimensional (2D) thin foils, where the limited specimen thickness, i.e., only a few grains are sitting on top of each other for nc materials, can provoke changes in GB structures near the free surfaces and/or enhance the dislocation activities, diffusion processes, grain

rotations, etc. Thus, precautions have to be taken when using TEM to reveal the deformation mechanisms.

The microstructure evolution determines the deformation mechanisms, which, in turn, affects the exhibited mechanical properties. In order to unveil the underlying deformation mechanisms in bulk nc metals and alloys, reliable and systematic information on the microstructure evolution for the bulk materials is necessary for accurately interpreting the bulk properties of nc metals and alloys.

In this dissertation, the microstructure evolution of a fully-dense nc Ni-Fe alloy during cold rolling deformation is systematically studied. A new characterization method consisting of the synchrotron high-energy X-ray, line-profile analysis, and texture analysis is introduced and employed in the study to accurately and systematically characterize the bulk nc Ni-Fe alloy. Hardness tests, differential scanning calorimetry (DSC), and TEM are also performed to corroborate the diffraction results. The deformation mechanisms are suggested based on the line profile analyses and texture analyses for the current nc Ni-Fe alloy in the end.

CHAPTER 2: BACKGROUND

The ultra-high strength of nc materials could reach the level of GPa, which has already been widely accepted. However, there is no agreement on the ductility. Most results are mainly obtained through the indentation, compression method. The tensile results on the mechanical properties are relatively limited due to the limitation of obtaining fully-dense and bulk nc materials. Some people state that the nc materials are inherently ductile, and the low ductility observed in the experiments is attributed to the not fully-dense initial materials [40]. Thus, how to obtain fully-dense bulk nc materials is the first problem that we need to solve in the investigation.

This chapter is intended to provide the background knowledge on the selected nc materials for the investigation in the whole thesis, from the initial materials selection, microstructure characterization, and the fundamental mechanical properties the selected materials exhibited based on the documented works.

2.1 Fabrication of Nanocrystalline Ni-Fe Alloys

How to obtain fully-dense bulk nc materials is the first challenge in the deformation study. In the past two decades, different laboratory-scale processing techniques have been developed to synthesize the nanostructured metals and alloys. Representatives of them are inert-gas condensation of particulates (IGC) [41-42], ball milling (BM) [43-44], sputtering [32], sol-gel (SG) technique [45], severe-plastic deformation (SPD) [46], and electrochemical deposition [47-48]. However, the first five methods have obvious disadvantages. In the case of IGC, the amount of nc materials

produced by this method is pretty small. For BM, the purity of initial materials is critical. However, the contamination of powders during mechanical processing is unavoidable, resulting in a high-impurity level in the prepared samples. In addition, the large amount of lattice disorder developed during milling is this technique's other flaw. The main deficiency of sputtering is that a significant amount of porosity is present in the specimens due to the consequential bombardment of the beam on the already deposited film. The sol-gel technique is preferred to be applied in metallic glass/oxide or composite materials rather than for obtaining pure metals and alloys. SPD could produce high-purity materials since the resulting samples only depend on the starting material, however, there are tons of dislocation generated during heavy deformation. This type of nc materials has characteristic of cold-worked materials, where the plastic deformation has been primarily exhausted. Furthermore, the grain size obtained by this method is generally on the level of more than 100 nm, which is not small enough for the investigation as nc materials, especially at the most interesting range of less than 50 nm.

The disadvantages above can be compensated using electrochemical deposition, which has been proved to be a simple, versatile, and inexpensive way to achieve fully-dense metals with a relatively narrow grain-size distribution. During the deposition process, the anodic ions are reduced into atoms on the cathode surface when the current is applied in the electrolytes. Thus, the electrochemical deposition is an atom-by-atom accumulation process. The material fabricated by this method could be fully dense. Furthermore, the grain size and thickness of the deposited materials can be controlled by the current density, agitation degree, species of electrolytes, and deposition time. In

principle, any kind of metals and alloys, as long as the corresponding electrolytes exist, could be fabricated by this kind of method.

In the current study, the nc material used is the electrochemical-deposited nc Ni - 18wt.% Fe (nc Ni-18Fe) alloy. Compared with the pure Ni (fcc), the strength of the current nc Ni-18Fe alloy is greatly improved with the Fe alloying effect. Furthermore, Li et al. [49] clearly states that the microstructures of the deposits are dependent on the Fe content in the electrodeposited Ni-Fe alloys. The reasonableness of the selected composition is stated clearly in the next few paragraphs.

Figure 2-1 shows the effect of iron content on the grain size of electrodeposited Ni-Fe alloys. Here, the substrate used in the electrochemical deposition is annealed (AN) and cold-worked (CW) copper. The lattice match between the copper and nickel is perfect, which is good for depositing thick materials without exfoliation from the substrate.

The grain size gradually decreases with increasing the Fe content in the deposits, suggesting that the addition of an alloying element, Fe, can miniaturize grains. However, the grain size will not unlimitedly decrease with the iron addition. As seen in Figure 2-1, after the iron content increased to 15 wt.%, the grain size remained approximately constant (~ 11 nm) with more iron content. When the iron content increased more than 55 wt.%, the grain size started to decrease further with raising the iron content. The minimum grain size was reached in the mixture of fcc and bcc (body-centered cubic) phases, which is in the range of 60 $\sim$ 70 wt.% Fe [50]. Below this range, the material is a single phase fcc structure, and bcc above this range. Thus, nc Ni-Fe alloys with iron

content of 15 ~ 55 wt.% will be selected for the investigation since they are single phase fcc structure with relatively good ductility compared with bcc structured materials.

However, the deposited nc Ni-Fe alloy with a high-iron content exhibits extensive microcracking due to the presence of large internal stresses. Figure 2-2 is the lattice strain evolution as a function of the iron content in the electrodeposited Ni-Fe alloys [49]. As seen, the lattice strain of the deposited fcc Ni-Fe alloy increased linearly with increasing the iron content beyond 20 wt.%.

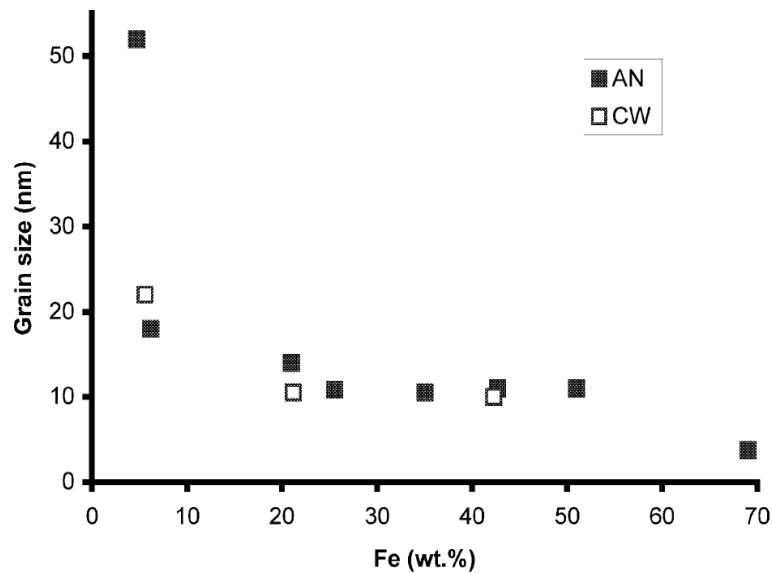


Figure 2-1. The effect of iron content on the grain size of electrodeposited Ni-Fe alloys [49].

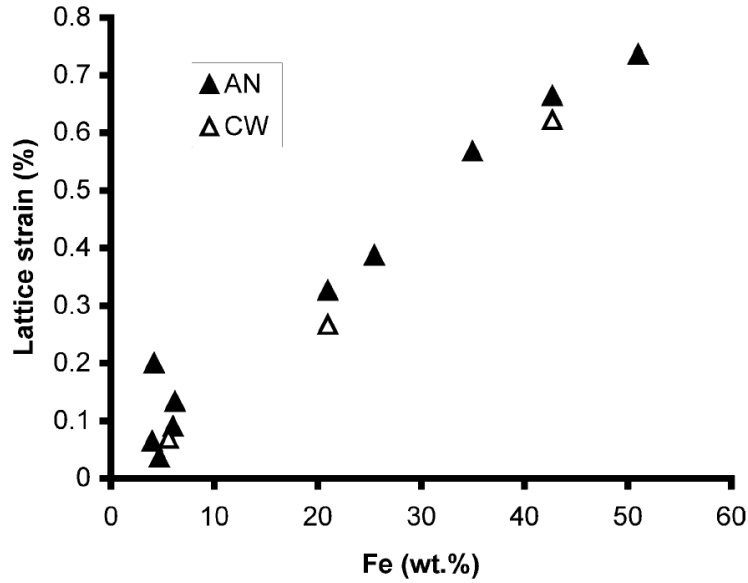


Figure 2-2. The lattice strain as a function of the iron content in the electrodeposited Ni-Fe alloys [49].

Based on the above information, we choose electrodeposited nc Ni-Fe alloys with the iron content of 15 wt.% ~ 20 wt.% as the initial nc materials for the current deformation study. The properties of Ni-Fe alloys within this range of the iron contents are pretty similar. Thus, the later literature reviews on the mechanical properties of the electrodeposited nc Ni-Fe alloys are based on the nc Ni-Fe alloy with the iron contents either 15 wt.% or 18 wt.% or 20 wt.% .

The electrochemical deposition provides fully-dense nc Ni-Fe alloy with a lower impurity level, and the appropriate iron addition (15 wt.% ~ 20 wt.%) in Ni produces nc Ni-Fe alloys with the grain sizes less than 20 nm, which is the most interesting region for the deformation study of nc materials.

2.2 Characterization of the Electrodeposited Nanocrystalline Ni-Fe Alloy

The nc Ni-Fe alloy is provided by Integran Technologies Inc. using the electrochemical deposition. The as-deposited alloy is a single phase with the *fcc* structure. The alloy sheets have dimensions of 70 x 70 x 3 mm³. 3 mm is in the materials-growth direction, as shown in Figure 2-3. These alloy sheets are large enough to prepare the bulk samples for the tensile and compression tests. Optical microscopy (OM) and scanning-electron microscopy (SEM) examinations reveal that the as-deposited plate is free of artifacts, such as the porosity and second-particle inclusions.

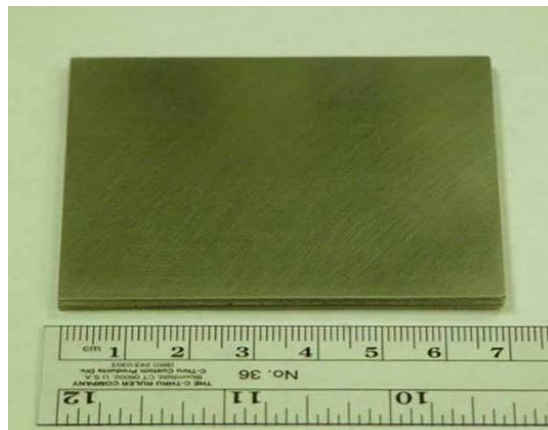


Figure 2-3. The dimension of the electrodeposited nc Ni-18Fe alloy in the current study.

2.2.1 Focused-Ion-Beam (FIB) Microscopy Observation

The nanostructure of the as-deposited nc Ni-18Fe alloy was first examined by FIB microscopy [51]. Figure 2-4(a) and (b) shows a graded nanostructure in the bulk nc Ni-18Fe alloy in the as-deposited state. The grain size distribution as a function of the distance to the top surface (away from the substrate during the electrochemical deposition) is shown in Figure 2-4 (c). As seen, the grain size is about 500 nm near the top surface and gradually decreases to a “steady state” value of ~ 10 nm at a distance of ~ 6 μm from the top surface. Thus, the top surface with a thickness of around 6 μm was polished away from the samples to achieve a uniform nanostructure prior to any mechanical tests.

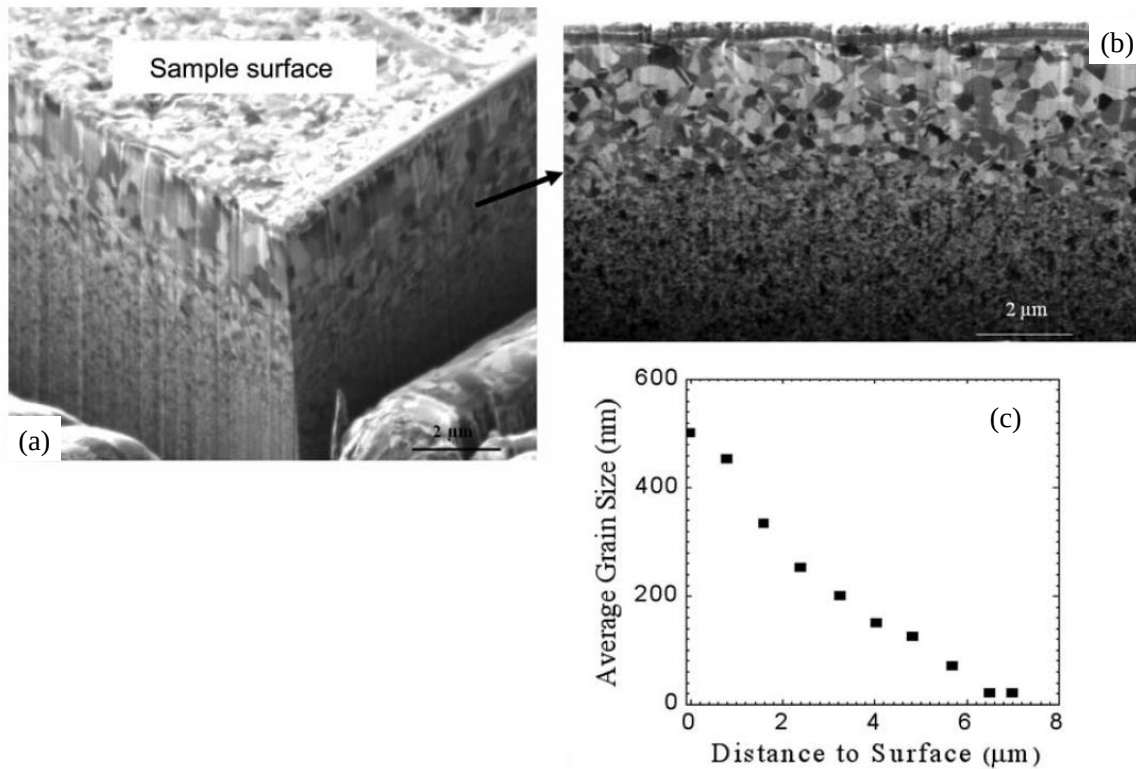


Figure 2-4. FIB images of the nanostructure of the bulk nc Ni-18Fe alloy [51].

2.2.2 Lab X-ray Characterization

Lab X-ray was used in the structure characterization [52-53]. Figure 2-5 shows the X-ray diffraction patterns in the plane view (the X-ray beam direction is parallel to the growth direction) and cross-sectional view (the X-ray beam direction is perpendicular to the growth direction), respectively. The peaks were indexed, and the normalized peak intensities were summarized in Table 2-1. The diffraction peaks indicate that the material is a single phase fcc structure. As seen, the intensities for all indexed peaks in the cross-sectional view are pretty close to those in the standard with randomly distributed grains. Thus, the random texture is observed in the cross-sectional view. From plan view, the intensity of (200) is the highest among the indexed peaks, which indicates the (200) texture. Thus, the material shows a moderate (100) texture in the growth direction and random texture perpendicular to the growth direction.

Table 2-1. Texture results of the as-deposited Ni-20Fe alloy from lab X-ray characterization [52-53].

fcc peaks	111	200	220	311	222
Standard. intensity (Ni ₃ Fe)	100	60	30	40	10
Cross-sectional	100	75	44	27	14
Plan view	90	100	8	11	7

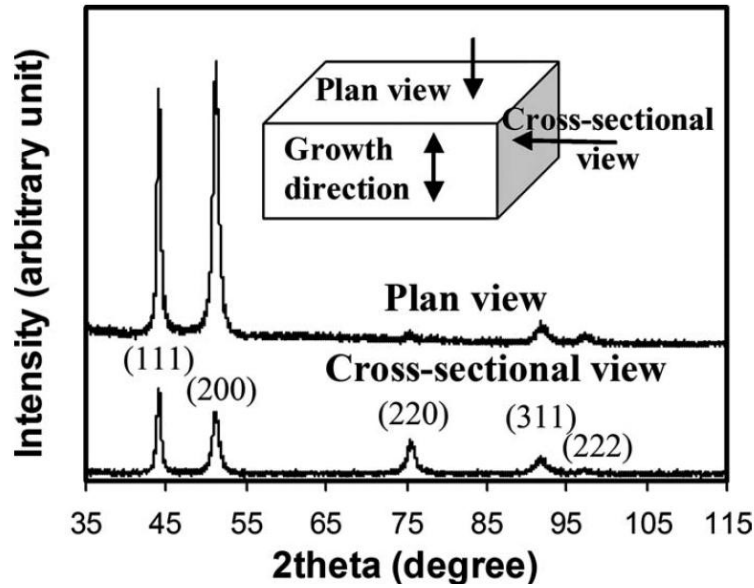


Figure 2-5. X-ray diffraction patterns of the nc Ni-20Fe alloy in the plane and cross-sectional views [52-53].

2.2.3 TEM Observation

Figure 2-6 shows dark-field TEM images of the (a) plane view, and (b) cross-sectional view, of the as-deposited nc Ni-20Fe alloy [52-53]. Figure 2-6 (a) demonstrates that this alloy has relatively narrow grain-size distribution, and grains exhibit an equiaxed shape. Statistics from 300 grains indicate that the average grain size is about 23 nm. However, for the cross-sectional view [Figure 2-6 (b)], the grains have a high aspect ratio of grain size, which indicates that the columnar grains developed along the growth direction during the electrochemical deposition. The length along the longitudinal direction is about twice or three times of the cross section. Thus, the (100) texture observed in the lab X-ray characterization is caused by these columnar grains with (100) oriented along the growth direction.

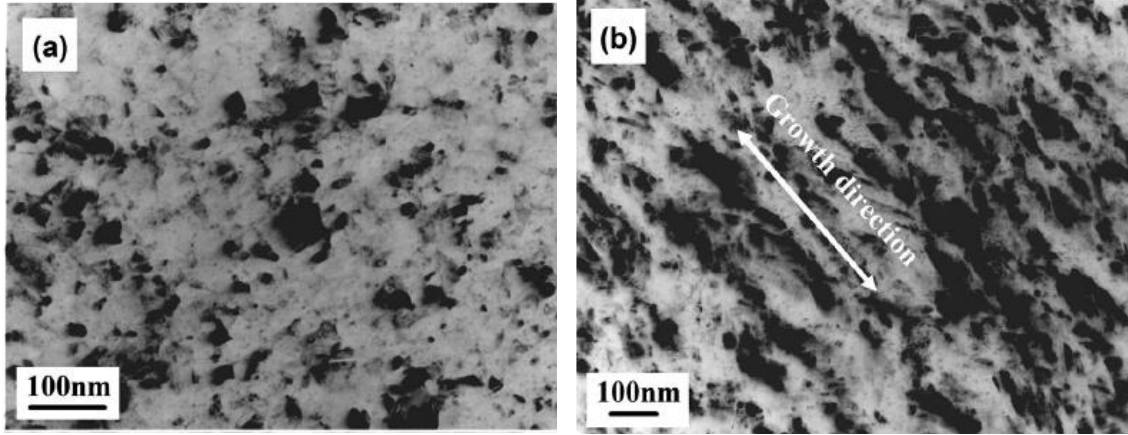


Figure 2-6. Dark-field TEM images of the (a) plane view, and (b) cross-sectional view for the as-deposited nc Ni-20Fe alloy [18, 52-53].

Growth defects are usually introduced in the materials during the materials fabrication. Figure 2-7 shows the bright-field TEM images of the as-deposited nc Ni-18Fe alloy in the (a) top view (the electron beam parallel to the growth direction) and (b) side view (the electron beam normal to the growth direction). The examinations reveal that many growth twins are observed in the side view, while they are almost invisible in top view. The reason for this type of growth twins is still unknown. Statistic TEM observations indicate that the above microstructural characteristics are exhibited in the whole sample. From the images, it is also found that the grain boundaries between grains in the as-deposited nc Ni-18Fe alloy are high-angle grain boundaries. Insets in (a) and (b) are selected-area diffraction (SAD) patterns from an area with a diameter of 500 nm.

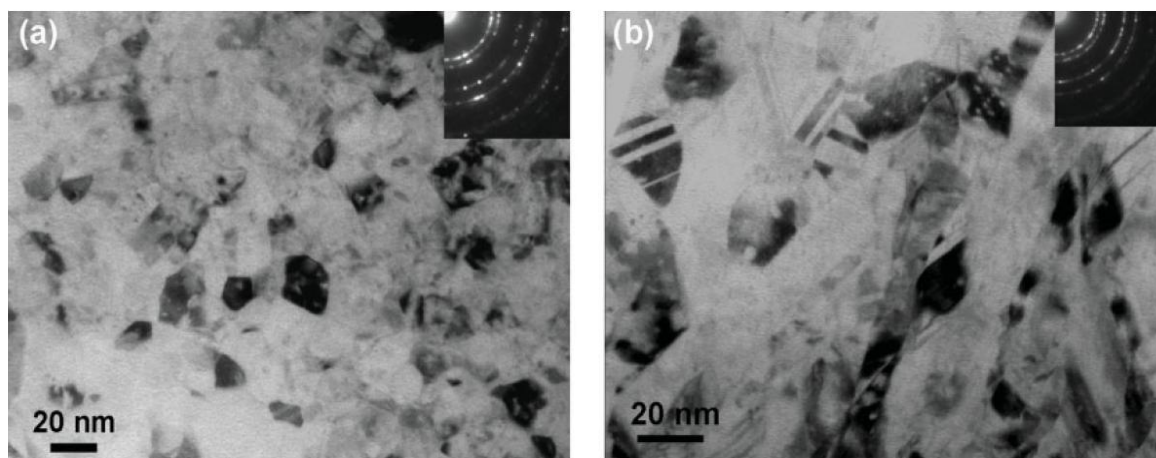


Figure 2-7. Bright-field TEM images of the as-deposited nc Ni-Fe alloy in the (a) top view, and (b) side view [18, 52-53].

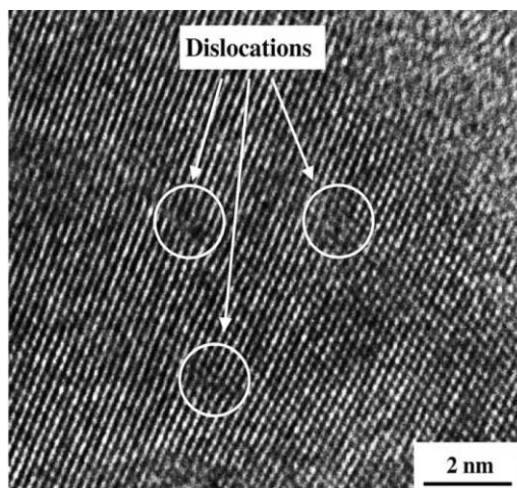


Figure 2-8. HRTEM image shows the growth dislocations in the as-deposited nc Ni-18Fe alloy [18, 52-53].

The high-resolution TEM (HRTEM) is also taken in the as-deposited materials to carefully study the growth defects, such as dislocations, within grains. Figure 2-8 presents the HRTEM observations of the as-deposited nc Ni-18Fe alloy [18, 52-53]. The HRTEM images taken here are perpendicular to the material growth direction. The growth dislocations (indicated by white circles in the figure) are observed in the as-deposited materials.

In summary, the as-deposited nc Ni-Fe alloy with the iron weight of 15 % to 20% consists of columnar grains with moderate (100) fiber texture in the growth direction. The growth dislocations and twins are found in this type of nc materials. High-angle grain boundaries are observed in the as-deposited nc fcc Ni-Fe alloys.

2.3 Mechanical Tests and Microstructure Characterizations

2.3.1 The Tensile Tests and Microstructure Evolutions

Figure 2-9 displays a typical engineering stress-strain curve at a strain rate, $\dot{\epsilon}$, of 10^{-2} s^{-1} for a dog-bone shaped specimen (nc Ni-18Fe alloy) [14] with a gauge section of $4 \times 3 \text{ mm}^2$ and a gauge length of 25 mm. Please see the figure inset for the sample geometry. The material-growth direction is normal to the dog-bone plate. The alloy exhibits a combination of high strength and appropriate tensile ductility. The yield strength of the as-deposited material is around 1.5 GPa with an appropriate plastic strain of $\sim 7 \%$. The elastic strain, ϵ_e , the uniform plastic strain, ϵ_p , and the postnecking plastic strain, ϵ_n , are illustrated in the figure as well.

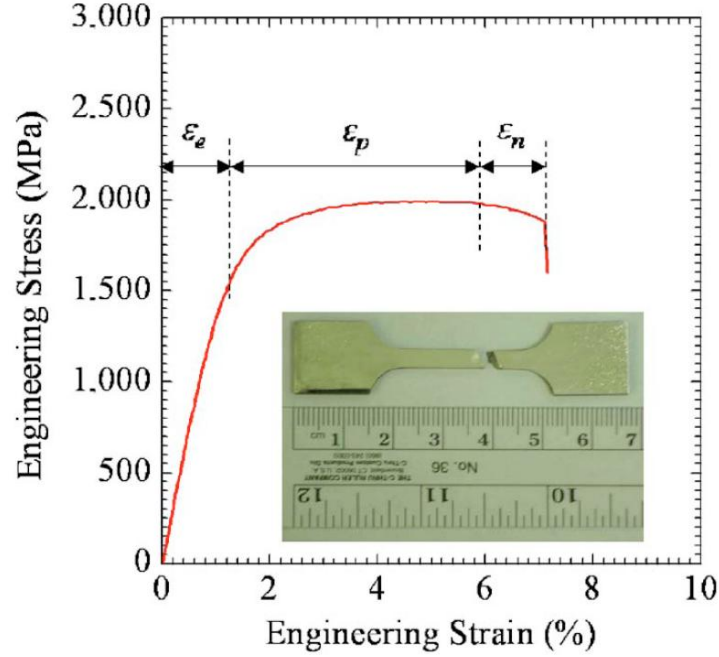


Figure 2-9. Engineering stress-strain curve for the as-deposited bulk nc Ni-18Fe alloy at a strain rate of 10^{-2} s^{-1} [14].

The sample after the tensile test was examined by high-energy synchrotron X-ray diffraction (HEXRD) with the beam energy around 115 keV. The fractured sample was examined by the transmitted beam from the fracture surface to the uniformly-deformed region with a spatial resolution of about 50 μm . The patterns were collected by a two-dimensional detector (Mar 345). This *ex-situ* HEXRD measurement was carried out at the beamline, 11-ID-C, at the Advanced Photon Source (APS), Argonne National Laboratory, USA.

The diffraction peaks are fitted by a Cauchy-peak shape, and the physical-peak shape is obtained by the deconvolution of the measured peaks from the instrumental peak (calibrated by Si powders). The Williamson-Hall (WH) integral-breadth method is used

to determine the grain size, d , and the microstrain, ε^M , from the (111) and (222) reflections [54-55] following,

$$\beta_i = \frac{1}{d} + 2\varepsilon^M S_i \quad (2-1)$$

where $S_i = 2 \sin(\theta_i) / \lambda$ is the length of the diffraction vector, $\beta_i = \beta_i^0 \cos(\theta_i) / \lambda$ is the integral breadth of the diffraction peak in the reciprocal space, θ_i is the Bragg angle, λ is the wavelength, β_i^0 is the integral breadth of θ_i for the diffraction peak. i stands for different hkl plane. As seen in the equation, the slope is proportional to the microstrain, ε^M , and the β_i intercept at $S_i = 0$ is inversely proportional to the grain size, d .

Figure 2-10 shows the distributions of the crystallite-domain size (d) and microstrain (ε^M) as a function of the distance from the fracture surface, L . The red arrows in the figure point to the place where the necking starts in the sample during the uniaxial tensile deformation.

The crystallite-domain size increases from 21.8 nm in the as-deposited state to about 32.5 nm during the uniform plastic deformation. Moreover, the crystallite-domain size increases rapidly from 32.5 nm to a maximum of 307 nm ($L = 0.075$ mm) when $L \leq 0.9$ mm. The literature attributes this abrupt increase in the crystallite-domain size to the large localized-plastic strain (around 20.3 %) in the necking area. Larger deformation will cause larger grain growth. However, as shown in the figure, the microstrain, which is microscopically related to the dislocation density, did not change after the plastic deformation in the uniformly-deformed region ($L > 0.9$ mm) within the experimental error. This result indicates that there is no dislocation storage during the uniformly-deformed region, which may be due to the limited plastic strain in that region or may be

due to the relaxation of dislocations to the grain boundaries after the deformation. However, there is a slight increase in the microstrain after entering the necking region, which may indicate that there are some lattice dislocations trapped.

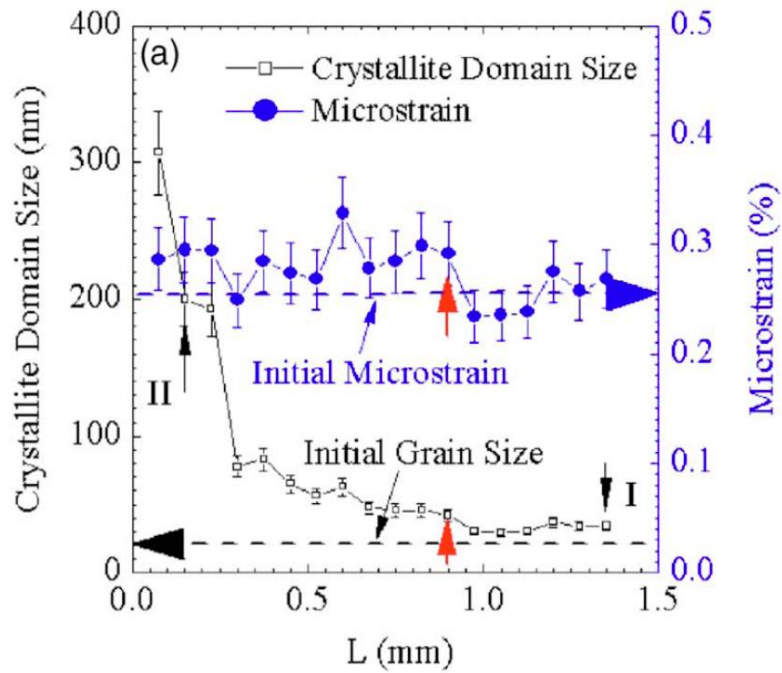


Figure 2-10. Crystallite-domain sizes and the microstrains measured by HEXRD as a function of the distance from the fracture surface, L [14].

The sample was examined by TEM after the tensile test to confirm the grain growth. The TEM foils were taken from the dog-bone plate, where the normal of the TEM foil is along the material-growth direction. The TEM sample was prepared for the uniformly-deformed region. Due to the small area of the necking region, no TEM foil was prepared for that region. Figure 2-11 (a) shows a typical bright-field TEM image after the tensile plastic deformation. The grain-size distribution shown in Figure 2-11 (b) reveals the average-grain size about 73 nm after the plastic deformation. This is a significant increase in the grain size, compared with 23 nm in the as-deposited, which is shown as the dash line in the figure. The big difference in the evaluated grain size from X-ray (33 nm) and the TEM observation (73 nm) is firstly due to the definition of grain size in these two techniques: X-ray characterizes the domain size, the boundary where the lattice coherency breakdown. However, the grains observed by TEM may consist of many subgrains. Thus, the grain-size value from the X-ray will be always smaller than that from the TEM observations. Furthermore, the HRTEM images [Figure 2-11 (c) and (d)] show that the grain boundaries change to small-angle grain boundaries (with an angle of around 6°) after the deformation.

In summary, grain growth is observed in the nc Ni-Fe alloy after the uniaxial tensile deformation. The grains remain equiaxed after the tensile deformation. The grain growth in the necking area is dramatically large, which may be due to the large localized-plastic strain (around 20.3 %) in the necking region. The larger the plastic strain, the larger the grain growth. High-angle grain boundaries change to smaller-angle grain boundaries after the deformation, indicating the grain rotation. No dislocation storage is

observed in the uniformly-deformed region. However, there may be tiny dislocation storage after entering the necking region.

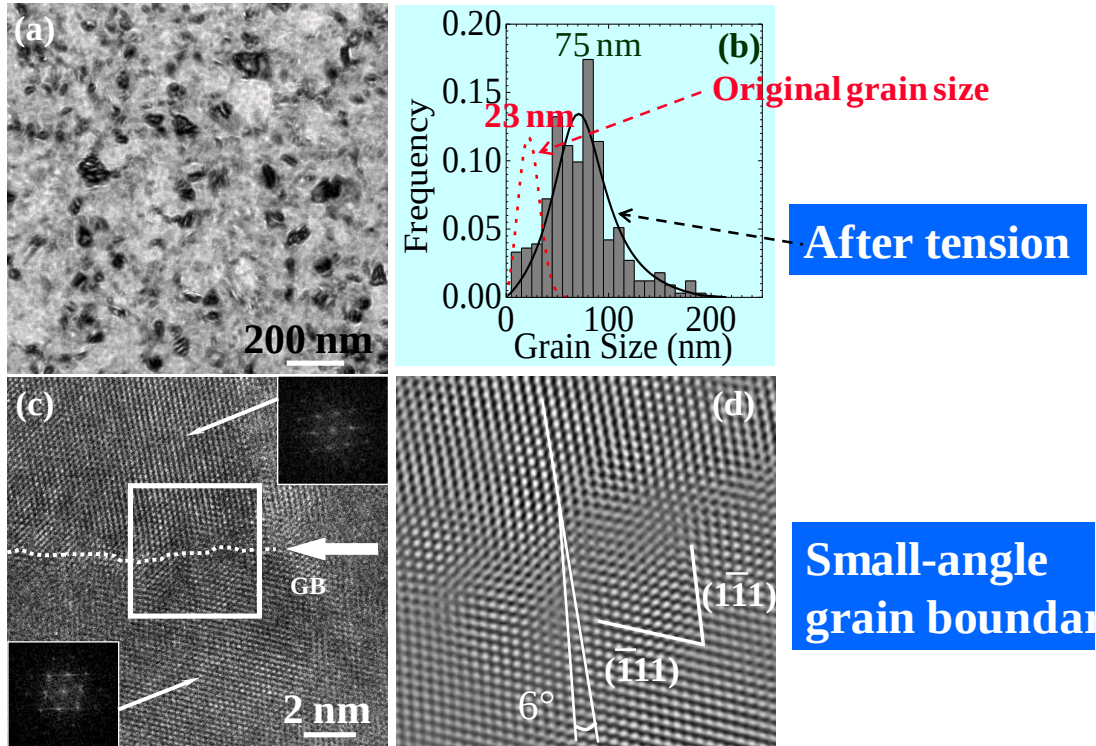


Figure 2-11. (a) Bright-field TEM image, (b) The grain-size distribution from TEM observations, (c) HRTEM around the grain-boundary region, and (d) the magnified photo of white box shown in (c), for the bulk nc Ni-18Fe alloy after the plastic deformation [14].

2.3.2 The Compressive Tests and Microstructure Evolutions

Rectangular specimens with dimensions of $1.5 \times 1.5 \times 3 \text{ mm}^3$ were prepared for the compression tests. The sample length is either parallel or perpendicular to the material-growth direction. In addition, larger samples with dimensions of $3.3 \times 3.3 \times 7 \text{ mm}^3$ were also made with the sample length perpendicular to the material-growth direction. The specimen ends were polished before compression tests to ensure that they were flat and normal to the loading axis. The compression tests were conducted at a strain rate of $5 \times 10^{-3} \text{ s}^{-1}$ at room temperature. All the specimens were cut from the same plate. At least two samples were tested per condition to ensure the result stability. Table 2-2 summarized the compression test results and revealed that the specimen size did not influence the mechanical property, i.e., there is no noticeable change in the strength and plastic strain with different specimen dimensions. However, some mechanical properties, such as the plastic strain, do depend on the grain orientation.

Table 2-2. A summary of the compression-test results on the nc Ni-20Fe alloy.
L=sample length; LA = loading axis; and GD = growth direction [17, 52-53].

Samples	Yield stress (MPa)	Ultimate stress (MPa)	Plastic strain (%)
$L=3 \text{ mm}$, LA $\perp$ GD	1720 ± 6	2448 ± 38	9.1 ± 0.6
$L=7 \text{ mm}$, LA $\perp$ GD	1705	2315	9.0
$L=3 \text{ mm}$, LA $\parallel$ GD	1705 ± 5	2410 ± 10	20.6 ± 1.4

Compressive stress-strain curves [17, 52-53] of the nc Ni-20Fe alloy with the loading direction parallel and perpendicular to the deposition direction are shown in Figure 2-12, respectively. The results show that the strength is independent of the grain orientation. However, there is a significant difference in the plastic strain under these two types of compressive tests. The plastic strain is increased from 9 % to 20 % without a sacrifice of strength when the loading direction changes from perpendicular to parallel to the direction of the grain columns. Thus, the mechanical performance of nc materials could be significantly improved using a special grain geometry.

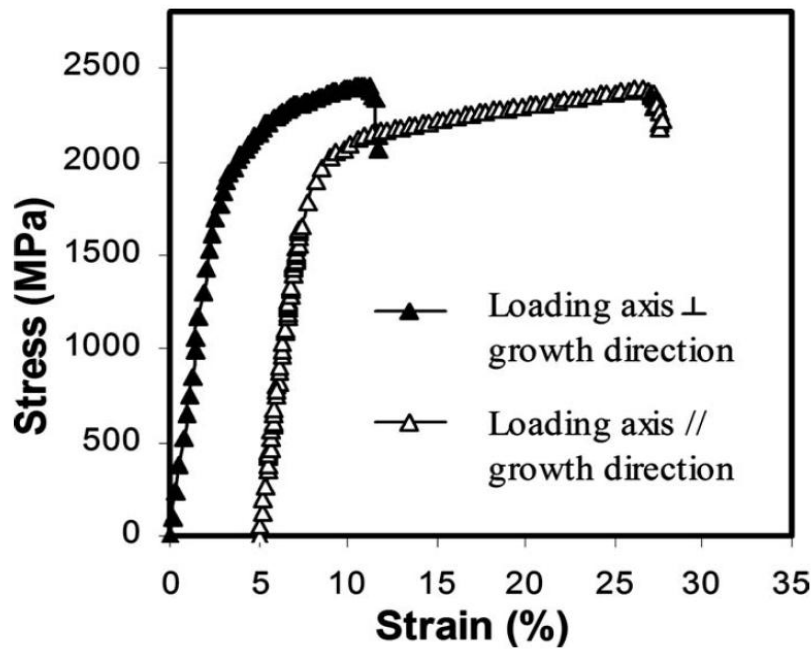


Figure 2-12. The compressive stress-strain curve of the nc Ni-20Fe alloy [17, 52-53].

A very interesting phenomenon, orientation grain growth, is observed during one of the compressive tests. The analyses and TEM observations are presented in the following paragraphs. Figure 2-13 shows the compressive stress-strain curve of the nc Ni-18Fe alloy with the loading axis perpendicular to the growth direction, which corresponds to one of the loading situations in Figure 2-12. Here, Z is the material-growth direction, and X-Y is the material-growth plane. The compressive load was applied along the Y direction. (The corresponding engineering stress-strain curve during the tensile test at the same strain rate is also included.) The inset is a schematic of a rectangular nc compressive test specimen.

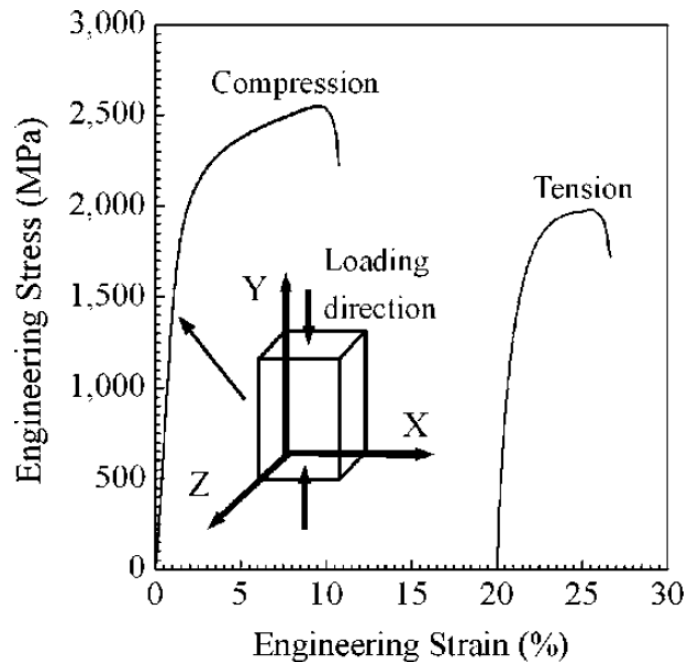


Figure 2-13. The engineering stress-strain curve of the bulk nc Ni-18Fe alloy during the compression test at a strain rate of 10^{-3} s^{-1} [17, 52-53].

Synchrotron HEXRD experiments were performed on the undeformed and deformed specimens after the above compressive test. The grain size and the microstrain were evaluated from the WH plots through integral breadths from the {111} and {222} diffraction peaks. This theory has been clearly stated in the above Section 2.3.1. Table 2-3 shows the average grain size d and the mean microstrain ε^M along the X, Y, and Z axes before and after the room-temperature compressive deformation [17, 52-53]. The grain sizes determined from the HEXRD are in a good agreement with the TEM observations for the as-deposited specimen (about 23 nm). The grain size along the Z axis (64 nm) is about two times larger than that observed in the XY plane, showing a characteristic grain structure typically observed in the as-deposited state. After the deformation, the grain sizes along the X, Y, and Z axes all increased. The grain growth is directionally inhomogeneous during the compression test. The grain growth in the X direction is much larger than that in the Y and Z directions. This orientation grain growth observed in the nc Ni-18Fe alloy depends on the stress distribution according to the grain orientation. The preferential grain growth was confirmed by TEM images taken at different plastic strains, 7 % and 11.6 %, respectively, shown in Figure 2-14. The TEM images were in the XY plane. It is observed that the equiaxed grains in the as-deposited state grow into the elongated grains after the compressive tests. The grain growth becomes more significant with increasing the plastic strain. The arrows in the images indicate the preferential grain-growth direction.

Table 2-3. The average grain size d and the mean microstrain ϵ^M along the X, Y, and Z axes before and after the room-temperature compressive deformation of the bulk nc Ni-18Fe alloy at a strain rate of 10^{-3} s^{-1} [17, 52-53].

	d_X	d_Y	d_Z	ϵ^M_X	ϵ^M_Y	ϵ^M_Z
As-deposited	21 nm	21 nm	64 nm	0.17%	0.17%	0.5%
Deformed ($\epsilon=11.6\%$)	42 nm	28 nm	78 nm	0.34%	0.19%	0.41%
Percentage changes due to deformation	100%	33%	22%	100%	12%	-18%

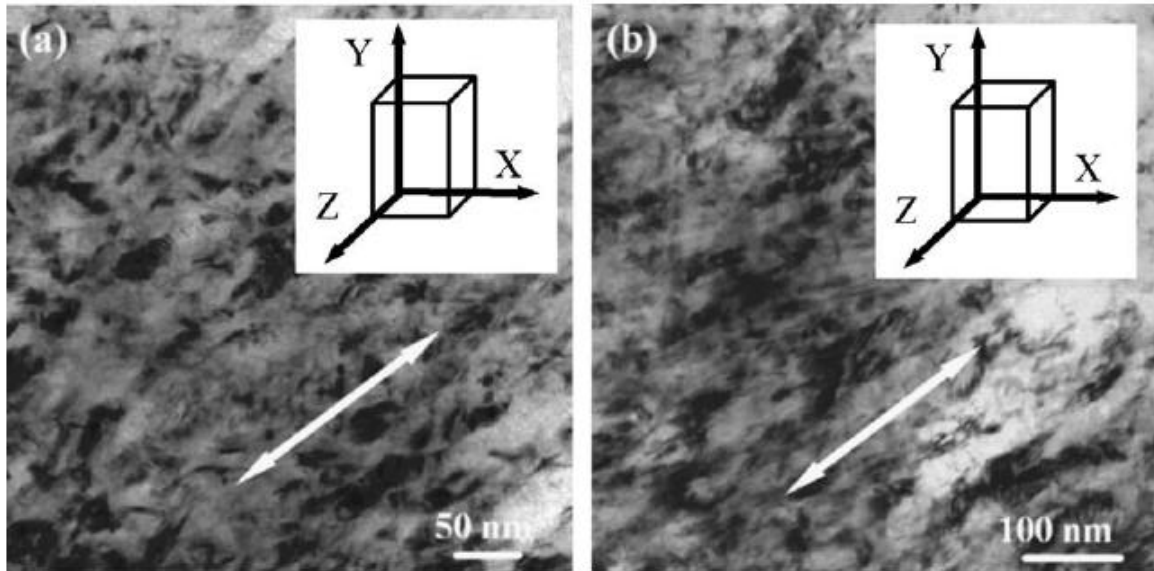


Figure 2-14. The bright-field TEM mages of the bulk nc Ni-18Fe alloy after the compressive deformation at $\dot{\epsilon} = 10^{-3} \text{ s}^{-1}$ to reach (a) $\epsilon = 7\%$ and to (b) $\epsilon = 11.6\%$, respectively [17, 52-53].

In summary, grain growth is observed in the nc Ni-18Fe alloy after the compressive deformation. However the grain growth here is anisotropic. The equiaxed grains become elongated grains after the compressive tests.

2.4 Summary

The electrodeposited nc Ni-Fe alloy exhibits a $\langle 100 \rangle$ fiber texture with the longitudinal direction of columnar grains in the growth direction. The grains have an equiaxed shape in the growth plane. The size in the longitudinal direction is around twice or three times of that in the growth plane. Growth dislocations and twins are observed within grains in the electrodeposited nc Ni-Fe alloy. The nc Ni-Fe alloy exhibits a high-angle grain boundary in the initial state. The following results are reached after the uniaxial tensile and compressive deformations:

- Grain growth is observed in the electrodeposited nc Ni-Fe alloy after both uniaxial tensile and compressive deformations. In contrast to the elongated grains after the compressive deformation, grains remain equiaxed after the tensile tests, suggesting that stress-induced grain growth in the nc materials depends on the stress loading condition.
- The grain growth in the necking region is much larger than that in the uniformly-deformed region in the tensile deformation, which may be due to the large localized-plastic strain.
- The plastic strain observed in the electrodeposited nc Ni-Fe alloy is grain-orientation dependent. There is a significant increase in the plastic strain in the

compressive test with the loading axis parallel rather than perpendicular to the materials-growth direction.

- The microstrains are calculated by WH plots using the integral-peak widths of {111} and {222} diffractions. The results show that there is no dislocation storage within the uniformly-deformed region in the tensile deformation. However, slight dislocation storage does exist in the necking area. The dislocation storage observed may be due to the large localized-plastic strains in the necking region. This results is consistent with Li, *et al*' prediction [56]: at low strains, the deformation is mainly accommodated by the GBs, however, at large strains, dislocation motion becomes probable and eventually dominates. Even though dislocation motion may not be the dominant mechanism in the deformation of the nc Ni-Fe alloy, dislocations do move during the deformation and can be trapped partly in the lattice, causing the slight increase in the microstrains. However, the slight increased microstrains observed can also be due to the overestimation of dislocations by WH plots (Please refer to the following paragraph for the overestimation).

Synchrotron HEXRD is introduced in the deformation study of the nc Ni-Fe alloy in recent years due to its good penetration and statistics of the diffraction patterns. This technique will provide us with the bulk information instead of the surface information from TEM. However, the current study on the nc Ni-Fe obtained from diffraction patterns are mainly based on WH plots, which will provide only qualitative microstructure information. For example, in the as-deposited nc Ni-Fe alloy, growth

twins are observed. However, this feature is not considered in the WH plots, where the microstrains caused by twins are compensated using extra dislocations. This replacement will cause the overestimation of dislocations in the materials. More effective and accurate microstructure analysis is needed for correctly interpreting the microstructures.

Furthermore, because of the complex initial state of materials, i.e., columnar grains aligning along the material-growth direction, a set of full-around, well-planned mechanical experiment is needed for the accurate deformation study since some mechanical properties may be orientation-dependent.

Finally, in order to accurately investigate the whole process of the plastic deformation, a large plastically-deformed region is needed for interpretation of the microstructure evolution.

These shortages mentioned above are overcome in the current thesis as you will find in the following chapters.

CHAPTER 3: QUANTITATIVE MICROSTRUCTURE EVOLUTION DURING COLD ROLLING IN A NANOCRYSTALLINE NI-FE ALLOY FROM X-RAY LINE PROFILE ANALYSIS

In the present study, rolling was performed on the nc Ni-18Fe alloy to study the microstructure evolution during the large plastic deformation. Rolling experiments were performed at both room temperature (RT) and liquid-nitrogen temperature (LNT) to investigate the temperature effect on the microstructures. Synchrotron high-energy X-ray, with good statistics and strong penetration capability, is employed in the current study to characterize the bulk nc Ni-18Fe alloy without any damage. X-ray line-profile analyses (XLPA) are used in the current study to provide the quantitative microstructure information from the diffraction patterns for the nc Ni-18Fe alloy. X-ray line-profile analysis is especially useful in the case of submicron or nanoscale materials where the X-ray line broadening becomes well pronounced and the observation of defects with a very large density is often not easy by the conventional TEM. The dislocation density, twin density, average grain size, and size distribution are systematically studied for the nc Ni-18Fe alloy before and after the cold rolling. The microstructure properties provided by XLPA are supported by TEM and DSC.

3.1 Experimental

3.1.1 Specimens

A bulk nc Ni-18Fe alloy sheet fabricated by a pulsed electrochemical-deposition technique with a thickness of 3 mm in the growth direction was acquired from the

Integran Technologies Inc. The as-deposited alloy is a single phase with fcc structure. Two bars with a cross section of 1 mm x 3 mm were machined from the as-deposited sheets and rolled at both room temperature (RT) and liquid-nitrogen temperature (LNT) through several passes to reach their maximal true strains (ϵ), - 0.6 and - 0.36, respectively, i.e., the final thickness of 0.55 mm for the RT-rolled specimen and 0.7 mm for the LNT-rolled specimen after the deformation. The growth direction (GD) becomes the transverse direction (TD) after rolling.

3.1.2 Synchrotron-Diffraction Experiments

The ex-situ synchrotron X-ray experiments were carried out at the beamline, 11ID-C, of the Advanced Photon Source (APS), Argonne National Laboratory (ANL) in US. Figure 3-1(a) shows a schematic of the synchrotron X-ray experimental setup. The monochromatic synchrotron high-energy X-ray beam with an energy of 115 KeV penetrated through the specimens, and the transmission-diffraction patterns were collected by a two-dimensional (2D) detector (Mar 345) positioned at about 1.4 m away from the specimen stage. In the texture experiments, the specimens were rotated every 10 degrees around the axis, which is parallel to the rolling direction (RD) in the sample-coordinate system.

Figure 3-1(b) presents one typical diffraction pattern collected by the 2D detector. The weaker and finer Debye-Sherrer rings, compared with the broader Debye-Sherrer rings of the nc Ni-Fe alloy, come from CeO₂, which was used as the standard in the synchrotron X-ray experiments (Standard LaB6 was used for obtaining the instrumental file in the later X-ray line-profile analysis).

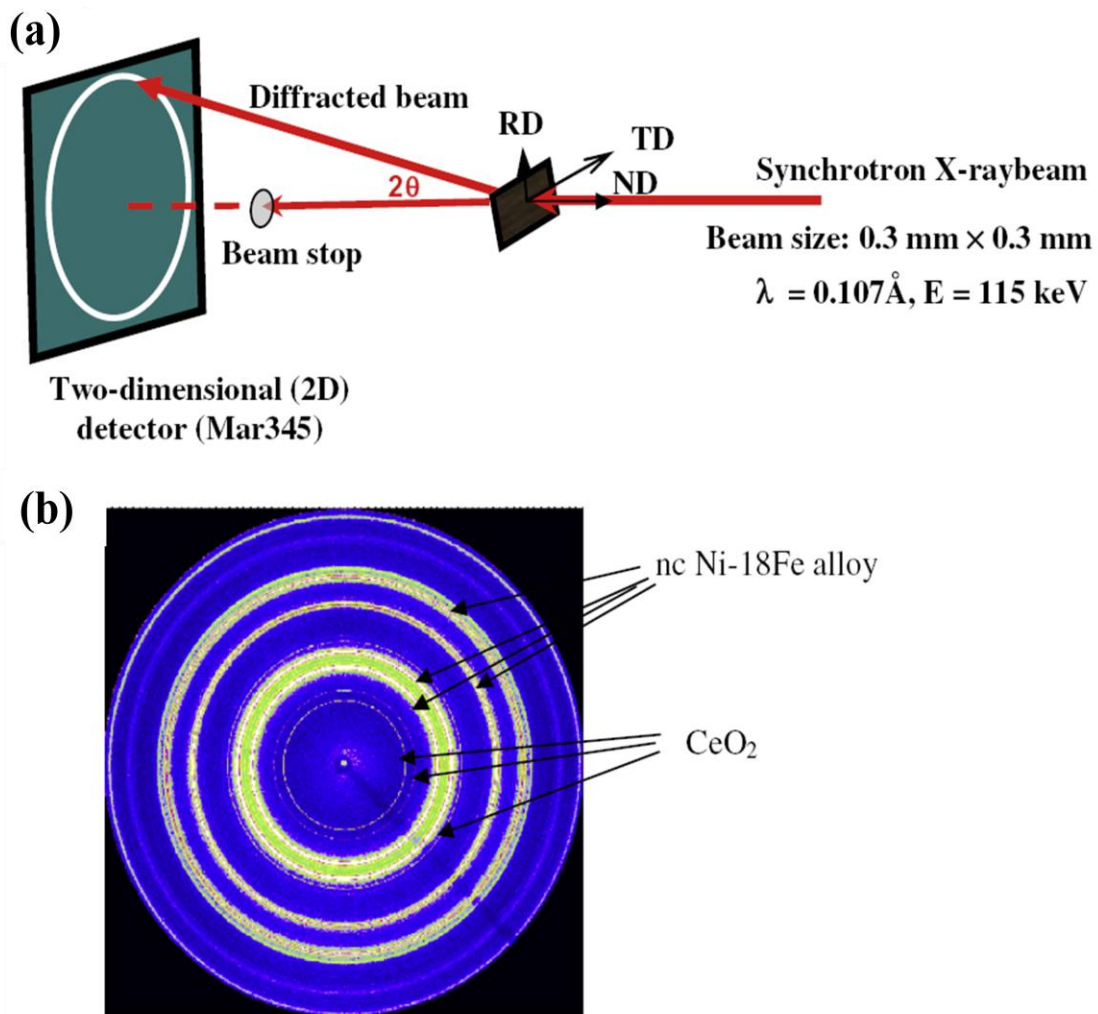


Figure 3-1. (a) Schematic figure of a synchrotron HEXRD experimental setup. (b) One typical diffraction pattern collected by the 2D detector.

3.1.3 The Methodology of X-Ray Line Profile Analysis

Generally speaking, diffraction peaks are Bragg peaks superimposed on the diffuse scattering background, which is caused by the point defects, such as interstitials and vacancies in the material. Diffraction peaks can be shifted, broadened, and become asymmetric after the plastic deformation. The peak can be shifted due to different kinds

of internal stresses, such as residual internal stress, stacking faults, and chemical inhomogeneities. The peak broadening is caused by crystallite size and strains. Peaks can also become asymmetric due to different kinds of internal stresses, such as gradient stress, coherency stress, stacking faults and chemical inhomogeneities. The above three main factors need special care before performing the line profile analysis. In this thesis, the extended convolutional multiple whole profile (eCMWP) fitting procedure works as a computer program developed for the determination of microstructural parameters from diffraction profiles of materials with cubic, hexagonal or orthorhombic crystal lattices [57], but works in principle, for all crystal systems [58]. In the calculation of the theoretical functions, it is assumed that the crystallite size and strain are two sources of line broadening, the Fourier transform of line profiles can be given by the following equation [59-60]:

$$\ln A(L) \cong \ln A_L^S - 2\pi^2 L^2 g^2 \langle \varepsilon_{g,L}^2 \rangle \quad (3-1)$$

where A_L^S are the size Fourier coefficients, L is the Fourier parameter, and g is the diffraction vector. Strain broadening is given by the mean-square strain that in dislocated crystals is [61-62]:

$$\langle \varepsilon_{g,L}^2 \rangle = (b/2\pi)^2 \rho C f(\eta) \quad (3-2)$$

where b is the Burgers vector, ρ is the dislocation density, $f(\eta)$ is the Wilkens function, $\eta = R_e/L$, R_e is the effective outer cut-off radius of dislocations, and C is the dislocation-contrast factor. Instead of R_e , it is better to use the dimension-free quantity: $M = R_e \sqrt{\rho}$, which characterizes the dislocation arrangement. When M is smaller or larger than unity,

the dipole character of dislocations is strong or weak, respectively. The values of C depend on the relative orientations between the line direction, Burgers vector of dislocations and the diffraction vector, and also on the elastic constants of the crystal. They can be calculated numerically. In cubic crystals, the dislocation-contrast factors can be averaged over the permutations of the hkl indices [63]:

$$\bar{C} = \bar{C}_{h00}(1-qH^2) \quad (3-3)$$

where $\bar{C}_{h00}$ is the average dislocation-contrast factor for the $h00$ reflections, q is a parameter depending on the elastic constants of the crystal and the edge or screw character of the dislocations [64], and $H^2 = (h^2k^2 + h^2l^2 + k^2l^2)/(h^2+k^2+l^2)^2$.

The size Fourier coefficients can be calculated for a given size-distribution-density function, $f(x)$. Assuming the crystallites have spherical or ellipsoidal shape with a log-normal size distribution, the size Fourier coefficients can be written as [62]:

$$A^S(L) = \int_{|L|}^{\infty} (\mu^2 - |L|\mu) \text{erfc} \left[\frac{\log(\mu/m)}{2^{1/2}\sigma} \right] d\mu \quad (3-4)$$

where erfc is the complementary error function, and m and σ are the median and the variance of the log-normal size distribution function, respectively. The area-weighted mean crystallite size is [65]:

$$\langle x \rangle_{\text{area}} = m \exp(2.5\sigma^2) \quad (3-5)$$

The effect of twinning is incorporated into the theoretically-modeled functions by Lorentzian-type profile functions following well-defined specific selection rules for the hkl indices [66].

The extended convolutional multiple whole profile (eCMWP) procedure [57, 66] is used for determining the microstructure from x-ray diffraction patterns in terms of the (a) crystallite size and size distribution, (b) dislocation density, and (c) planar faults, in the present case, twin-boundary frequency. The whole measured diffraction pattern is fitted directly by the sum of the background and the theoretically-constructed profile functions convoluted with the instrumental pattern. The theoretical profile functions are calculated as the convolution of the size, strain, and faulted profile functions.

The method used in the fitting is the Java frontend of eCMWP. Run the program *evaluate* directly (which is part of the eCMWP package). The *evaluate* program is a frontend written in the shell script language *zsh* and it is enhanced with graphical functions written in the JAVA programming language. All the parameters can be adjusted in JAVA panel and all the functions of the fitting can be reached by pressing the appropriate buttons [58]. The evaluation follows:

1. Running the *evaluate* program through `./evaluate/directory` (where the data files put), then a JAVA panel will pop up.
2. Selection of the crystal system in the JAVA panel. The possible selections are: cubic (default), hexagonal or orthorhombic. Cubic is picked in the current study.
3. Setting the values of the input parameters. The lattice constants, the values of the Burgers' vector, dislocation contrast factor of $\{h00\}$ C_{h00} , and the wavelength of the X-ray measurement are needed for the evaluation.
4. Specification of the instrumental profiles. The instrumental profiles are obtained from the diffraction experiment with intensity versus diffraction

angle, $I \sim 2\theta$. The profile is converted into the reciprocal space in terms of $I \sim (K-K_0)$. Here $K = 2\sin\theta/\lambda$, $K_0 = 2\sin\theta_0/\lambda$.

5. Determining the background by push the *mkspline* button. The base points of the background spline should be manually defined.
6. Indexing peaks. Push the *peak-index* button and right click the mouse to zoom in for the maximum of the peaks, then click the middle mouse. After that go to *zsh* shell to input the corresponding peak index.
7. Specification of the interval used for fitting and plotting. Specify the lower and upper limit, which is used for fitting and plotting.
8. Selection of the size function. The possible selections are: no size effect, spherical size function or ellipsoidal size function.
9. Specification of the sampling of the simulated powder pattern data. The value of N_1 , N_2 and the profile cutting parameter should be specified here. Input 1024 for N_1 and N_2 . If not working, use 512 instead.
10. Specification of the initial values of the parameters. The initial values of the fitting parameters have to be specified. They are always saved for subsequent runs. There is an option for fixing the value of any parameter, which means that the values of that parameter will not be refined during the fitting procedure. Fixing b means no size effect, which can be used when the size is very large (e.g. 10 micrometer). Fixing the value of d^*e means that the value of the parameter M is fixed. This option can be used if the program enters into an asymptotic minimum (the values of ρ and R_e^* tend to infinity and zero, respectively, and the asymptotic standard errors of the parameters

d and e become extremely large, larger than 100%). The scales of the fitting parameters can also be specified here for improving calculation velocity.

11. Peak parameter refinement and weighting. Here the refinement of the peak positions and peak intensities can be chosen. If the peaks have very different intensities, you can choose here to use weights in the fitting algorithm. In this study, no weight is chosen.
12. Fit control. The fitting is stopped if the specified maximum number of iterations is reached or if the relative change between two iteration steps is less than the specified limit 10^{-9} .
13. Fitting. In this step, the values of the parameters are refined using the *gnuplot* program. The measured and the fitted theoretical pattern are plotted for each iteration, thus, one can continuously trace how the theoretical pattern approaches the measured data. The figure and solution is saved after the convergence.

If the fitting is not good after following above, then think about trying to adjust the background spline since the initial background spline defined manually may not close to the real situation in the material.

3.1.4 Transmission-Electron Microscopy

After mechanical polishing, TEM thin-foil specimens of the as-deposited, RT-rolled, and LNT-rolled Ni-18 Fe alloys were prepared by the conventional twin-jet electropolishing technique using a solution of 25 volume percent (vol.%) nitric acid and 75 vol.% methanol.

3.1.5 Differential-Scanning-Calorimetry Measurements

A Perkin Elmer DSC-2 differential-scanning calorimeter was employed to determine the excessive stored enthalpy. DSC curves were obtained at a heating rate of 20 Kmin^{-1} in the temperature range of 350 K - 1,000 K. Three consecutive heatings were performed for each case. Second and third heatings were performed to check for reversible processes. All calorimetric measurements were carried out in a nitrogen (99.999% purity) flux in order to protect specimens against oxidation.

3.2 Results

3.2.1 X-ray Line-Profile Analyses

Figure 3-2 presents the X-ray line profiles for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys after caking and integrating the whole 2D diffraction patterns. It apparently shows the peak narrowing after cold rolling at both LNT and RT, indicating that either grain is coarsening, or strain is reduced, or these two happen concomitantly. The narrowing of the peaks is most pronounced after rolling at RT.

The full widths at half maximum (FWHMs) of the first six reflections for each specimen are shown in the conventional WH plots [67] as a function of K in Figure 3-3(a). Here, $K = 2\sin\theta/\lambda$, $\text{FWHM} = \Delta K = 2\cos\theta(\Delta\theta)/\lambda$, θ and λ are the Bragg angle and the wavelength, respectively. The open triangles, open squares, and open circles stand for the as-deposited, LNT-rolled, and RT-rolled specimens, respectively. It can be seen that line broadening does not increase monotonously with the order of reflection. This phenomenon is due to the strain anisotropy, which is typical when the strain is caused by dislocations [68].

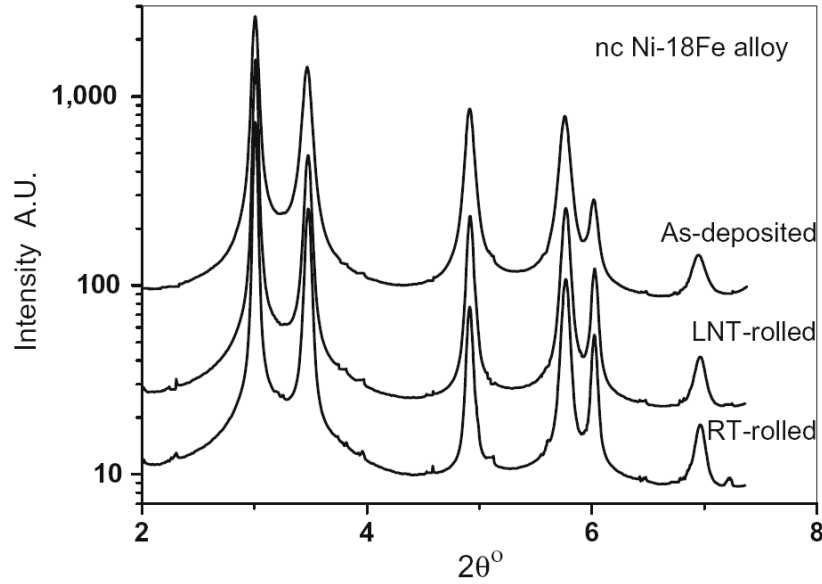


Figure 3-2. Comparison of diffraction patterns for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys.

The strain anisotropy is rectified in the *modified* WH plot by a dislocation contrast factor, C , as shown in Figure 3-3 (b). From the plot, it is found that both RT-rolled and LNT-rolled specimens show smaller FWHM intercepts and slopes, compared with the as-deposited one after fitting the experimental data by a straight line using a standard least-squares method. Since the intercepts at $KC^{1/2} = 0$ and the slopes in the *modified* WH plots are proportional to the reciprocals of the crystallite size and microstrain, respectively, the results indicate the grain coarsening and microstrain reduction after cold rolling at both temperatures, RT and LNT.

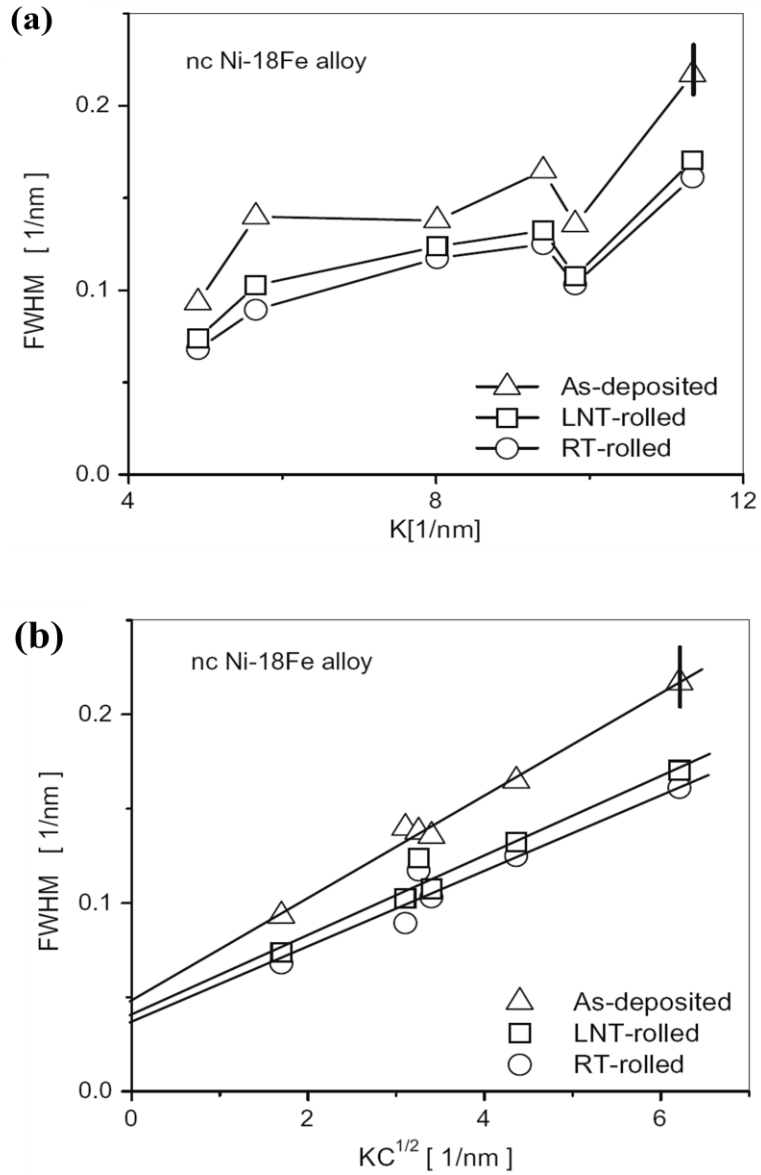


Figure 3-3. (a) WH plots and (b) modified WH plots for the nc Ni-18Fe alloy.

A quantitative study of diffraction patterns was performed by the eCMWP method. Figure 3-4 presents one typical fitted diffraction pattern by the eCMWP procedure. Measured and fitted data are indicated by the open circles and the solid line through the circles, respectively. The difference between the measured and fitted data is

shown by a thin line at the bottom of the figure. The inset shows a blow-up of the fitted (311) and (222) peaks, indicating a perfect fitting. The values of the quantitative evaluation of diffraction patterns for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys are given in Table 3-1.

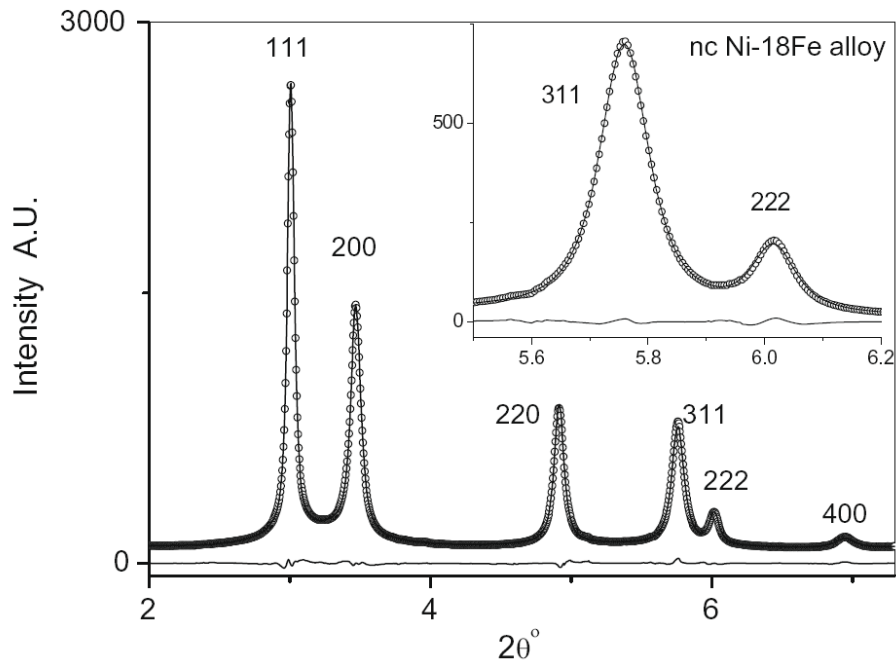


Figure 3-4. The measured diffraction pattern and the calculated pattern by the eCMWP procedure for the as-deposited specimen.

Table 3-1. The eCMWP fitting values for the median (m) and variance (σ) of the size-distribution function, area-average crystallite size ($\langle x \rangle_{\text{area}}$), q parameter, and twin-boundary frequency (β) for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys, respectively.

Specimens	m [nm]	σ	$\langle x \rangle_{\text{area}}$ [nm]	q	ρ [10^{16} m^{-2}]	β [%]
As-deposited	6.8 (± 0.5)	0.54 (± 0.05)	14 (± 1)	1.8 (± 0.1)	3.7 (± 0.5)	3.2 (± 0.8)
RT-Rolled	26 (± 2)	0.27 (± 0.05)	31 (± 3)	2 (± 0.1)	2.2 (± 0.4)	1.5 (± 0.3)
LNT-Rolled	7.5 (± 0.5)	0.7 (± 0.08)	26 (± 3)	1.8 (± 0.1)	1.8 (± 0.3)	2.2 (± 0.3)

It is found that the as-deposited samples contains an extremely high dislocation density of $3.7 \times 10^{16} \text{ m}^{-2}$, an average grain size of 14 nm, and a large twin-boundary frequency of 3.2 %. After cold rolling, The dislocation density decreases from $3.7 \times 10^{16} \text{ m}^{-2}$ to $2.2 \times 10^{16} \text{ m}^{-2}$ and to $1.8 \times 10^{16} \text{ m}^{-2}$ after rolling at RT and LNT, respectively. The twin-boundary frequency, defined as the number of twin boundaries for each 100 closed-packed layers, decreases from 3.2 % to 1.5 % and to 2.2 % after RT and LNT rolling, respectively. In conventional metals and alloys, during plastic deformation, especially cold rolling, the grain size generally decreases together with the increase of the dislocation density. When the stacking-fault energy is low enough, deformation twins may be formed. In that sense, the present nc Ni-18Fe alloy is rather unconventional: the

grain size increases, while both the dislocation density and twin density decrease during cold rolling. This simultaneous reduction of these two types of defects is contrary to all previous observations in coarse-grained materials and has not been reported so far in other nc materials. This simultaneous reduction of these two types of defects with grain growth during rolling deformation is consistent with the information provided above by the most commonly used analysis, *modified* WH plots: grain coarsening and decreased microstrain after cold rolling. The grain-size-distribution functions for the undeformed and deformed specimens are plotted from the fitting values provided in Table 3-1. The log-normal size-distribution density functions determined from the measured m and σ values are shown in Figure 3-5.

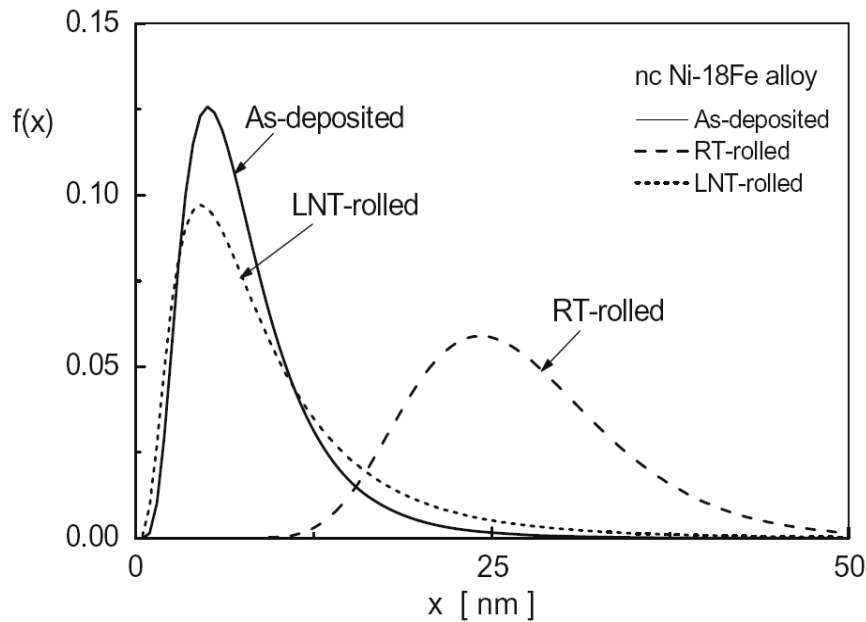


Figure 3-5. The log-normal grain-size probability distribution functions for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys.

It can be seen that the size distribution of the RT-rolled specimen (a dash line) is shifted much more, relative to that of the as-deposited one (a solid line). In the case of the RT-rolled specimen, all three, the TEM micrograph, the area-average mean crystallite size, and the size-distribution function indicate a considerable grain growth in unison. In the case of the LNT-rolled specimen, the change is not as great as that for the RT-rolled one. The size-distribution function of the LNT-rolled specimen (a short-dash line) is hardly shifted relative to the as-deposited one, but it becomes wider. However, the area-average mean crystallite size of the LNT-rolled specimen, 26 nm, is apparently much larger than that of the initial one, 14 nm. The slight shift towards a smaller size observed in Figure 3-5, however, is not opposite to the TEM observations. The size-distribution function, used in the X-ray line-profile analysis, is a “density function”, which has different moments that are characteristic of different size “averages” in the specimen. The two parameters describing the log-normal size distribution are the median, m , and variance, σ . (In fact, the variance, as used here, is the “logarithmic” variance, but it is usual to omit the attribute “logarithmic”). The value of m is at a higher value than the maximum position of the log-normal size distribution (*max-of-LG-SD*) and is, nevertheless, at lower values than any of the three physically-relevant average values. The three physically-relevant mean values are:

$$\langle x \rangle_{\text{arithmetic}} = m \exp(0.5\sigma^2) \quad (3-6)$$

$$\langle x \rangle_{\text{area}} = m \exp(2.5\sigma^2) \quad (3-7)$$

$$\langle x \rangle_{\text{volume}} = m \exp(3.5\sigma^2) \quad (3-8)$$

where $\langle x \rangle_{arithmetic}$, $\langle x \rangle_{area}$, and $\langle x \rangle_{volume}$ are the arithmetic, area, and volume averages of the mean crystallite or subgrain sizes, respectively. The sequence in the different size values is:

$$max-of-LG-SD < m < \langle x \rangle_{arithmetic} < \langle x \rangle_{area} < \langle x \rangle_{volume} \quad (3-9)$$

The sequence above indicates that neither the value of *max-of-LG-SD* nor that of *m* are characteristic of an “average” grain or subgrain size. The whole size-distribution function has to be considered for determining physically-relevant average size values. In Figure 3-5, it can be seen that the tail of the size-distribution function corresponding to the specimen deformed at LNT is higher than that of the as-deposited one, i.e., the size distribution extends to larger grains far away. This is the reason why the area-average crystallite size for the LNT specimen is larger than that of the as-deposited one. It is also noted that the *area-average value* of the mean crystallite or subgrain size is one of the most stable size values in the evaluation of line broadening. This trend means, even if the actual values of *m* and σ vary slightly within the experimental error with the X-ray line-profile evaluation run at different starting values, the $\langle x \rangle_{area}$ value does not change. Both the average grain size and the size distribution will influence the deformation mechanisms [69-70], which, in turn, determine the mechanical properties that the materials exhibit.

The parameter, *q*, in Table 3-1 is used to describe the dislocation type, screw or edge. For Ni, the Zener constant is $A_z = 2c_{44}/(c_{11}-c_{12}) = 2.54$, where c_{11} , c_{12} , and c_{44} are the elastic constants [71]. From the literature [64, 72], based on the *q* versus A_z curve, *q* is equal to 2.2 and 1.5 for the pure screw and edge dislocations, respectively. The *q*

parameters in our nc Ni-18Fe alloys lie between 1.8 and 2, indicating a mixed edge and screw dislocation character.

3.2.2 TEM Observations

Figure 3-6 shows bright-field TEM observations for the (a) as-deposited specimen [perpendicular to the deposition-growth direction (GD)], and (b) LNT-rolled specimen with a marked sample coordinate. There is an obvious grain growth after rolling deformation even at LNT. The grains increased from around 25 nm in the as-deposited material to around 40 ~ 50 nm after rolling at LNT.

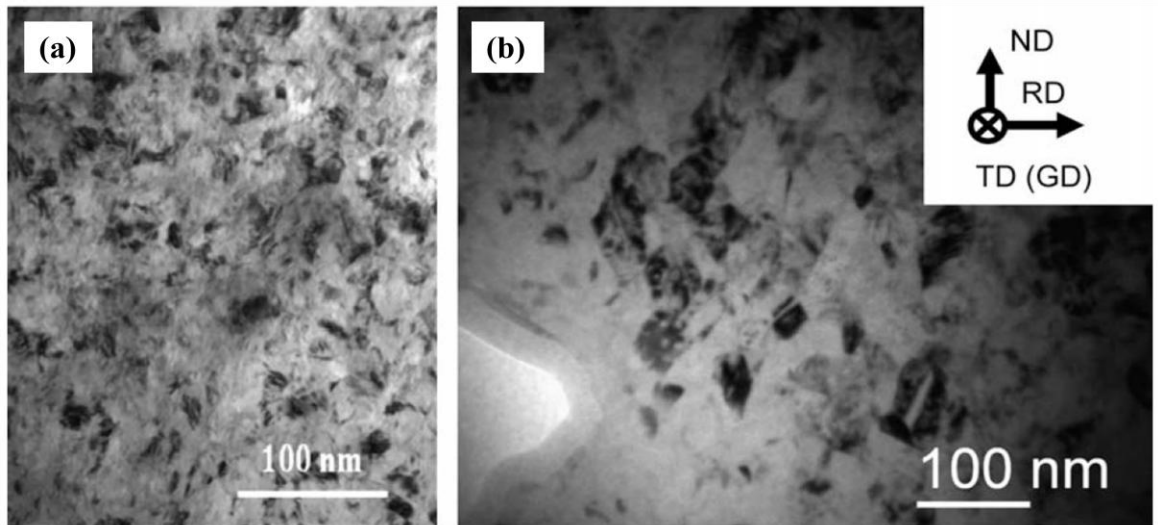


Figure 3-6. Bright-field TEM images of the (a) as-deposited (perpendicular to the deposition growth direction), and (b) LNT-rolled nc Ni-18Fe alloys.

The TEM micrograph corresponding to the RT-rolled specimen is rather similar to that of the LNT-rolled one. The grain-coarsening phenomenon in the LNT-rolled specimen is not as obvious as that in the RT-rolled one, which could be due to the slightly lower reduction in the LNT-rolled specimen or to the lower deformation temperature. Besides, twins are observed in the above TEM micrographs. These TEM observations are consistent with the XLPAs analysis results.

3.2.3 DSC Measurements

Each specimen was heated three times, consecutively, at a heating rate of 20 Kmin^{-1} within the temperature range of 350 K - 1,000 K. Second and third heatings were performed to check for reversible processes. The heat-release curves for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys in the first heating are shown in Figure 3-7(a). The graph corresponding to the as-deposited specimen is truncated for the sake of a better representation of the other two curves. The unit, MPa, is selected in order to have an easier comparison with the elastic-stored energy per volume corresponding to dislocations, where MPa is used as the unit. The conversion between Joule/g and MPa by a mass density is $1 \text{ J/g} = 8.63 \text{ MPa}$.

It is shown that in the case of the as-deposited and LNT-rolled specimens, the heat release starts at about 400 K with a relatively low rate, which is followed by a sharp peak maximized at around 680 K to 700 K, and, finally, there is a heat-absorption peak with the negative maximum around 840 ~ 850 K.

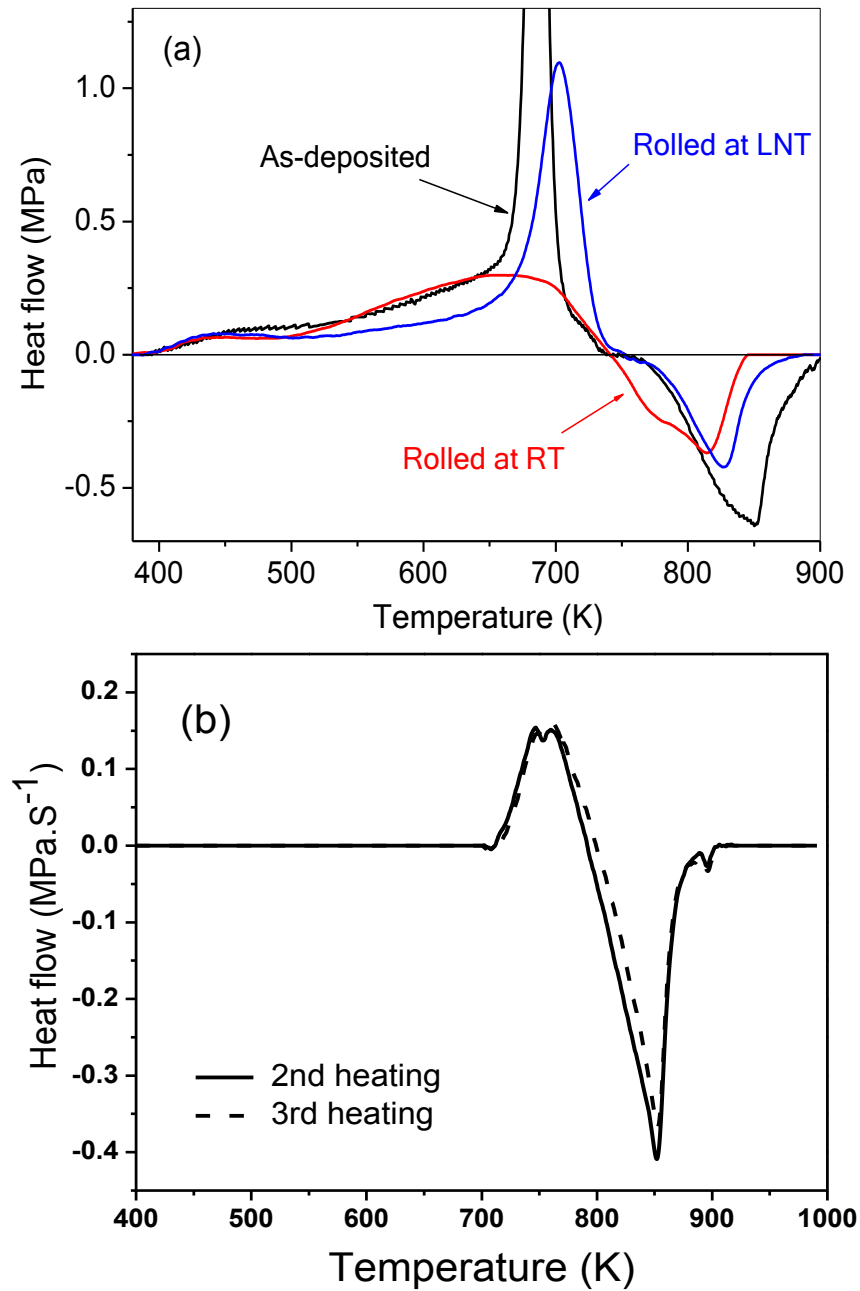


Figure 3-7. (a) DSC curves for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys in the temperature range of 350 K - 1,000 K for the first heating, (b) DSC curves for the second and third heating of the as-deposited nc Ni-18Fe alloy.

The heat flow of the RT-rolled specimen has the same characteristic temperatures, but the second heat-release peak following the first low-rate peak is smeared out over a wider temperature range than the as-deposited and LNT-rolled specimens. This phenomenon may be due to the adiabatic process of rolling at RT. The second heat-release peak is the sharpest in the as-deposited specimen (black), somewhat damped in the LNT-rolled specimen (blue), and the least sharp in the RT-rolled specimen (red).

The second and third heating curves for the as-deposited, RT-rolled, and LNT-rolled specimens are similar. Figure 3-7(b) shows the second and the third heating curves for the as-deposited specimen. They were identical within the experimental error, which indicates the reversible process.

The Ni-Fe phase diagram shown in Figure 3-8 indicates that the Ni_3Fe intermetallic phase may appear during the heating of Ni-18Fe alloy. The intermetallic phase, Ni_3Fe , is ordered below about 700 K and disordered above about 800 K. Thus, the sharp heat release in Figure 3-7 (a) corresponds to the formation of the stable Ni_3Fe phase from the metastable solid solution, and the heat absorption is due to the disordering of this Ni_3Fe phase.

In order to cross-check the presence of Ni_3Fe precipitates, additional X-ray diffraction experiments were carried out on the heated specimens. Figure 3-9 shows the full X-ray diffraction patterns of the initial-state specimen measured in a special high-resolution double-crystal diffractometer after heating up in the DSC calorimeter.

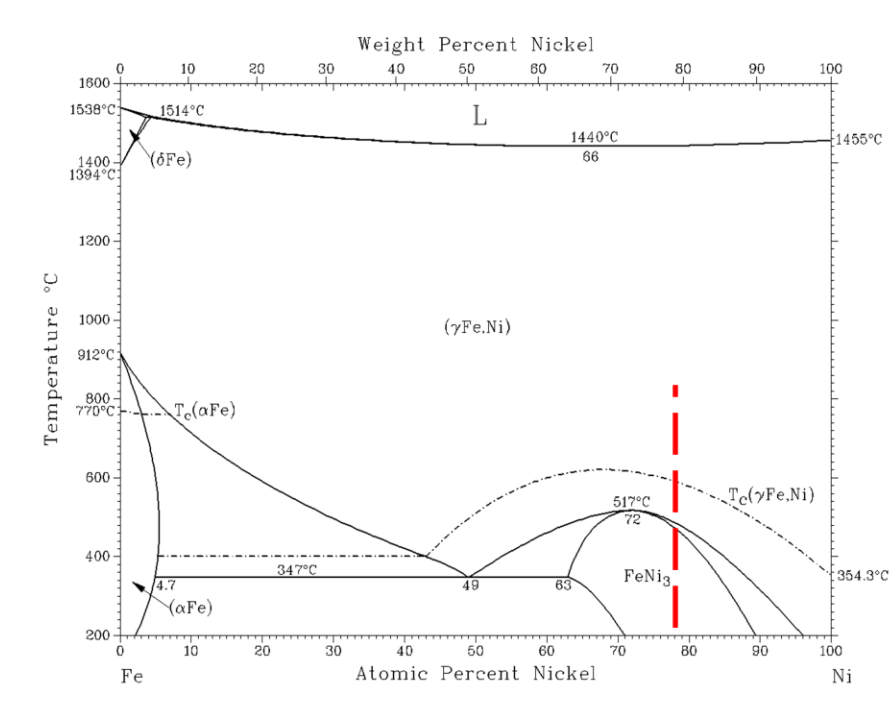


Figure 3-8. Phase diagram of the binary Ni-Fe system.

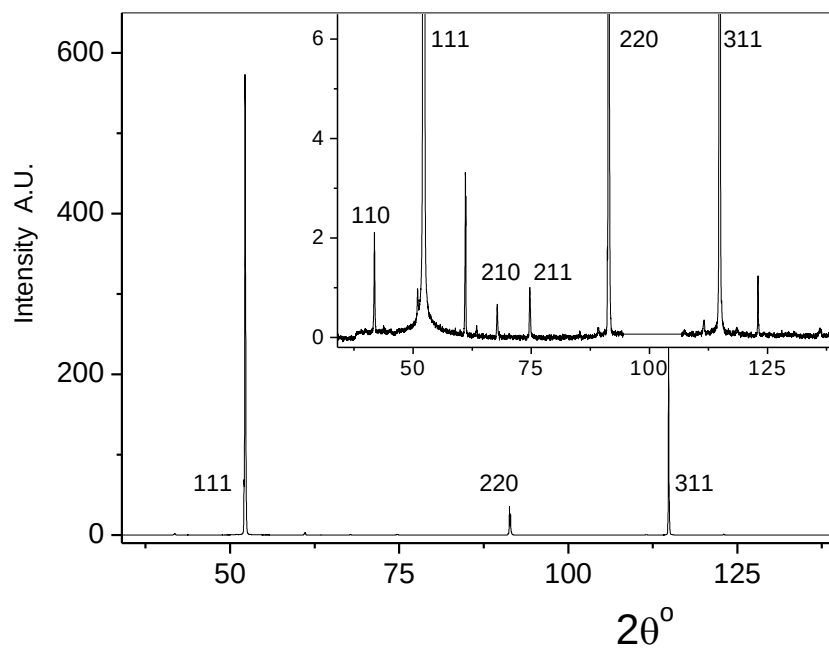


Figure 3-9. Diffraction patterns of the initial-state specimen after heating up in the DSC.

Three fundamental reflections of (111), (220), and (311), which correspond to the fcc structure, were indexed. The inset in the figure shows the pattern where the intensity scale has been reduced by a factor of 100 to better see the superreflections of the ordered Ni₃Fe precipitates, (110), (210), and (211). The x-ray diffraction patterns of the RT-rolled and LNT-rolled specimens after heating in the calorimeter were similar to that of the as-deposited one. The intermetallic phase, Ni₃Fe, does precipitate from the matrix Ni-18Fe alloy during the heating. Thus, heat absorptions in the DSC curves correspond to the disordering of the Ni₃Fe precipitates formed during the first heating.

Figure 3-9 also presents that the volume fraction of the Ni₃Fe phase is of the order of a few percents. The deformation process may be changed by controlling the volume fraction of Ni₃Fe precipitates in the nc Ni-18Fe alloy matrix. Furthermore, the drastic line narrowing indicates a full recovery and recrystallization during heating up to about 900 K.

3.3 Discussion

3.3.1 Stress Softening after Rolling Deformation

Due to the limited deformed specimen dimension, nanoindentation tests were performed on the undeformed and deformed specimens to obtain the hardness information. The measured hardness values are listed in Table 3-2. Note, $\langle x \rangle_{\text{area}}$ is listed in the same table for easy reading. Table 3-2 shows that the hardness and grain size in the nc Ni-18Fe still follows the Hall-Petch relation: increased hardness with finer grains. The nc Ni-18Fe alloy becomes soft because of the grain growth and the reduced dislocation density after cold rolling.

Table 3-2. X-ray measured dislocation density (ρ), mechanical-test measured yield strength [σ_Y (measured)], hardness (H), and the calculated yield strength from hardness [σ_Y (calculated)], and constant, α , for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloy, and heavily-deformed pure nc Ni [14].

Specimens	$\langle X \rangle_{\text{area}}$ [nm]	σ_Y [MPa] (measured)	H (MPa)	σ_Y [MPa] (calculated)	α
As-Deposited	14 (± 1)	1,500 (± 80)	7,600	-	0.12
RT-Rolled	31 (± 3)	-	5,500	1,100	0.10
LNT-Rolled	26 (± 3)	-	4,900	980	0.10
Ni [73] (8ECAP + 5HPT)	48 (± 6)	1,100 (± 50)	-	-	0.38

ECAP: equal-channel-angular processing

HPT: high-pressure torsion

The macroscopic flow-stress, σ_Y , and the average dislocation density, ρ , can be related to each other by the Taylor equation [74]:

$$\sigma_Y = \sigma_0 + \alpha M_T G b \sqrt{\rho} \quad (3-10)$$

where σ_0 is the friction stress, α is a constant between 0 and 1, b is the Burgers vector, G is the shear modulus, and M_T is the Taylor factor. In the present case, $b = 0.25$ nm, and $G = 76$ GPa. The value of σ_0 has recently been determined for Ni-Fe alloys by Durst and Göken [75], which for the present alloy, provides $\sigma_0 = 210$ (± 10) MPa. After considering the texture influence on the Taylor factor [76], $M_T = 2.952$, 3.097, and 3.028 for the as-deposited, RT-rolled, and LNT-rolled specimens, respectively.

A tensile test provides the flow stress, $\sigma_Y = 1,500$ MPa, for the as-deposited specimen [14]. Due to the limited deformed specimen dimension, nanoindentation tests were performed on the undeformed and deformed specimens to obtain the hardness. Then the yield strengths were calculated and listed in Table 3-2. A factor 5, obtained from the ratio of the measured hardness over the measured yield strength in the as-deposited specimens, is used in our experiment for converting the hardness into the yield strength. The yield strength is 1,110 MPa for the RT-rolled specimen and 980 MPa for the LNT-rolled specimen, respectively. Nanocrystalline Ni-Fe alloys become soft after cold rolling at either RT or LNT. Using Equation (3-10), α values were obtained as 0.12, 0.10, and 0.10 for the as-deposited, RT-rolled, and LNT-rolled specimens, respectively. These α values are similar, which is consistent with the mild change of the dislocation density during cold rolling. For the sake of comparison, the σ_Y and α values of a heavily-deformed Ni specimen [73] with eight equal-channel angular passes (ECAP) followed by five high-pressure-torsion (HPT) turns are also shown in the table. The flow stress of this latter specimen is close to that of the two cold-rolled specimens. However, its α value is more than three times larger than that of the rolled specimens. The values of α are in correlation with dislocation-dislocation interactions. As the dislocation density increases, the dipole character of dislocations increases, i.e., the screening of the strain field becomes stronger. This effect was experimentally verified in a compression-deformed single-crystal copper, where α decreased from 0.28 to 0.17 while the dislocation density increased from $0.2 \times 10^{14} \text{ m}^{-2}$ to $6 \times 10^{14} \text{ m}^{-2}$ [77].

3.3.2 Strong Diffuse-Background Scattering

The presence of the amorphous fraction in the specimens is evidenced by the diffuse-background scattering in the X-ray diffractograms. Figure 3-10(a) shows the measured x-ray diffraction pattern (a solid line) and the diffuse-back ground scattering (a dash line) together on a logarithmic intensity scale for the as-deposited specimen. The background shows a variation with the diffraction angle, which is identical in shape to the diffuse scattering of amorphous materials [78-79]. Diffuse-background scattering most likely comes from the strongly-disturbed grain boundaries in the form of amorphous materials since the contribution from point defects is nominal within such a small grain.

The amorphous volume fraction in the specimens can be estimated by either the measured diffuse-background scattering or the estimation from the grain size. The amorphous volume fraction can be estimated from the ratio of the integrated intensities of the diffuse background, I_{DBG} , and the total scattering curve, I_{Tot} . For the as-deposited specimen, this ratio is:

$$\frac{I_{DBG}}{I_{Tot}}(as - deposited) \cong 0.15 (\pm 0.05) \quad (3-11)$$

The same amorphous volume fraction can be estimated by assuming that the grain-boundary region is a strongly-disturbed amorphous region of the material with the crystallite size in the as-deposited state is about 15 nm. Assuming that the grain boundary has the thickness of 2 or 3 atomic distances, i.e., 0.5 or 0.76 nm, the amorphous region is again obtained to be about 15 vol.%. This ratio reduced to approximately 10 % (± 5 %) after rolling at either LNT or RT, which is in agreement with the grain growth.

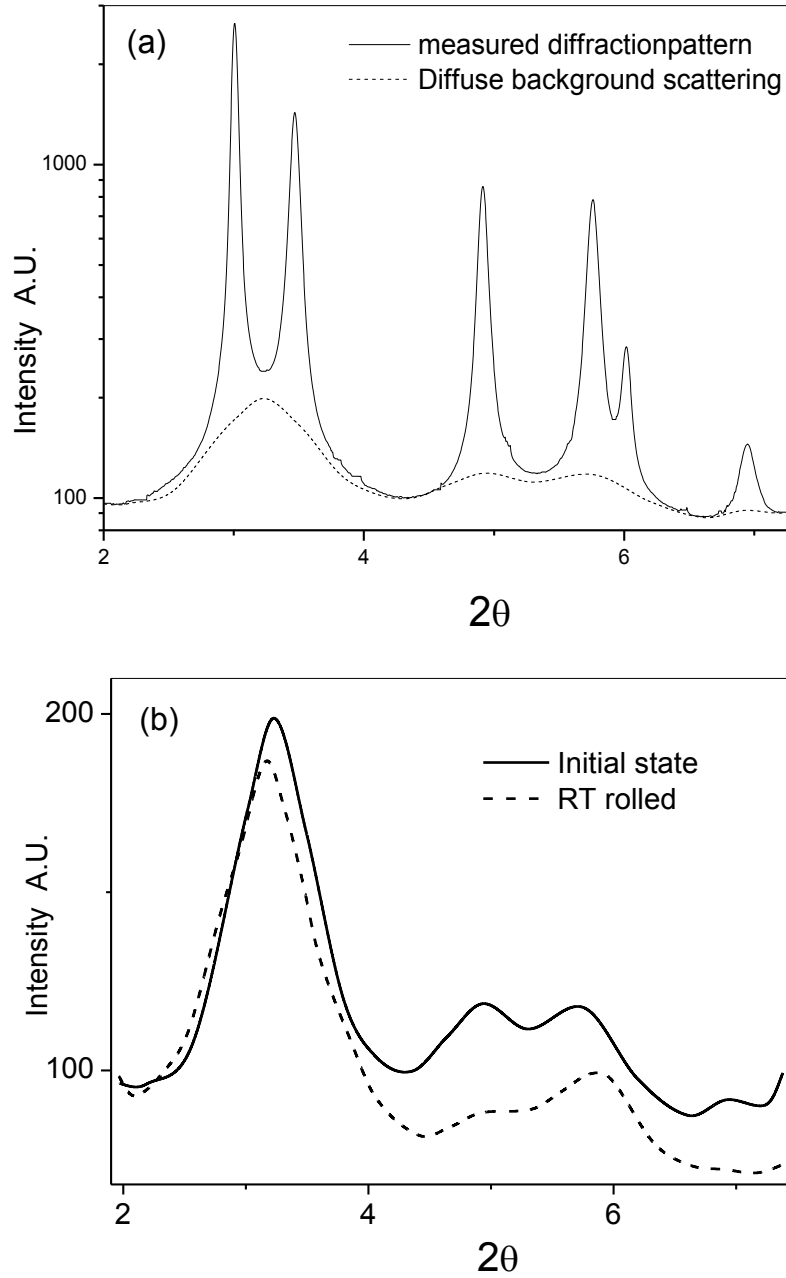


Figure 3-10. (a) The measured diffraction pattern and diffuse-background shown on a log-intensity scale, and (b) The diffuse-scattering background for the as-deposited (solid line) and RT-rolled (dash line) nc Ni-18Fe alloys, respectively.

3.3.3 Inequilibrium State of the As-deposited nc Ni-18Fe Alloy

The elastic-stored energy of dislocations per unit volume can be obtained from the dislocation density, ρ , and the effective outer cut-off radius, R_e , [80]:

$$E_{\text{Sto}}(\rho) = AGb^2\rho \ln \frac{R_e}{r_o} \quad (3-12)$$

where $A = \frac{1}{4\pi}$ for screw and $\frac{1}{4\pi(1-\nu)}$ for edge dislocations, respectively. Assuming a mixed edge and screw dislocation character, taking the Poisson's ratio, $\nu = 0.31$, the shear modulus, $G=76$ GPa, approximating R_e with the average dislocation distance, and putting the inner cut-off radius, r_0 , equal to the Burgers vector, b , the elastic stored energies for the as-deposited, RT-rolled, and LNT-rolled Ni-Fe alloys are calculated and given in Table 3-3.

Table 3-3. The dislocation-stored energy [$E_{\text{stor}}(\rho)$], total heat release (E_{Tot}), the energy corresponding to the formation and ordering of the Ni_3Fe precipitates (E_{OD}) in the first heating, and grain-boundary-related energy (E_{gb}) for the as-deposited, RT-rolled, and LNT-rolled specimens.

Specimen	$E_{\text{stor}}(\rho)$ [MPa]	E_{Tot} [MPa]	E_p [MPa]	E_{gb} [MPa]
As-Deposited	40 (± 5)	328 (± 30)	121 (± 20)	167 (± 25)
RT-Rolled	26 (± 4)	164 (± 20)	65 (± 15)	73 (± 15)
LNT-Rolled	22 (± 4)	207 (± 20)	60 (± 15)	125 (± 20)
Ni [45] (8ECAP+5HPT)	4.3 (± 1)	—	—	—

The maximum dislocation density that can be pumped in a similar specimen, Ni, which is deformed by 8 ECAP and subsequent 5 HPT turns, and its corresponding elastic stored energy are also given in the table for comparison. In this latter specimen, the dislocation density (ρ) was also determined by the X-ray line-profile analysis using the same eCMWP code as employed here.

The elastic-stored energy in the as-deposited Ni-Fe specimen was about one order of magnitude higher than that in the strongly-deformed Ni. To further investigate this phenomenon, the stored energies were measured by heating the Ni-Fe specimens in the calorimeter, as mentioned in Section 3.2.3. The broad exothermic process between 400 K and 750 K consists of a lower very broad peak and a superimposed sharp exothermic peak. The superimposed sharp peak is attributed to the precipitation of the Ni_3Fe phase. The endothermic process corresponds to the disordering of the Ni_3Fe precipitates. A similar two-step heat release was observed in ball-milled nc Fe powders [81] and HPT-deformed Cu-Zr-Ti alloys [82-83]. In the first exothermic process, i.e., the temperature between 400 K and 500 K, the grain size remains essentially constant, and a structure relaxation takes place in the grain interior by the annihilation of dislocations and point defects or point-defect clusters. In the second exothermic reaction, the grains grow and simultaneously Ni_3Fe precipitates are being formed.

Based on the above considerations, the total heat release, E_{Tot} , comprises the energies corresponding to (i) dislocations, $E_{\text{sto}}(\rho)$, (ii) grain boundaries, E_{gb} , and (iii) the formation and ordering of the Ni_3Fe precipitates, E_{OD} . Note that the energy of twin boundaries is negligible due to the low stacking-fault energy in the present alloy.

$$E_{\text{Tot}} = E_{\text{Sto}}(\rho) + E_{\text{gb}} + E_{\text{OD}} \quad (3-13)$$

E_{OD} can be estimated as the disordering heat, E_{Disord} , measured from the heat absorption. $E_{\text{Sto}}(\rho)$ is obtained from Equation (3-12). The balance provides the energy related to the grain-boundary region. The energy values corresponding to the different defects are listed in Table 3-3.

The reduced grain-boundary-related energy after cold rolling is due to the grain growth, which ultimately results in a reduction of the fraction of atoms in the grain-boundary region. The reduced volume fraction of the grain-boundary region after cold rolling is consistent with the reduced diffuse-background scattering observed in the X-ray diffraction shown in Figure 3-10(b).

The as-deposited state of the alloy contains dislocations, twin boundaries, and grain boundaries, all in such a large abundance that the material is extremely far from equilibrium. In the mechanical sense, the material is in a "highly-excited state." The high purity and nonequilibrium structure are necessary conditions for mechanical grain growth. Cold rolling, either at RT or at LNT, reduces all different types of the defects-stored energies. In this context, rolling is a "mechanical perturbation," which brings the state of the material somewhat closer to equilibrium.

3.3.4 The Model of Dislocation Annihilation during Cold Rolling

Plastic deformation of crystalline materials is mainly carried by the generation, motion, interaction, storage, and annihilation of dislocations. The extremely high dislocation density within the small grain of the nc materials make the dislocation

annihilation possible during the deformation. It is assumed that when dislocations come close enough to each other, they may annihilate. In the as-deposited state, the materials contained an initial dislocation density, ρ_{init} . During the rolling deformation, part of these dislocations and part of dislocations probably emitted from the grain-boundary regions, denoted as ρ_{flown} , are “flowing” through the grains to provide the dislocations necessary to carry the plastic deformation. These flowing dislocations annihilate either in the grain-boundary regions or within the grains, especially when passing within the annihilation distance of opposite dislocations. The annihilated dislocation density is denoted as $\rho_{annihil}$. Note that neither ρ_{flown} nor $\rho_{annihil}$ appears explicitly as a real density in the material. These values show only the amount of dislocations that passed a unit area during the entire deformation procedure. Then the balance equation shows the remnant dislocation density after deformation in the specimen, which is measured by the X-ray, is:

$$\rho = \rho_{init} + \rho_{flown} - \rho_{annihil} \quad (3-14)$$

The value of ρ_{flown} is given by the Orowan equation:

$$\gamma = \rho_{flown} b d \quad (3-15)$$

where γ and b are the plastic strain and the Burgers vector, respectively. Note that d is the mean free path of dislocations, which can be taken as the area-average mean crystallite size, $\langle x \rangle_{area}$, measured by the X-ray method. The value of γ can also be obtained from the annihilation process where two dislocations will annihilate within the annihilation distance. Denoting the annihilation distance of opposite dislocations within a band of y thickness, the average distance between dislocations parallel to the shear direction is $1/(\rho y)$ (See Figure 3-11). The shaded region is the band with a thickness of y

perpendicular to the shear direction, where two dislocations annihilate when passing. The zebra region between two dislocations is the area containing one dislocation.

Again,

$$\gamma = \frac{\rho_{annihil} b}{\rho y} \quad (3-16)$$

Insert Equations (3-15) and (3-16) into (3-14),

$$\rho - \rho_{init} = \Delta\rho = \frac{\gamma}{b} \left(\frac{1}{d} - \rho y \right) \quad (3-17)$$

where $\Delta\rho$, d , and γ are quantities measured by the X-ray method and given by the deformation procedure, respectively. Then the dislocation-annihilation distance, y , is determined as

$$y = \frac{1}{\rho d} - \frac{\Delta\rho b}{\gamma\rho} \quad (3-18)$$

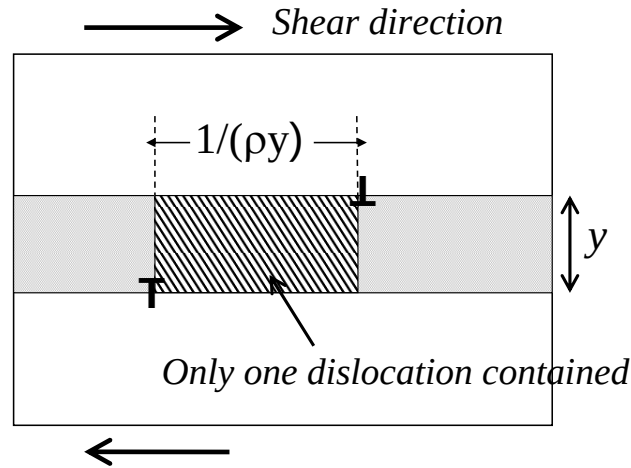


Figure 3-11. Schematic figure for explaining the notations used in the dislocation annihilation model.

In this model, the “flowing” dislocations are assumed to be initiated from the grain boundaries, travel across the grains, and be absorbed in the opposite grain boundaries without the multiplication and annihilation within grains. The mean free path is taken as the area-average crystallite size, $\langle x \rangle_{\text{area}}$, since the crystallite sizes of 14 nm, 31 nm, and 26 nm for the as-deposited, RT-rolled, and LNT-rolled specimens, respectively, are orders of magnitude smaller than the usual dislocation-mean-free paths, 1 μm , for the fatigued Cu single crystals [84]. It is physically unlikely to have a shorter mean free path than the area-average crystallite size in the current nc specimen. Table 3-4 lists the dislocation-annihilation distances, the flowing and annihilation dislocation densities in the RT and LNT-rolling processes. Here, $\gamma = \sqrt{3}|\varepsilon|$ for the fcc structure, and ε is the true strain in the thickness reduction.

Table 3-4. The X-ray-measured average dislocation density (ρ), shear strain (γ), the calculated annihilation distance (y), spontaneously-flowing dislocation density (ρ_{flown}), annihilating dislocation density (ρ_{annihil}) for the as-deposited, RT-rolled, and LNT-rolled nc Ni-18Fe alloys, respectively.

Specimen	ρ [10^{16}m^{-2}]	γ	y [nm]	ρ_{flown} [10^{16}m^{-2}]	ρ_{annihil} [10^{16}m^{-2}]
As-Deposited	3.7 (± 0.5)	-	-	-	-
RT-Rolled	2.2 (± 0.4)	1.04	2 (± 0.5)	13.2 (± 1)	14.7 (± 1)
LNT-Rolled	1.8 (± 0.3)	0.62	3 (± 0.5)	9.4 (± 1)	11.3 (± 1)

Considering that pinning may play an important role in our solid-solution material and the overwhelming weight of edge dislocations in the averaged annihilation distance, the γ values, 2 and 3 nm for RT and LNT rolling, respectively, are in good agreement with the values reported for fatigued copper specimens in [85] and the numerical calculations in [86], where the annihilation distance for edge dislocations is 1.6 nm. The remnant dislocation density is smaller than the initial one. However, both the initial and the remnant densities are considerably smaller than the flowing and annihilation dislocation densities during the deformation, since the deformation reduction, i.e., 45 % and 30 % at RT and LNT, is large. There is a huge flux of dislocations during the deformation, but only a small fraction remains stored in the specimens after the deformation. The γ , ρ_{flown} , and ρ_{annihil} values corresponding to the RT and LNT deformation are also in correlation with the effect of temperature on dislocation dynamics. At RT, both ρ_{flown} and ρ_{annihil} are larger than those at LNT, whereas the annihilation distance at RT is shorter than that at LNT. This result is in good correlation with the observation that the specimen could not be deformed to the same extent at LNT as at RT. This model together with the experimental facts indicate that extremely large dislocation currents are flowing through the grains of the nc materials during the plastic deformation in a similar manner to that in the coarse-grained materials. In this model, deformation is assumed to be carried solely by dislocations. No allowance for grain-boundary sliding has been made. However, this deformation mode cannot be excluded completely. Nevertheless, the low temperatures and large deformation rates, applied in the present case, substantiate that the major mode of deformation is the dislocation mechanism.

The reduction in the twin density after the deformation is contrary to all previous observations in coarse-grained materials and has not been reported so far in other nc materials. In nc materials, plastic deformation can take place by deformation twins formed by partial dislocations [87]. If some fractions of the dislocations in our specimens are such “partials” and “partials” emitted from grain boundaries, it is easily possible that a fraction of the huge dislocation flux flowing through the specimen during the deformation is a flux of partials. Then the flux of partials may leave behind the twins, which are observed as “remnant” twins just like the “remnant” dislocations mentioned above. The decreased twin density after the deformation may be explained by a similar mechanism like the reduced dislocation density.

3.3.5 Estimation of Partial Dislocation Separation

Slip occurs on the $\{111\}$ plane in the $\langle 110 \rangle$ direction for the fcc lattice. The Burgers vector is $(a_0/2)[110]$. The perfect dislocation can dissociate into two partial dislocations with a stacking fault (SF) since it is more energetically favorable for the strain energy [88],

$$\frac{a_0}{2} [10 \bar{1}] \rightarrow \frac{a_0}{6} [2 \bar{1} \bar{1}] + \frac{a_0}{6} [11 \bar{2}] \quad (3-19)$$

Then the partial dislocation separation, r , is

$$r = Kb^2 / 2\pi\gamma_{SF} \quad (3-20)$$

where b is the Burgers vector of two partial dislocations binding the stacking fault (SF), $b=(a_0/6)[2-1-1]$ or $(a_0/6)[11-2]$, γ_{SF} is the SF energy, the constant, K , depends on the

elastic modulus of the material and the partial-dislocation type. $K = G$ (shear modulus) for pure screw partials and $G/(1-\nu)$ for pure edge partials, here ν is the Poisson's ratio. Ni has a high SF energy, $\gamma_{\text{SF}} = 120 \sim 150 \text{ mJ/m}^2$ [89-90], whereas the Ni-18Fe has a smaller SF energy, supposing around 80 mJ/m^2 . $a_0 = 3.524 \text{ \AA}$, $b = 1.439 \text{ \AA}$, $G = 76 \text{ GPa}$, and $\nu = 0.31$. Thus, the separation of partial dislocations is estimated as 3 nm and 5 nm for pure screw and edge partial dislocations, respectively. The partial-dislocation separation is smaller than the average initial grain size of 14 nm. Thus, from the deformation map in [37], it is probable that complete, extended dislocations nucleated from the GBs propagate across the grains. That's also consistent with our x-ray investigations that a symmetric-peak shape is observed in all diffraction patterns. The stacking faults will cause asymmetric-peak shape. However, for the extremely small grain size, partial dislocations still exist in the materials during the deformation, just not playing a dominant role.

3.4 Conclusions

Synchrotron high-energy X-ray has been employed for the microstructure study of the bulk nc Ni-18Fe alloy before and after cold rolling at RT and LNT. The microstructures are characterized by the line-profile analyses. Visual, qualitative, and quantitative X-ray line-profile analyses have been systematically conducted to obtain the microstructure information, such as the grain size (average grain size and size distribution), dislocation structure (dislocation density, and type), planar faults (stacking-fault or twin density). These microstructure changes are consistent with the experimental

observations from the nanoindentation, DSC, and TEM. Based on the framework above, the following conclusions are reached:

- a) The stress softening after cold rolling are verified in the current nc Ni-18Fe alloy.
- b) Two independent, though indirect, evidences support the presence of an amorphous fraction in the form of grain-boundary regions. One is the diffuse-background scattering in the diffraction patterns, and the other is the GB-related energy in the DSC results: the diminished diffuse-background scattering and the decreased GB-related energy with the increase of the grain size during cold rolling.
- c) The as-deposited state contains: (i) dislocations, (ii) twin boundaries, and (iii) an amorphous fraction in the form of grain-boundary regions. All defects are in large abundance. The as-deposited material is in a mechanically-high excited far-from-equilibrium state. In this study, rolling is a "mechanical perturbation," which brings the state of the material somewhat closer to the equilibrium.
- d) Cold rolling of the nc Ni-18Fe alloy, at either RT or LNT, concomitantly reduces the dislocation and twin densities, and increases the grain size. These quantitative results from eCMWP are consistent with the qualitative results from the modified WH plots. Grain growth is confirmed by TEM observations. This simultaneously decreased dislocation and twin densities have never been observed before in coarse-grained and other nc metals and alloys. However, the reduction of these properties and the increase of the grain size are moderate.
- e) A model based on the dislocation mean-free path and annihilation distance is suggested for the explanation of the dislocation change. The calculation of the

partial-dislocation separation further suggests that most likely, complete, extended dislocation activities are dominant in the cold rolling.

- f) The deformation process may be changed by controlling the Ni_3Fe precipitates in the nc Ni-18Fe alloy using heating.

CHAPTER 4: GRAIN GROWTH IN THE NANOCRYSTALLINE NI-FE ALLOY DURING COLD ROLLING

Recent studies (as shown in chapter 1) on the microstructure of nc metals and alloys under various deformations show that grain growth occurs in these types of materials when they are severely deformed. In nc materials, unlike in coarse-grained materials, the dislocation mechanisms are accompanied by various grain-boundary (GB) - mediated processes, e.g., GB sliding/migration, grain rotation, and GB diffusion. GBs are actively involved in the deformation when the grain size becomes below about one micrometer. The simultaneous appearance of dislocation and GB processes needs special care in explaining the grain growth of nc materials during deformations. Furthermore, most growth was observed using TEM. The extremely-thin TEM foil with around one grain thickness for the nc sample will cause the surface microstructure relaxation, misleading the correct microstructure characterization for the bulk material. Moreover, TEM provides the two-dimensional plane information only. Special attention is necessarily needed for deciding a three-dimensional problem - whether the grain growth is genuine or only a change of the grain shape.

In this study, the orientation dependency of the deformation-induced grain growth was investigated in an electrodeposited nc Ni-18Fe alloy. The grain-size distributions in three dimensions are studied through the XLPA in a similar manner as mentioned in the last chapter. Changes of the average volume of grains during the deformations are determined. The grain-size values provided by the method of XLPA are

discussed in terms of the texture evolutions, and possible mechanisms are suggested for the observed grain growth.

4.1 Experimental

The bulk nc Ni-18Fe alloy sheets fabricated by electrochemical deposition were provided by Integran Technology Inc. The as-deposited alloy is a single-phase *fcc* material with an initial $\langle 100 \rangle$ fiber texture along the electro-deposited direction (ED) [91]. The specimens were characterized earlier by TEM in Chapter 2. The material consists of columnar grains, where the columns can be described as elongated ellipsoidal bodies with three different average main diameters: d_1 , d_2 , and d_3 . The longitudinal direction (d_3) of columnar grains is along the ED. In the initial state, the elongated columns have equiaxed cross-sections in the deposition plane, i.e., $d_1 = d_2$, and $d_3 > d_1, d_2$.

The nc Ni-18Fe alloy was machined from the alloy sheets and cold rolled. Two cases are studied: (I) ED//TD (transverse direction during rolling), Figure 4-1(a); and (II) ED//ND (normal direction during rolling), Figure 4-1(b). In both cases, the flat specimens were rolled through several passes at room temperature (RT) to reach the reductions of 10%, 20%, and 30% in thickness, respectively. (RD: rolling direction)

Synchrotron-diffraction experiments were performed at the beamline, 11 ID-C, Advanced Photon Source, Argonne National Laboratory. Figure 4-1 also shows the schematic of synchrotron X-ray measurements for obtaining the three-dimensional grain size in the two cases. First, all plate specimens, undeformed and deformed, were X-rayed normal to the TD-RD surface in transmission with the beam energy of 115 keV. The diffraction patterns were recorded by a two-dimensional MAR-345 detector.

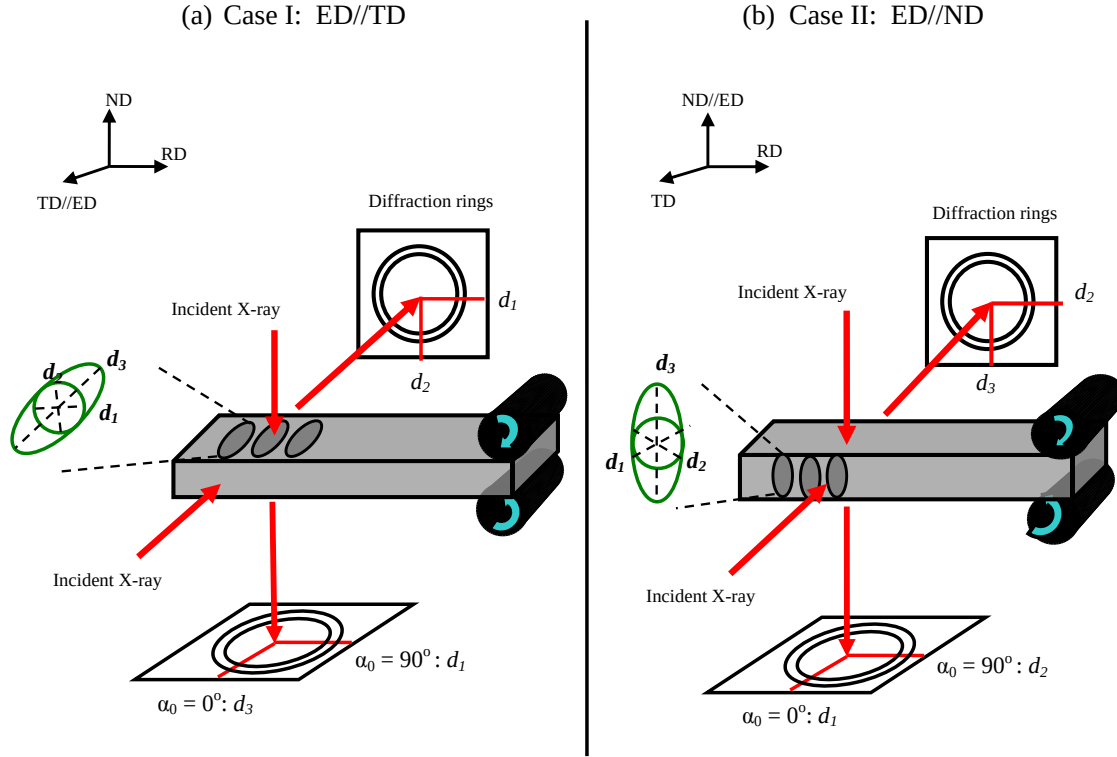


Figure 4-1. Schematic of synchrotron X-ray measurements for three-dimensional average grain size evaluations in two cases of rolling deformation, (a) Case I: ED//TD and (b) Case II: ED//ND.

X-ray line profiles used for studying two-dimensional grain sizes were obtained by integrating along the Debye-Scherrer rings in different azimuthally angular ranges, $\Delta\alpha$. Integration is carried out within $\alpha = \alpha_0 \pm 10^\circ$ around either the vertical direction ($\alpha_0 = 0^\circ$) or the horizontal direction ($\alpha_0 = 90^\circ$), respectively. Since the energy of X-ray is relatively high, the diffraction angles are small. Even with the long distance of about 1.2 m between the specimen and detector, the first eight reflections have been recorded within $2\theta = \pm 8^\circ$. This means that all recorded Bragg reflections correspond to lattice planes “almost”

parallel to the incoming beam. The diffraction conditions are somewhat similar to TEM geometries. Therefore, the size values provided for the vertical and horizontal directions in diffraction rings correspond to those for the two perpendicular directions in the specimen, which is perpendicular to the beam. Second, by rotating the specimens by 90° and measuring through the ND-RD surface of the specimen, the third average size is measured. It is noted here that the widths along TD of the specimens were kept narrow enough so that even in this geometry, the transmission X-ray measurements could be carried out. In addition, texture measurements were performed for undeformed and deformed samples with 30% reductions for both cases. The specimens were rotated every 10 degrees around the axis of the rolling direction (RD) with 10 steps, and the diffraction patterns for each step were collected for the texture analysis.

4.2 The Methodology of Texture Evaluation

In the synchrotron X-ray texture analysis, each Debye-Sherrer ring was caked and integrated over 72 continuous angular sections from 0 to 2π to obtain 72 X-ray line profiles. Then, these line profiles were fitted by the General Structure Analysis System (GSAS) software created by the Los Alamos National Laboratory [92] to obtain the intensity information of (111), (200), and (220) peaks for the 72 in-plane directions. From the rotation angles, we can deduce all the positions that correspond to their intensities in the (111), (200), and (220) pole figures. Then three complete pole figures of (111), (200), and (220) were obtained for the nc Ni-18Fe alloy using the (111), (200), and (220) reflections.

4.3 Results

4.3.1 XLPA results

The X-ray line profiles obtained by the integration were evaluated by the extended CMWP procedure as mentioned in the last chapter to obtain the quantitative grain-size information, such as the area-average grain size and size-distribution functions. Assuming that the grains are ellipsoids with the three dimensions, d_1 , d_2 , and d_3 , then the average-grain volume, V , can be calculated as $V = (4\pi/3)(d_1/2)(d_2/2)(d_3/2)$. The three average sizes, d_1 , d_2 , and d_3 and the average grain volumes provided by the eCMWP fittings are shown in Figure 4-2.

In Case I, there is an obvious increase in the cross-sectional region (d_1 and d_2) with little change in the longitudinal dimension (d_3). The volume increase is significant (a 300% increase compared to the initial volume). However, in Case II, an increase along the cross section with a decrease in the longitudinal dimension is observed. The overall effect is a 100% increase in the average grain volume compared to the initial state. In both cases, cold-rolling caused the grain growth. However, the grain growth in Case II is not as significant as in Case I. Note that the grain shape in the cross section always remains circular during the rolling deformation in both cases, indicating that the grain growth along the cross section is isotropic during the rolling process. This phenomenon is different from the observation of Fan et al. [17], where the anisotropic grain growth is observed in a similar material during the compressive plastic deformation. This difference may be due to the different stress conditions in the two kinds of deformations: rolling and compression.

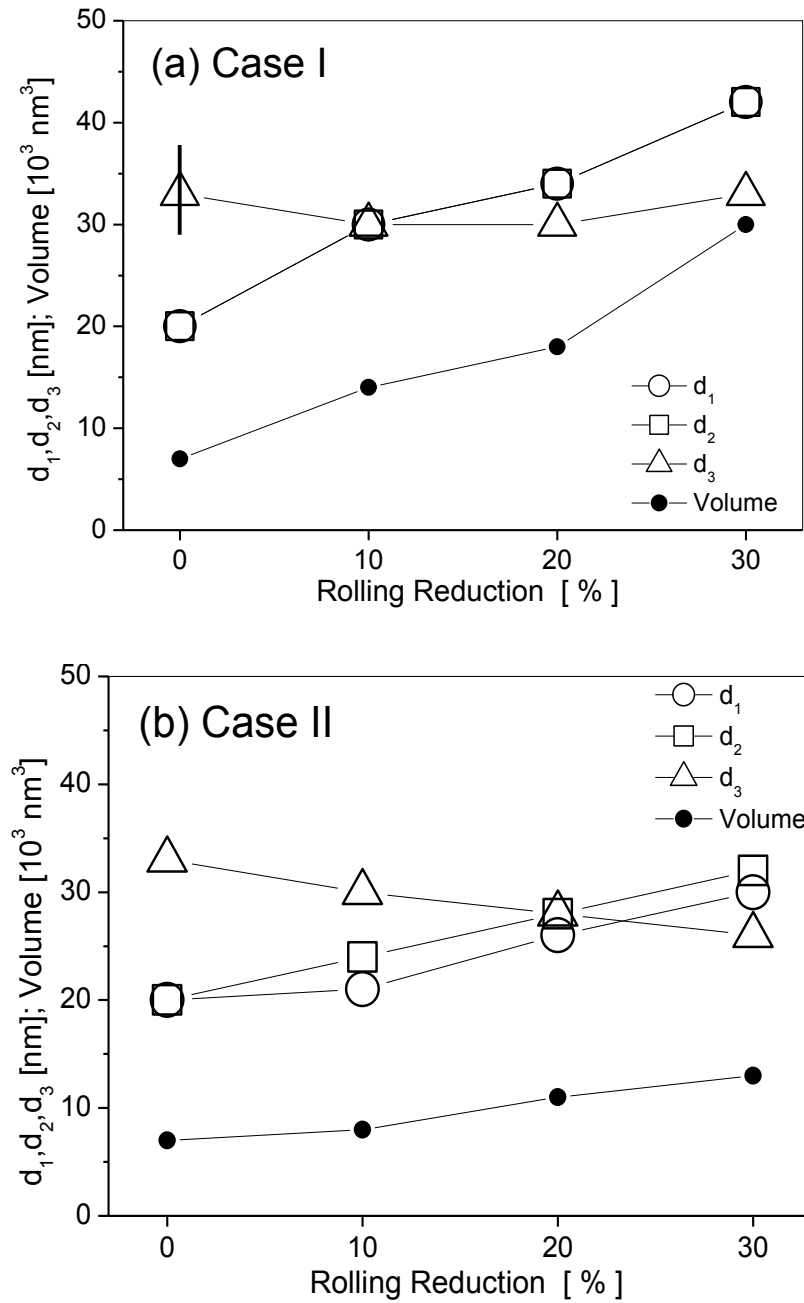


Figure 4-2. The eCMWP analysis results of three-dimensional area-average grain sizes, d_1 , d_2 , d_3 , and the average grain volumes for the rolling (a) Case I and (b) Case II.

The eCMWP procedure also provides the median and the logarithmic variance, m and σ , of the log-normal size distribution function. From these two values, the size distribution functions can be given and are shown in Figure 4-3 for both cases. The grain-size-distribution functions are always shifted to larger values, which indicate that grains grow at the expense of smaller grains for both cases. Note that in Figure 4-3(b), the relative right shift of d_3 size-distribution function of the deformed sample (with the 30 % reduction) to that of the undeformed sample does not conflict with the smaller average-grain size (compared with the initial grain size) presented in Figure 4-2(b), since the average-grain size is the area-weight-mean crystalline size. The size distribution function shown here is a density function. The average grain size is always the most stable size values in the evaluation of the X-ray line broadening [91].

4.3.2 Texture evolutions

Figure 4-4 shows the pole figures of (111), (200), and (220) for the undeformed sample in Case I sample-coordinate system, Figure 4-4 (a), and in Case II sample-coordinate system, Figure 4-4 (c). Note that (c) is the same pole figure as (a), but with a simple rotation of 90° for a better comparison between the undeformed and their corresponding deformed samples in their own coordinate systems, respectively; Figure 4-4 (b) and (d) are the pole figures for the cold-rolled samples in Case I and Case II with a 30% reduction, respectively.

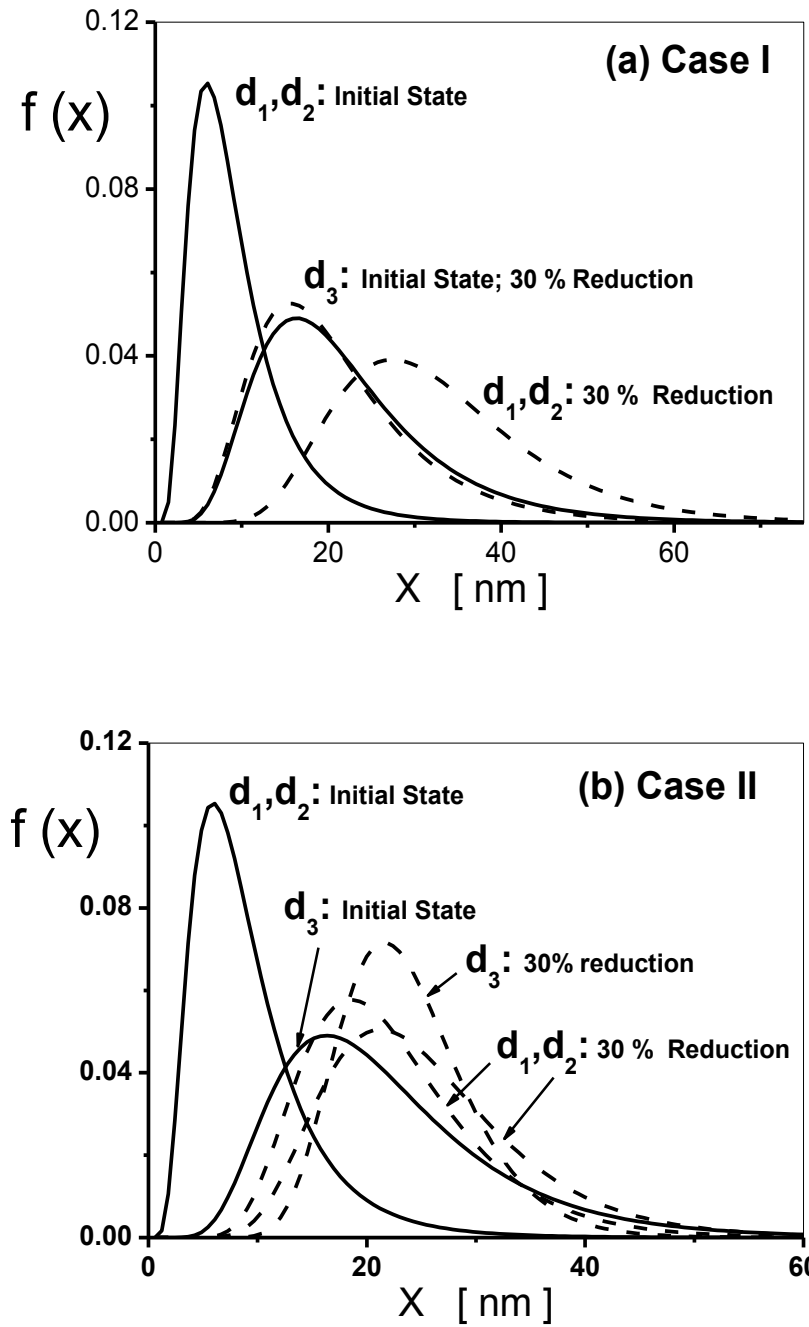


Figure 4-3. Average grain-size distribution functions before (solid line) and after 30% reductions (dash line) for the rolling (a) Case I and (b) Case II.

First, from Figures 4-4(a) and (c), the initial electrodeposition texture is clearly observed with $\{100\}$ poles parallel to TD (Case I) and to ND (Case II). After Case-I rolling, the number of $\{100\}$ poles along TD increases dramatically with $\{110\}$ poles simultaneously emerged towards ND. This indicates that the $\langle 110 \rangle$ -oriented population in the initial random texture components (e.g., $\langle 001 \rangle$, $\langle 010 \rangle$, $\langle 110 \rangle$, which are perpendicular to the fiber axis, $\langle 100 \rangle$) consumes other texture components. This new texture has already been confirmed as $\{110\}\langle 110 \rangle$ [91]. This texture is different from all *fcc* rolling textures in the conventional metals and alloys [93]: $\{100\}\langle 001 \rangle$ (“cube” texture), $\{112\}\langle 111 \rangle$ (“copper” texture), $\{123\}\langle 634 \rangle$ (“S” texture), $\{110\}\langle 112 \rangle$ (“brass” texture), $\{011\}\langle 100 \rangle$ (“Goss” texture), and $\{4,4,11\}\langle 11,11,8 \rangle$ (“Dillamore” texture). The newly-developed texture component of $\{110\}\langle 110 \rangle$ is also different from the mixed texture components recently found in a heavily-rolled nc Ni [94].

This novel texture points to new deformation mechanisms beyond merely dislocation slips. Both GB sliding (accommodated by the GB diffusion) and dislocation glide in the preferred active slip systems can induce grain rotation. Grain rotation due to GB sliding will not introduce a texture [95], whereas grain rotation due to a dislocation mechanism will introduce a texture in the sample. The newly-developed strong texture indicates the occurrence of grain rotations together with dislocation activities during the cold-rolling processes.

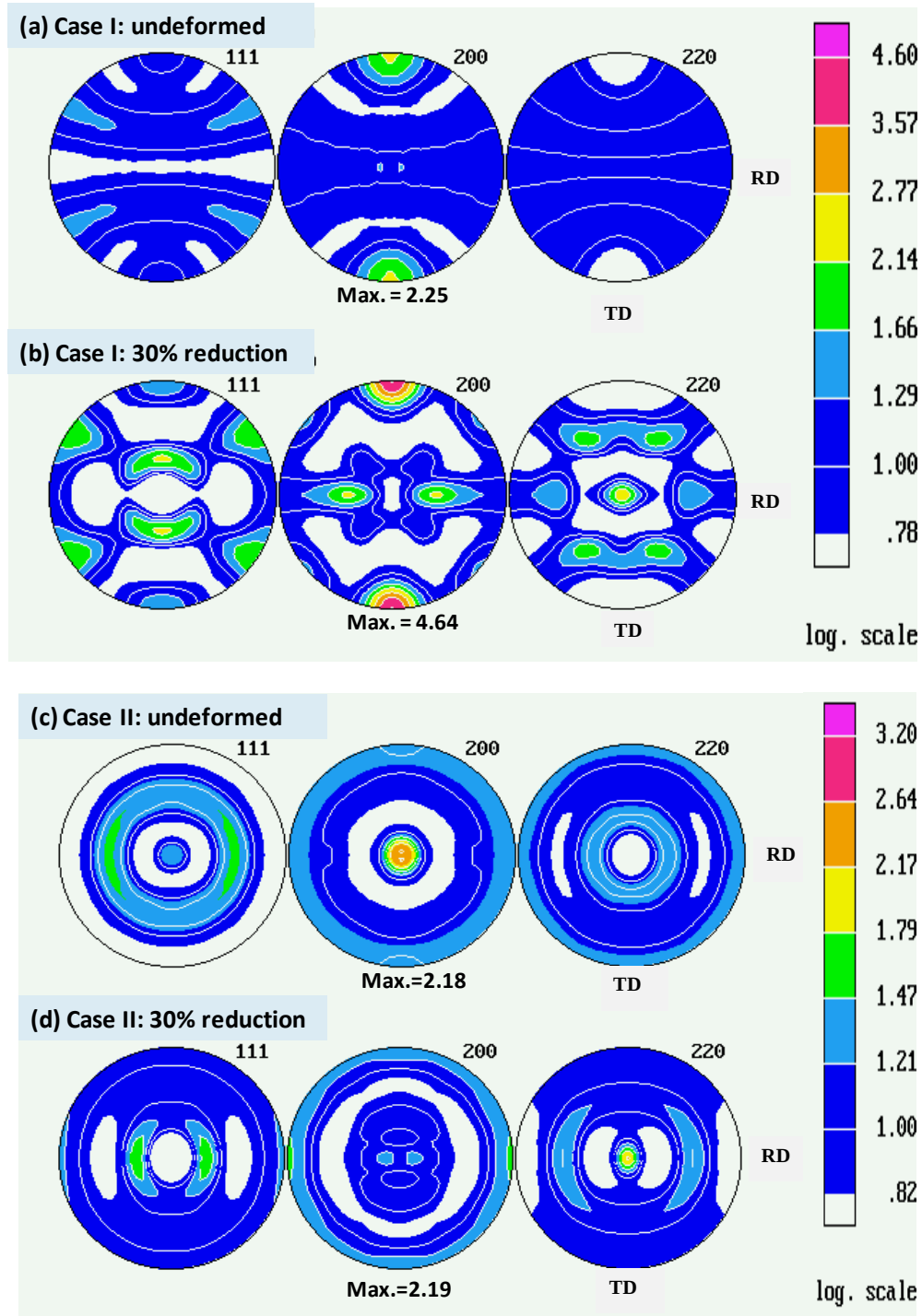


Figure 4-4. (111) (200) (220) pole figures of (a) Case I: undeformed, (b) Case I: 30% reduction, (c) Case II: undeformed (note that there is the same pole figure as (a), but with a simple rotation of 90° for better comparison with (d)), and (d) Case II: 30% reduction.

For Case-II rolling, the $\{100\}$ poles originally orientated along ND weaken greatly with the $\{110\}$ poles emerging in the same direction. The initial $\langle 100 \rangle$ fiber texture changes to $\{110\}\langle 100 \rangle$ (Goss texture), which is a typical rolling texture in coarse-grained *fcc* metals and alloys. A conventional route of texture development established in coarse-grained *fcc* polycrystals is the grain rotation due to dislocations glide in the preferred active slip systems.

Similar XLPAs analyses and texture analyses are also applied for samples dipped in liquid nitrogen and rolled through several passes to reach 10%, 20%, and 30% reductions, respectively. The results demonstrate no significant difference due to the temperature effect.

4.4 Conclusions

Deformation-induced grain growth is observed in the cold rolling. However, the extents of grain growth are different, which are due to the different deformation mechanisms.

In Case I, GB activities, are enhanced since the shear stress is perpendicular to the initial longitudinal axis of columnar grains during the rolling, i.e., grain rotation can be easily initiated by the shear stress. Most grains rotate around the initial fiber axis, $\langle 100 \rangle$, until they have the same orientation and coalesce to become one. It is most likely that this grain growth is caused by the grain-rotation-induced grain coalescence.

As for Case II, most columnar grains in the initial material are along ND, which is not a preferred orientation for grain rotation by a shear stress during the rolling

deformation. The stress-induced grain growth is suggested by the curvature-driven GB migration since larger grains grow on the expense of smaller grains. This curvature-driven GB migration is observed for both cases. When the two mechanisms are closely coupled, the grain growth will be considerably larger. The significant grain growth in Case I may indicate that both growth mechanisms are active and closely coupled during the deformation.

In summary, the preexisting texture influences on the deformation of the nc Ni-18Fe alloy. The nc Ni-18Fe alloy deforms differently in the two types of rolling. In Case I, where ED//TD, the columnar grains preferably align to their longitudinal direction, ED, and rotate around ED. Grains grow significantly through the grain-rotation induced grain coalescence and curvature-driven GB migration. In Case II, where ED//ND, curvature-driven GB migration is suggested for the moderate grain growth. The grain growth in the Case I is much larger than that in Case II since both deformation mechanisms (curvature-driven GB migration and grain-rotation-induced grain coalescence) operate and may be closely coupled in Case I.

CHAPTER 5: SUMMARY AND FUTURE WORK

Cold rolling conventional metals and alloys, like other plastic deformation, leads to hardening due to the strong dislocation interactions by the dislocation accumulation and propagation on the well-defined slip systems. However, cold rolling, at both RT and LNT, softens the current nc Ni-18Fe alloy instead of hardening. This phenomenon demonstrates the unusual mechanical properties of the present system.

The microstructure evolution determines the deformation mechanisms, which, in turn, governs the exhibited mechanical properties. In order to accurately interpret the mechanical properties of bulk nc metals and alloys, synchrotron high-energy X-ray is adopted in the diffraction experiments for the deformation study. High-energy X-ray with energy of around 115 KeV can penetrate through the bulk samples without any damage on the samples. Synchrotron with a good angular resolution and high flux make the diffraction patterns having good statistics. XLPA is employed in the evaluation study of the diffraction patterns since it can provide the quantitative microstructure information, such as the dislocation density, planar fault density, average grain size and size distribution, dislocation arrangement, etc. Texture analysis is also applied in the current study to complement the XLPA results. The combination of texture and XLPA help better understanding these processes. Both GB and dislocation activities are active in the current nc system with grain size of around 20 nm. Dislocation-induced grain rotation or GB sliding/diffusion/migration-induced grain rotation are operative in the current system.

The electrodeposited nc Ni-18Fe alloy is a kind of unusual nc materials due to the special deposition technique. In the macroscopic view [52], the exhibited plastic

strain is strongly dependent on the grain orientation and grain geometry. A significant increase in the ductility can be obtained with the loading axis along the material growth direction. The columnar grains along the $\langle 100 \rangle$ axis (material growth direction) make the dislocation slip systems equally operated in the current fcc structured nc materials. Thus both GB and dislocation activities are enhanced when the loading axis is parallel to the growth direction since the high stress component is parallel to the GB plane.

In the microscopic view, the as-deposited nc Ni-18Fe alloy contains a huge amount of dislocations, twins, and a large fraction of the amorphous region in the form of grain boundaries. The as-deposited nc materials is in a far-from-equilibrium state. Cold rolling of the nc Ni-18Fe alloy, at either RT or LNT, concomitantly reduces the dislocation and twin densities, and increases the grain size. These microstructure changes will relax the as-deposited materials, releasing the mechanical energy initially stored in the materials. In this study, rolling is a "mechanical perturbation," which brings the state of the material somewhat closer to the equilibrium.

Genuine grain growth are confirmed through three-dimensional grain size characterization. The increased average grain volumes after the deformation indicate the genuine grain growth. Orientation-dependent grain growth is observed in the current nc Ni-18Fe alloy. This orientation-dependent grain growth is related to the stress distribution on the nc materials. The shear stress in the Case-I rolling leads to the grain-rotation-induced grain coalescence. However, the shear stress in the Case-II rolling is not in a preferred direction for the grain rotation as that in Case-I rolling. In the Case-II rolling, the shear stress leads to the dislocations slipping in the preferred systems, causing grain rotations. The curvature-driven GB migration is observed in both cases. The extent of the

grain growth is related to the coupling effect between the grain-rotation-induced grain coalescence and the curvature-driven GB migration [96]. Strong coupling in Case-I rolling causes larger grain growth than that in Case-II rolling.

GB sliding/migration/diffusion and dislocations slip in the preferred slip system can cause grain rotation. However, pure GB-mediated processes will not result in the new texture. The texture evolution observed in the current nc Ni-18Fe alloy indicates the combination of dislocation activities and GB activities.

For most metals and alloys, grain-size reduction occurs during the cold rolling. Dislocation pile-ups at the grain boundaries contribute to the stress hardening. With further grain refinement, especially when the dislocation distance or partial dislocation separation are comparable to the grain size, dislocation process becomes less effective and GB-mediated processes take over. In the absence of grain growth, Hall-Petch behavior transitions to inverse Hall-Petch behavior at sufficiently small grain sizes [3, 37], leading to a “strongest” grain size. However, the current nc Ni-18Fe alloy exhibits strong GB effects (as indicated by the grain growth and newly-developed texture presented in Chapter 4) even though the grain size is larger than the partial dislocation separation.

The deformation in nc Ni-18Fe alloy shows a combined perfect dislocation slip and GB-mediated deformation, which corresponds to the boundary region between region I and region III in the deformation map proposed in Figure 1-2, shown in Chapter 1. The “strongest grain size” has been predicted to arise in this crossover region. However, the current material did not show the “strongest” behavior. This does not conflict with the theoretical prediction since the initial state of the material in the prediction and in the current experiment are different: no or a few dislocations for the initial material in the

theoretical work compared with the extremely high dislocation density in the as-deposited nc Ni-18Fe alloy in the present work. Our nc Ni-18Fe alloy still follows the Hall-Petch behavior: the materials soften as the grain size becomes larger. The unusual grain growth during cold rolling directly leads to both larger grains and lower dislocation densities, causing the softening behavior.

Based on the above information, the following could be followed as the future work in this alloy system:

1. The pair-distribution-function (PDF) study of the current nc Ni-Fe alloy through neutron scattering.

The difference in the DSC curves (shown in Chapter 3) of the undeformed and deformed specimens indicates that Ni and Fe atoms in the materials could be relocated during the plastic deformation. There may be atom segregation occurring, most likely around the grain boundaries. The PDF study through the neutron-full scattering could be applied to diagnose this phenomenon. However, the software PDFfit, which is used for PDF data fitting, doesn't have a model for the ellipsoidal grains now. Investigators have to create their own model for data fitting.

2. The cross-over behavior in hardness for annealed nc Ni-Fe alloys.

In this study, the initial nc Ni-Fe alloy is an “abnormal” material exhibiting softening rather than hardening after cold rolling. Samples before cold rolling soften with increasing annealing time. Samples with short annealing times and then cold rolled will also soften, mimicking the effects of the mechanical relaxation as mentioned in Chapter 3.

However, well-annealed samples exhibit normal “hardening” behavior. A series of specimens with different microstructures can be prepared by annealing the nc Ni-Fe alloy through holding-time control. Hardness studies will be performed before and after cold-rolling experiments for all the specimens, to establish the cross-over behavior. This work, if successful, will establish not only this unusual crossover behavior, but will demonstrate regimes of dislocation densities and grain sizes where unusual mechanical processes may occur. Note the selection of temperature and hold time is critical for the achievement since the Ni_3Fe precipitates may occur.

3. In-situ deformation study in the current nc Ni-Fe alloy system.

In-situ deformation study through synchrotron HEXRD is highly recommended for the current nc system. The dislocation and annihilation model constructed in Chapter 3 could be confirmed by these in-situ studies. It is not necessary to be in-situ rolling, in-situ compressive test with the loading axis perpendicular to the material growth direction could reach similar effects.

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VITA

Li Li was born in 1980, China, the daughter of Suzhi Gao and Hongming Li. After completing her undergraduate study in the Applied Physics at Jilin University - China, she went on to Fudan University – China to further her study and received her Master degree in Optics in 2005. She entered the Graduate School at the University of Tennessee in the fall 2005. She has broad interests in science and technology. Her particular interest would be the structural materials and scattering techniques.