ABSTRACT

KOTAN, HASAN. Thermal Stabilization and Mechanical Properties of Nanocrystalline Fe-Ni-Zr Alloys. (Under the direction of Prof. Ronald O. Scattergood and Prof. Carl C. Koch).

Ultrafine grained and nanostructured materials are promising for structural applications because of the high strength compared to coarse grained counterparts. However, their widespread application is limited by an inherently high driving force for thermally induced grain growth, even at low temperatures. Accordingly, the understanding of and control over grain growth in nanoscale materials is of great technological and scientific importance as many physical properties (i.e. mechanical properties) are functions of the average grain size and the grain size distribution within the microstructure.

Here, we investigate the microstructural evolution and grain growth in Fe-Ni alloys with Zr addition and differentiate the stabilization mechanisms acting on grain boundaries. Fe-Ni alloys are chosen for stability investigations since they are important for understanding the behavior of many steels and other ferrous alloys. Zirconium is proven to be an effective grain size stabilizer in pure Fe and Fe-base systems.

In this study, nanocrystalline alloys were prepared by high energy ball milling. In situ and ex situ experiments were utilized to directly follow grain growth and microstructural evolution as a function of temperature and composition. The information obtained from these experiments enables the real time observation of microstructural evolution and phase transformation and provides a unique view of dynamic reactions as they occur. The knowledge of the thermal stability will exploit the potential high temperature applications.
and the consolidation conditions (i.e. temperature and pressure) to obtain high dense materials for advanced mechanical tests.

Our investigations reveal that the grain growth of Fe-Ni alloys is not affected by Ni content but strongly inhibited by the addition of 1 at% Zr up to about 700 ℃. The microstructural stability is lost due to the bcc-to-fcc transformation (occurring at 700℃) by the sudden appearance of abnormally grown fcc grains. However it was determined grain growth can be suppressed kinetically at higher temperatures for high Zr containing alloys by precipitation of intermetallic compounds. Eventually at high enough temperatures the retention of nanocrystallinity was lost, leaving behind fine micron grains filled with nanoscale intermetallic precipitates. Despite the loss of stability the in-situ formed precipitates were found to induce an Orowan hardening affect. The results from the mechanical tests show that Orowan particle strengthening can be as significant as Hall Petch hardening is at the smallest grain sizes.
Thermal Stabilization and Mechanical Properties of Nanocrystalline Fe-Ni-Zr Alloys

by
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DEDICATION

This work is dedicated to my family for the constant support and encouragement. I am thankful for everything they have done for me.
BIOGRAPHY

Hasan was born in Sakarya, Turkey to Osman and Meryem on September 1, 1983. He attended Sakarya University to major in Metallurgy and Materials Engineering. He graduated from Sakarya University with a B.S. in that discipline with the highest GPA in the spring of 2006 along with another Bachelor’s degree in Electrical and Electronics Engineering in the fall of 2007. Hasan attended nationwide exam and earned a scholarship from Turkish Government for graduate studies in the US. He came to US in 2007 to attend an English course in Charlotte, NC and took his master degree from University of Pittsburgh in the spring of 2010 in Materials Science and Engineering department. He continued his education by enrolling at North Carolina State University in the fall of 2010 in the Materials Science and Engineering doctorate program. Under the direction of Dr. Carl Koch and Dr. Ronald Scattergood he worked on stabilizing nanocrystalline Fe-Ni alloys and investigating their mechanical properties.
ACKNOWLEDGMENTS

This work would not have been possible without the assistance of a number of individuals and I am grateful to each one. First, I would like to thank Dr. Koch and Dr. Scattergood for their great supervision, guidance, knowledge, and support throughout this work.

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1. INTRODUCTION

1.1. Nanocrystalline Materials

Materials with nanocrystalline or ultra-fine grain sizes offer the intriguing properties such as high strength and toughness [1, 2]. Numerous reports now indicate that an order of magnitude increase in strength is possible in metals and alloys that exhibit grain size approaching the lower limit of nanocrystallinity [3-5]. The Hall-Petch relationship relates the grain size of a material to yield stress. It predicts that there is an inverse relationship between the material’s strength and the average grain size, as illustrated in Eq. (1.1) [6] and the largest improvements of which occur at the finest grain size (<100 nm), Figure 1.1.

\[ \sigma_y = \sigma_0 + k d^{-1/2} \]  

(1.1)

\( \sigma \) is yield stress, \( \sigma_0 \) is the intrinsic yield stress, \( k \) is a constant for a given material, and \( d \) is the grain diameter. The main mechanism causing the Hall-Petch relationship is the pileup of dislocations at grain boundaries. Thus, smaller grain size result in more grain boundaries and cause enhanced plastic flow.
**Figure 1.1** Effect of grain size on strength. Largest improvements of strength occur at the finest grain.

**1.2. Motivation and Significance.**

Achieving high strength has never been a problem. The ability to preserve the nanocrystallinity that increases the strength and to achieve any amount of uniform elongation and appreciable ductility has been a challenge in the past [7-9]. The reason is the following; grain boundaries are sources of internal energy due to the high atomic disorder and such small grain size configurations account for a large increase at the total free energy of the system (Figure 1.2) according to Eq. (1.2) [10], making the nanomaterials unstable.

\[dG \approx \gamma \, dA\]  

(1.2)
As grain boundaries have a surface energy term $\gamma$, decreasing the grain boundary area can decrease the internal stored energy. Thus, the reduction of this excess free energy $dG$, Figure 1.2, provides a strong driving force for grain growth during the processing steps (i.e. consolidation) and/or product’s life time that being potentially at high temperatures. It is therefore critical to determine the grain size evolution of such microstructures, as it can drastically change the mechanical properties.

![Free energy of the system increases as the grain size decreases](image)

**Figure 1.2** Free energy of the system increases as the grain size decreases

Here, we describe the microstructural evolution and grain growth in Fe-Ni alloys with Zr addition and differentiate the stabilization mechanisms acting on grain boundaries. Fe-Ni alloys are chosen for stability investigations since they are important for understanding the behavior of many steels and other ferrous alloys. In addition, Ni in Fe is a $\gamma$-stabilizer and it
alters the fcc to bcc transition temperature offering an ideal model to study processes in commercial austenitic steels. Zirconium is proved to be an effective grain size stabilizer in pure Fe and Fe-base systems [11] and will be investigated in this study. We found that the addition of Ni to Fe did very little to stabilize the Fe-Ni system against grain growth whereas the onset of the grain growth process occurs at higher annealing temperatures with increasing zirconium additions. We present experimental evidence that reveal the possible reasons for the microstructural stability and elevated mechanical properties in spite of micron size grains formed in some compositions.

1.3. References


2. LITERATURE REVIEW

2.1. Thermal stabilization of nanocrystalline materials

Thermal stability is of interest for nanocrystalline materials prepared by any method. Grain growth in nanostructured materials has been reviewed by many authors [1-4] and a number of investigations on the thermal stability of nanocrystalline materials have been conducted based on controlling the parameters for the velocity $v$ of a grain boundary undergoing curvature-driven grain growth [5].

$$v = MP = M_0 \left[ -\frac{Q}{RT} \right]^{2\gamma} r$$

(2.1)

$M$ is the mobility, $Mo$ is the pre-exponential factor for the mobility term, $Q$ is the activation energy for grain boundary mobility, $R$ is the ideal gas constant, and $T$ is the absolute temperature. The pressure $P$ is entirely curvature driven and therefore related to the interfacial energy per unit area, $\gamma_b$ and the radius of the grain, $r$. The stabilization of nanocrystalline materials can be carried out in two principal manners: the reduction of grain boundary energy (i.e. thermodynamic stabilization) or grain boundary mobility (i.e. kinetic stabilization).

Eliminating the grain boundary energy from Eq. (1.2) is considered the thermodynamic stabilization route and can be written as [6]:

$$\gamma = \gamma_o - \Gamma (\Delta H^{seg} + kT\ln X)$$

(2.2)
$\Gamma$ is the specific solute excess at the grain boundary which lowers the enthalpy by the enthalpy of segregation, $\Delta H^{seg}$, and raises the entropy via $kT \ln X$ ($kT$ is the thermal energy and $X$ is the composition). Thermodynamic stabilization of nanostructures has been proposed both theoretically [6-9] and experimentally [10-15] based on the elimination of the thermodynamic driving force, that is grain boundary energy, for grain growth due to solute atoms that preferentially segregate to the grain boundaries. Solute segregation to grain boundaries occurs if there is an attractive grain boundary-solute interaction that decreases the energy of the system [8]. Weissmuller [16] explained this interaction (1) by the elastic strain energy due to atomic mismatch between the solute and solvent atoms which is released when solute segregates to the grain boundaries and (2) by the total defect energy of the grain boundaries in nanostructure materials which is reduced with solute segregation.

Kinetic stabilization of grain size is based on grain boundary pinning which may occur with solute drag [17] or Zener pinning [18] as a result of a reduction in grain boundary mobility.

$$P_z = \frac{3fy}{D_p}$$  \hspace{1cm} (2.3)

$P_z$ is the pinning pressure by second phases, $f$ is the volume fraction of particles, and $D_p$ is the diameter of second phases. For successful pinning, the pinning pressure $P_z$ must be larger than the pressure $P$ driving the grain growth and it gives the Zener pinning of the grain boundaries [5].

$$d = \frac{D_p \alpha}{0.75f}$$  \hspace{1cm} (2.4)
$d$ is the limiting grain size and $\alpha$ is a factor that can vary from 0.25 to 0.5 [5]. Although solute drag has been found to be unable to completely prevent grain growth at elevated temperatures, secondary particle pinning, also known as Zener pinning [19], has been successful in increasing thermal stability to moderately high temperatures. To be successful at elevated temperatures, destabilization via particle coarsening must be suppressed otherwise this would lead to a fast grain growth as reported in [20, 21]. Nevertheless, grain boundary mobility has Arrhenius temperature dependence meaning that eventually the pinning pressure will be overcome allowing further grain growth. Therefore, recently thermodynamic stabilization is considered to be a compelling way limiting the grain growth.

Despite the high driving force and tendency for grain growth, significant stabilization of nano size grains has been reported for different binary systems exposed to high temperatures either for the purpose of consolidation or for annealing studies, such as: Fe [12, 22], Cu [23, 24], W [25] and Pd [10, 11] to name few. Recently, Darling et al. [12] studied the influence of solute Zr atoms on the stability of the grain size of nanocrystalline pure Fe produced by ball milling. It was reported that 1 and 4 at. % Zr additions to nanocrystalline Fe resulted in significant stabilization of the grains with little difference between the 1 and 4 at. % Zr alloys. Chookajorn et al. [25] reported that nanometer-sized grains can be retained in W-20 atomic % Ti alloy after annealing seven days at 1100 °C.
2.2. Nanocrystalline materials produced by high energy ball milling

Ball milling, that consists of repeated welding, fracturing, and rewelding of powder particles [26], produces powder with nanocrystalline grain size [27]. During ball milling the powder particles are subjected to severe plastic deformation from collisions with the milling media. Plastic deformation occurs within the particles at high strain rates reducing the average grain size to a few nanometers after extended milling times. Figure 2.1 shows the schematic sketch of the process of mechanical attrition of metal powders [28]. The grain size decreases and the lattice strain increases with milling time as seen in Figure 2.2. Once the grain size reaches a constant size, further refinement ceases. The minimum grain size obtainable by milling depends on the balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes [28, 29] of milling.

Figure 2.1 Ball-powder-ball collision of powder mixture during mechanical alloying [34].
Figure 2.2 The average grain size and micro strains as a function of milling time for iron powder determined from x-ray line broadening [28].

The ball milling emphasizes the maximum number of individual particles in a powder mass to undergo plastic deformation. Every time two balls collide they trap particles between them. The force of the impact deforms the particles creating clean new surfaces. When the clean surfaces come into contact, they weld together. Since such surfaces readily oxidize, the milling is carried out in an inert atmosphere or vacuum [30].

The structural changes occur via the accumulation of defects which are induced by the plastic deformation of milling. Initially, the deformation is localized in shear bands consisting of high density of dislocation. The strain level in the early stages of ball milling increases due to the increased dislocation density. At a critical dislocation density these
dislocations annihilate and recombine to small angle grain boundaries separating the individual grains. The subgrains formed via this route are already in the nanometer size range with diameters often between 20 and 30 nm [31]. During further attrition the sample volume exhibiting small grains extends throughout the entire specimen. The orientations of the grains with respect to their neighboring grains become completely random due to grain boundary sliding. The competitive processes of grain refinement by the severe plastic deformation of milling and the thermal recovery determine the minimum grain size obtainable by ball milling [28, 29].

As the metal particle is plastically deformed, most of the mechanical energy expended in the deformation process is converted into heat but the remainder is stored in the metals, thereby raising the internal energy [28]. When a metal is plastically deformed by cold welding, most of the mechanical energy of the deformation gets converted into heat increasing the temperature of the powder. If it raises above a critical temperature, the cold worked particles may undergo recovery and recrystallization leading to an undesired grain growth. Thus, the temperature of the vial should be kept below the critical temperature for the duration of milling by forced air cooling as the minimum nanocrystalline grain size attained is the result of the competition between defect creation and recovery. The remainder of the mechanical energy of the deformation is stored in the metals, thereby raising the internal energy [28].
2.3. Consolidation of nanocrystalline powders

The mechanical attrition produces powder particles with a nanoscale microstructure. These particulates must be consolidated into the bulk form to have bulk samples for mechanical testing and for the applications of structural nanocrystalline materials [32]. Cold compaction of metal powders requires plastic yielding, therefore high pressures for strong nanocrystalline metals of the order of several gigapascals are needed [32]. Warm compaction assists densification by allowing for plastic deformation for metals at high temperatures and pressures. The problem is that a combination of pressure and temperature is required for a good particle bonding in order to reach the theoretical densities. This should be done without significant coarsening of the nanoscale microstructure. Thus, the attainment of thermal stability can exploit the consolidation conditions (i.e. temperature and pressure) to obtain high dense materials for advanced mechanical tests for structural applications.

The major methods to consolidate nano-powders were reviewed [33] and those that have received the most attention are high pressure torsion (HPT) and equal-channel angular extrusion (ECAP). High Pressure Torsion (HPT) involves torsion at high hydrostatic compression stresses that basically enhances the strain to fracture. In the HPT, a disked shape sample is compressed and then one of the dies is moved with respect to the other. With enough rotation, significant shear strains can be achieved. It should be mentioned that due to the nature of the HPT process, the central part of HPT disks may remain undeformed even after large shear strains [34].
Equal Channel Angular Extrusion (ECAE), which is also commonly known as Equal Channel Angular Pressing (ECAP), is used for the deformation of bulk samples by pure shear [32] as well as for obtaining high density materials from powders. In this method powder or a billet is pressed through a die that is constructed containing a channel that is bent through an abrupt angles of intersection typically 90 to 120°. The deformation process imposes high strains without any concomitant change in the cross sectional area of the sample, Figure 2.4 [35].
Multiple passes through the die provide accumulative strain [35]. When samples are pressed repetitively, different slip systems may be introduced by rotating the samples about the X-axis. Four separate processing routes have been identified for use in ECAP [37].

1. Route A: the sample is pressed repetitively without rotation.
2. Route $B_A$: the sample is rotated through $90^\circ$ in alternate directions between each pass.
3. Route $B_C$: the sample is rotated by $90^\circ$ in the same sense between each pass.
4. Route $C$: the sample is rotated by $180^\circ$ between passes.
Figure 2.5 The four processing routes in ECAP [35].

2.4. References


3. EXPERIMENTAL PROCEDURE

3.1. Mechanical Milling/Alloying of Powders

For our investigations, appropriate masses of Fe (99.9 %), Ni (99.9 %), and Zr (99.7 %) powders were used with 440C stainless steel balls and sealed in a hardened steel vial under an argon atmosphere (O₂ < 2 ppm) prior to milling. Oxygen (Inert gas fusion – ASTM E 1019-08) and carbon (Combustion infrared detection – ASTM E 1019-08) amounts in the received powders were determined prior to milling. Three samples analyzed by Luvak Inc. and results are given in Table 3.1.

### Table 3.1 Oxygen and Carbon content of received powders prior to milling

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Carbon (wt %)</th>
<th>Oxygen (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.07</td>
<td>0.366</td>
</tr>
<tr>
<td>Ni</td>
<td>0.081</td>
<td>0.102</td>
</tr>
<tr>
<td>Zr</td>
<td>---</td>
<td>0.320</td>
</tr>
</tbody>
</table>

A ball-to-powder mass ratio of 10:1 with a powder charge of 5.1 g was loaded into the vials (Figure 3.1(c)) and milled for 20 h using a SPEX 8000 model mixer-mill (Figure 3.1(d)). It causes repeated welding, fracturing, and rewelding of powder particles and produces powder with nanocrystalline grain size (Figure 3.1(a-b)). The temperature of the vial was kept below about 50 °C for the duration of milling by forced air cooling as the
The minimum nanocrystalline grain size attained is the result of the competition between defect creation and recovery.

![Figure 3.1](image)

**Figure 3.1** Schematic view of mechanical alloying. (a) ball-powder movement during milling, (b) ball-to-powder interaction, (c) milling media, balls and vial, (d) SPEX 8000 mill

At the early stages in the process, the metal powders are still rather soft and the tendency for them to weld together into larger particles predominates [1]. A broad range of particles develops, with some particles being two to three times larger in diameter than the original ones. As the process continues, the particles get harder and their ability to withstand deformation without fracturing decreases [2]. The smaller particles tend to weld into larger pieces. The larger particles, on the other hand, are more likely to incorporate flaws and to
break apart when they are struck by the balls. In time, the tendency to weld and the tendency to fracture come into balance, and the size of particles becomes constant within a narrow range [3-5]. The mechanical milling/alloying for the different alloy compositions resulted in powders with a particle range of 10-100µm and a nanocrystalline microstructure of approximately 8-12nm (see Figure 3.2).

**Figure 3.2** Particle range of powders after 20 hrs room temperature milling; a)Pure Fe, b)Fe-8Ni, c)Fe-8N-1Zr, d)Fe-8Ni-2Zr, e)Fe-8Ni-3Zr, f)Fe-8Ni-4Zr

### 3.2. Thermal Treatments

As-milled powders were isochronally and isothermally annealed up to 1000 °C and 24 hrs, respectively in a 98% Ar + 2% H₂ gas atmosphere with subsequent cooling in the furnace where the cooling rate was less than 2-3 °C per second. The furnace used for the
annealing studies was Lindberg tube furnaces 2” in diameter. The powders were placed into a quartz tube along with a thermocouple and the tube was pumped down to < 40 mtorr and refilled with 98% Ar + 2% H₂ gas atmosphere. The as-milled powder was used as the starting material for annealing at each temperature.

3.3. Consolidation of Powders

Mechanical properties are best measured on bulk samples [6]. Thus, as-milled and/or annealed powders have to be compacted by temperature/pressure assisted compression in order to be able to obtain the theoretical density. Therefore, the knowledge of the thermal stability of nanocrystalline Fe-Ni-Zr alloys is crucial for the consolidation steps of the powders.

Heat Treatment, Hot Uniaxial Pressing, and Sintering

For advanced mechanical characterization the powders that had been milled for 20 hours followed by 1 hour annealing at elevated temperatures were compacted into pellets. Thin, disk-shaped specimens were prepared through uniaxial hot pressing (Ar/2%H atmosphere) of the annealed powders at 3-3.5GPa and 500 °C in a tungsten carbide 7 mm diameter die as seen in Figure 3.3. For this purpose, as-milled powders were annealed at elevated temperatures (between 800 – 1000 °C). Then, the powders were loaded into a WC die with a diameter of 7 mm. In order to eliminate oxidation, the die was evacuated before hot pressing and continuously purged with argon throughout the pressing until the
consolidation is complete and the temperature drops to room temperature. Next, the powders were heated up to 500 °C in Ar/2%H atmosphere and kept approximately 30 min. Finally, the load was applied at 500 °C for 10 min to produce disk-shaped specimens. These disks were subsequently sintered at 250 °C below the annealing temperatures to make interparticle bonding stronger before mechanical tests. The samples were polished and density was determined by measuring the dimensions and the weight of the samples. Densities varied between 92 and 97 % of the theoretical values. Hardness measurements confirmed that no significant grain growth had occurred after hot compaction.

Figure 3.3 Compacted disk through uniaxial pressing

*Equal channel angular extrusion (ECAE)*

Powder was processed in Ni 200 cans ~ 0.735 x ~ 0.735 x 4.5in long with a 0.4in diameter hole drilled into the top ~3.0in deep. The top of the hole was drilled and tapped to
.5in x 24 thread one inch deep, Figure 3.4. Cans were cleaned with ethanol in a sonicator and then dried. Powder was filled into the hole giving a total sample size of 1.25in long. Powder was loaded in a glove box, filled and compacted by hand using a push rod. Once the total height of desired sample size was met, a stainless steel hex cap screw that was turned down on the end to fit into the remaining 0.4in dia. channel was threaded into place. The screw was torqued down until no more compression on powder was possible without deforming the can. The cans were then coated with a high temperature glass based die processing paint to provide lubrication at 800+ degrees Celsius. The cans individually were heating in a box furnace to the desired processing temperature and soaked for 30 minutes, while the die was heated independently to ~300 degrees Celsius. Once the 30 minutes had passed the press was placed in the load position where the can was removed from the furnace (located directly next to die) with steel forged tongs and loaded into the die within 8 seconds. The can was then processed at a rate of 0.25in/sec. After the extrusion was complete the can was then ejected from the die after ~20 total seconds from the time leaving the furnace. ECAE consolidations were done at U.S. Army Research Laboratory, in collaboration with Dr. Kris A. Darling.
3.4. Microstructural Characterization

X-Ray Diffraction

X-ray diffraction analysis of the as-milled and heat treated powders was performed using a Rigaku X-ray diffractometer with CuKα (λ = 0.1542) radiation. The instrumental broadening was removed as a function of 2θ using a well-annealed standard alumina sample and assuming a Gaussian peak shape.

\[
\beta_{Exp}^2 = \beta_{Size}^2 + \beta_{Strain}^2 + \beta_{Inst}^2
\]  

(3.1.)
The grain sizes of the as-milled and heat treated samples were estimated using the Scherrer formula [7].

\[ d = \frac{K\lambda}{\beta \cos \theta} \]  

(3.2)

\( \beta \) is the peak broadening, \( \lambda \) is the wave length of the incident radiation, \( \theta \) is the center of the peak, \( d \) is the determined grain size and \( K \) is a shape factor. The four intense peaks (110, 200, 211, and 220) were used to calculate the grain size, and the standard deviation of an average value was taken as the error. The determination of grain size by the Scherrer equation gave inconsistent results for the larger grain size at high annealing temperatures. Therefore, it will be used only to determine the grain size of as-milled, at 400 °C (for pure Fe and Fe-Ni alloys) and at 600 °C (for Fe-Ni-Zr alloys) annealing temperature where the grain size is less than 30 nm.

The lattice strain was estimated from Williamson-Hall analyses [8] by plotting \( \frac{\beta \cos \theta}{\lambda} \) vs \( \frac{\sin \theta}{\lambda} \). Three reflections (110, 211 and 220) were used in the strain analysis because the elastic moduli of iron in these crystallographic directions are identical [9]. The room temperature lattice parameter was calculated using Cohen’s method [10].

**Optical Microscopy**

The microstructure of pure Fe and Fe-Ni samples annealed at high temperatures yielded > 5 micron grain sizes and was characterized by optical microscopy (Nikon Epiphot). The samples were polished with silicon carbide sanding papers unidirectionally after
consolidation and then rotated 90° after each polishing stage to insure that all scratches from the previous grit size is removed. Samples were then polished with suspension of alumina particles in water until a mirror finish was seen on the sample. The samples were then etched 15 s at room temperature in a 2% Nitol solution.

**Scanning Electron Microscopy**

A Hitachi S3200 Variable Pressure Scanning Electron Microscope was used for the work presented here. This is a conventional high resolution thermionic SEM which allows the operator to control the specimen chamber vacuum level by introduction of He gas. A non-conductive specimen maybe inserted directly into the VPSEM and observed in its natural state without the need for metalized coatings. A 4Pi Isis EDS system is also attached to the instrument for digital image acquisition and elemental analysis.

**Transmission Electron Microscopy**

JEOL 2000FX and Hitachi HF2000 TEMs were used at an accelerating voltage of 200kV in this work to image the microstructures for precise quantitative information on average grain size and grain size distribution. Bright field and dark field images were used to determine grain size distribution of the samples. The production of all samples reported in this work was particulate form. Thus, TEM sample preparation was problematic due to the high hardness and low interparticle bonding. This made it impossible to prepare electron transparent samples with electro jet polishing as the particles fall apart in the TEM under the
strong magnetic field. Therefore, electron transparent TEM samples were prepared using FEI Quanta 3D focused ion beam system that has an Omniprobe for in-situ TEM sample lift-out.

**Focused Ion Beam Imaging**

The FEI Quanta 3D focused ion beam system is used for ion channeling contrast imaging (FIB-CCI) and to prepare electron transparent samples for TEM. FIB-CCI images were obtained using backscattered electrons produced by the ion beam from a single powder particle. The contrast in the images is due to the changes in the grain orientations that cause variations in ion channeling efficiency [11]. The FEG that is a DualBeam instrument that combines a traditional Field Emission column with a FIB column to complement characterization laboratory tools and extend application range to 3D characterization and nanoanalysis.

**In situ X-Ray Diffraction**

High temperature XRD analysis was carried out using an Anton Paar HTK 2000. Samples consisted of a thin layer of powder place onto a Pt strip. A given sample was then brought into alignment on the optical axis of the diffractometer. The heating chamber was pumped down, under a vacuum of approximately $10^{-3}$ Torr and backfilled with a He 3 % hydrogen forming gas to prevent oxidation of the powders during examination. The sample was then resistively heated to temperature at a rate of 60 °C/min, at which point it endured a 10 min isothermal anneal, before performing a 17 min long diffraction scan at the respective
temperature. The sample temperature was increased to the next desired set point and the isothermal/scanning process repeated as done previously. This process was repeated to cover the following temperature range of 30 °C, 500 °C, 600 °C, 700 °C, 750 °C, 800 °C, 900 °C and again at 31 °C to complete the test. The grain size at temperature was calculated using the Scherrer Method.

**In situ Transmission Electron Microscopy**

The ion beam was used to prepare an electron transparent sample from as-milled powder for the *in situ* transmission electron microscopy (TEM) annealing experiments. The sample was mounted in the Aduro holder [12] and imaged in a Hitachi HF-2000 TEM. The Aduro system uses a flat, ceramic membrane as the active specimen support to enable fast, stable and accurate thermal analysis. The membrane has a small thermal mass, which allows for extremely fast heating rates up to $10^6$ °C/sec with virtually instantaneous temperature stabilization and accuracy of ± 0.5-3 °C. The whole experiment was recorded with a video imaging in bright field (BF) mode to directly observe grain growth in the initially nanocrystalline sample. The increment of the temperature was 50 °C during *in situ* annealing from room temperature to 900 °C.
3.5. Mechanical Properties

**Micro Hardness**

There is a general relation between material’s hardness and its yield point. Thus, hardness testing was used to get a quick general understanding of a material’s mechanical properties. For the microhardness measurements, annealed powders were cold-compacted into 3mm discs under a uniaxial pressure of 3-3.5GPa. Compaction of the as-milled powder was not successful and the powder particles were fixed into epoxy resin. All samples were mechanically polished and microhardness was measured using a Vickers hardness tester with a 50g load. The standard deviation was taken as the error after 8-10 measurements.

**Shear Punch Tests**

Shear punch tests samples were compacted into 7mm diameter compacts under an applied uniaxial pressure of 3-3.5GPa and at a temperature of 500 °C in tungsten carbide dies. Hardness measurements confirmed that no significant grain growth had occurred after
hot compaction. Densities varied between 92 and 95 \% of the theoretical values. Compacted samples were polished to ~400nm thickness and shear punch tests were run with an MTS Alliance RT/10 tensile frame at a speed of 0.01 mm/min. The punch and sample are 1.00 and 3.00mm in diameter, respectively. Details of the experimental setups for shear punch tests were described elsewhere [13].

### 3.6. References


[12] www.protochips.com

4. EFFECT OF ANNEALING ON MICROSTRUCTURE, GRAIN GROWTH, AND HARDNESS OF NANOCRYSTALLINE Fe-Ni ALLOYS PREPARED BY MECHANICAL ALLOYING

H. Kotan, M. Saber, C.C. Koch, R.O. Scattergood


4.1. Abstract

Fe-xNi alloys from x=0 to x=15 with an as-milled grain size and hardness in the range of 8-11 nm and 8.5-9.5 GPa, respectively, were synthesized by ball milling. Microstructural changes, hardness, and grain growth due to annealing were characterized using X-ray diffractometry, microhardness, focused ion beam channeling contrast imaging, and optical microscopy. It was found that the composition range of single bcc phase was extended by ball milling. Subsequent annealing of MA samples resulted in reduction of hardness and extensive grain growth. It indicates that nickel has no significant effect on thermal stabilization of iron. Retained austenite was observed for Fe-8Ni and Fe-10Ni alloys annealed in the two-phase region and effect of as-milled structure on retained austenite formation was discussed.

Keywords: nanostructured materials; mechanical alloying; grain growth;
4.2. Introduction

This study of iron-nickel alloys has the primary motivation of investigating the effect of annealing and nickel content on microstructure, grain growth, and mechanical properties of nanocrystalline iron-nickel alloys prepared by ball milling. The iron-nickel system has attracted considerable attention for the understanding of steels and other ferrous alloys. Therefore, several studies were performed to investigate phase stability, microstructural, and mechanical properties of iron-nickel alloys [1-7]. Studies of MA iron-nickel alloys showed that the single-phase bcc and fcc concentration ranges may be extended significantly as compared with those produced by conventional techniques [8, 9]. Another important feature of iron-nickel system is that the annealing of cold-worked alloys in two-phase (α + γ) region may lead to retained austenite formation [10]. The presence of retained austenite has a beneficial influence on the cryogenic toughness of ferritic steels [11]. However, limited research has been done, so far, to determine the effect of nickel content and annealing on grain growth and phase transformation of nanocrystalline iron-nickel alloys prepared by ball milling. Darling et al. [12] reported grain growth behavior of ball-milled Fe-Ni but it was limited to 1 at% Ni and intermediate annealing temperatures.

Ball milling, that consists of repeated welding, fracturing, and rewelding of powder particles [13], produces powder with nanocrystalline grain size [14] and consolidation of the powders into bulk shapes is necessary for potential applications [15]. The problem is that a combination of pressure and temperature is necessary for complete inter-particle bonding
However, grain growth limits the processing of nanocrystalline powders metals since there is a thermodynamic driving force for reduction of the total grain boundary area [17].

In the present study, we present an attempt to extend single phase α solid solution and determine the effect of annealing temperature on grain growth and hardness of iron-nickel alloys obtained by mechanical alloying. We compare the obtained results with the published data for pure iron and Fe-Ni alloys.

4.3. Experimental

Fe-Ni alloys with Ni content from 0 to 15 at% (0, 2, 4, 6, 8, 10, and 15) were prepared by mechanical alloying. As starting materials, appropriate masses of elemental Fe (99.9%) and Ni (99.9%) powders were mixed with 440C stainless steel balls and sealed in a hardened steel vial under an argon atmosphere (O<sub>2</sub> < 2 ppm) prior to milling. The weight of the mixed powders was 5.1 g and the ball-to-powder weight ratio was 10:1. Ball milling was performed with SPEX 8000 model mixer-mill for 20 h. The temperature of the vial was kept approximately below 50 °C for the duration of milling by forced air cooling.

Following the milling processing, powders were isochronally annealed at 400 °C, 600 °C, 800 °C and 1000 °C in a 98% Ar + 2% H<sub>2</sub> gas atmosphere for 1 h with subsequent cooling in the furnace where the cooling rate was less than 2-3 °C per second. In what follows, all cooling is in-furnace cooling unless otherwise stated. The as-milled powder was used as the starting material for annealing at each temperature.

X-ray diffraction analysis of the as-milled and heat treated powders was performed using a Rigaku X-ray diffractometer with CuKα (λ = 0.1542) radiation. The instrumental
broadening was removed as a function of 2θ using a standard alumina sample and assuming a Gaussian peak shape. The grain sizes of the as-milled and heat treated samples were estimated using the Scherrer formula [18]. The four intense peaks (110, 200, 211, and 220) were used to calculate the grain size, and the standard deviation of an average value was taken as the error. The determination of grain size by the Scherrer equation gave inconsistent results for the larger grain size at high annealing temperatures. Therefore, it will be used only to determine the grain size of as-milled and at 400 °C annealing temperature where the grain size is less than 30 nm. The lattice strain was estimated from Williamson-Hall analyses [19]. Three reflections (110, 211 and 220) were used in the strain analysis because the elastic moduli of iron in these crystallographic directions are identical [20]. The room temperature lattice parameter was calculated using Cohen’s method [21].

Microstructure of the samples annealed at high temperatures is characterized by optical microscopy (Nikon Epiphot) and focused ion beam contrast (FEI Quanta 3D FEG). Light microscopy was done using polished and etched samples (15 s at room temperature in a 2% Nitol solution). Focused ion beam (FIB) preparation was used to prepare ion channeling contrast imaging (FIBCCI) samples. ImageJ software was used to estimate the volume averaged grain size. For the microhardness measurements, annealed powders were cold-compacted into 3 mm discs under a uni-axial pressure of 3 GPa. Compaction of the as-milled powder was not successful and they were fixed into epoxy resin. All samples were mechanically polished and microhardness was measured using a Vickers hardness tester with a 50 g load. The standard deviation was taken as the error after 8-10 measurements.
4.4. Results

Figure 4.1 shows X-ray diffraction patterns from powders of Fe-xNi with $0 \leq x \leq 15$ for ball-milling for 20 hours. In what follows, all compositions are given in atomic percent. In our investigation, mechanical alloying (MA) of elemental iron and nickel powders leads to the extension of single phase solid solutions up to 15 at% Ni. Equilibrium solubility of nickel in the iron lattice was reported to be around 3.5 wt % Ni [22, 23] by conventional technique, and extended up to 30 at% Ni [8] by ball milling. The diffraction peaks of the as-milled alloys exhibit a significant broadening due to the refinement of grain size and the increase of internal lattice strain. The calculated grain size and lattice strain for the as-milled powders were found to be within the ranges 8-11 nm and 0.5% - 0.7% respectively.
Figure 4.1 X-ray diffraction patterns from as-milled Fe–xNi alloys with x = 0, 2, 4, 6, 8, 10, 15. Materials were milled for 20 h at room temperature.

Room temperature lattice parameters of α-(Fe,Ni) bcc solid solutions as a function of alloy compositions are shown in Figure 4.2. Lattice parameters of bcc phase for equilibrium alloys from different authors reported by [24] are also presented on the same figure. It is evident that there is excellent agreement between the lattice parameter data from our bcc powders and from those reported previously. There is only a small increase in the lattice parameter with increasing nickel content due to the small atomic size difference between nickel and iron atoms [25]. The lattice parameter of as-received pure iron was calculated to be 0.2866 nm and the change in lattice parameters, from un-milled iron powder to as-milled 15 at% Ni alloy, has been estimated to be 0.31%. Generally, the increase of the lattice
parameter has been attributed to a solid solution formation as the nickel content increases [26]. MA alloys lattice parameters are larger than those of equilibrium alloys reported by [24] (see Fig. 4.2) due to vacancy complexes and dislocations induced by plastic deformation [27]. The same effect was observed by different authors for Fe-Ni [28] and Fe-Mn alloys [29].

![Figure 4.2 Lattice parameters as a function of compositions for the bcc phases at room temperature from this work and from different authors reported by [24].](image)
Figure 4.3 X-ray diffraction patterns for Fe–4Ni alloy annealed at 400 °C, 600 °C, 800 °C and 1000 °C.

Figure 4.3 shows X-ray diffraction patterns of Fe-4Ni alloy annealed at different temperatures for 1 hour. Similar patterns were obtained for Fe-xNi alloys where x ≤ 6, but are not shown here. The diffraction peaks sharpen and peak intensity increases with annealing at increasingly higher temperatures as a result of stress relaxation and grain growth. One hour annealing of mechanically alloyed Fe-xNi alloys where x ≤ 6 did not cause any discernable structural change for annealing up to 1000 °C, meaning that single phase α-(Fe,Ni) solid solution was observed at room temperature. However, retained austenite was detected in X-ray diffraction results (Figure 4.4) for Fe-8Ni and Fe-10Ni alloys annealed at 600 °C. Annealing at other temperatures did not lead to any change of the structure for the
same compositions. The lattice constant obtained ($a = 0.3591$ nm) indicates that the austenite which forms at $600 \, ^\circ\text{C}$ contains approximately $32\, \text{at}\%\, \text{Ni}$ [24]. Using the X-ray diffraction pattern, we calculated the amount of retained austenite as $16\%$ [10].

![X-ray diffraction pattern](image)

**Figure 4.4** X-ray diffraction patterns for Fe–8Ni alloy annealed at $600 \, ^\circ\text{C}$ for 1 h.
Figure 4.5 X-ray diffraction patterns for Fe–8Ni alloy after 1 h annealing at 600 °C, 1000 °C, and 1000 °C followed by 1 h annealing at 600 °C.

In the generally accepted Fe-Ni phase diagram [24], the equilibrium phases in this region (600 °C annealing for Fe-8Ni and Fe-10Ni compositions) are ferrite (α) of low nickel content and austenite (γ) of high nickel content. It is also well documented that cold-working prior to annealing in this two-phase region increases the rate of austenite formation [10]. We did further annealing to investigate the effect of defective and nanocrystalline as-milled structure on retained austenite formation. First we annealed as-milled powders at 1000 °C to eliminate the majority of the defects introduced by ball milling, and to reduce grain boundary area. Then we annealed the same sample at 600 °C for 1 hour. No evidence of retained austenite was observed in X-ray diffraction scans, suggesting that defects and grain boundaries played
an important role in the kinetics of austenite formation in the two-phase region. X-ray diffraction scans of additional annealing are shown in Figure 4.5.

**Figure 4.6** Vickers hardness vs. 1 h isochronal annealing temperatures for pure Fe and Fe–Ni alloys.
Figures 4.7 Grain size vs. isochronal annealing temperature for 1 h annealing with data for pure Fe and Fe–Ni alloys.

Figures 4(6-8) respectively show hardness, grain size, and internal lattice strain as a function of annealing temperatures for the six alloys prepared by mechanical alloying. The as-milled powder was used as the starting material for annealing at each temperature. In the as-milled state, the microhardness of Fe-Ni alloys is in the range of 8.5 to 9.5 GPa. The initial annealing at 400 °C causes a small decrease in the hardness (Figure 4.6) whereas the grain size does not increase significantly, and remains below 30 nm (Figure 4.7). Analysis of the X-ray diffraction peak profiles also reveals (Figure 4.8) that the strain decreases from a high level of ~0.65% in the as-milled state to around ~0.2% at 400 °C, and becomes negligible beyond 600°C. It was reported [30] that dislocations are the primary cause of
strain in ball milled iron. Ashby [31] separated the dislocations into geometrically necessary ones that are associated with the existence of grain boundaries and statistically stored dislocations that are associated with plastic deformation. This suggests that the decrease in hardness below 400 °C is mostly due to the annihilation of the statistically stored dislocations that were generated by the heavy plastic deformation during milling and grain boundary relaxation, while the decrease in hardness above 400 °C is due to grain growth which resulted in reducing the density of geometrically necessary dislocations.

**Figure 4.8** Internal lattice strain as a function of temperatures for Fe–Ni alloys.
The nanocrystalline grain size of ball-milled Fe-Ni alloys did not begin to coarsen, and remained less than 30 nm up to 400 °C (T/T_M=0.38). Annealing at 600°C causes a sudden decrease in hardness for the alloys (see Figure 4.6) which have α-ferrite solid solution upon cooling, indicating rapid grain growth between 400 °C and 600 °C. It is worth noting that there is a wide range in hardness and grain size at this temperature for different nickel compositions. Hardness of Fe-8Ni and Fe-10Ni alloys annealed at 600°C is 5.5 – 6 GPa, whereas it is less than 4.5 GPa for single α-phase Fe-Ni alloys, and is 3 GPa for pure iron. Optical microscopy images (not shown here) revealed that the microstructure of nanocrystalline pure iron had undergone extensive grain growth, reaching a value of approximately 4000 nm for annealing at 600 °C. At the same annealing temperature, the grain sizes for Fe-8Ni and Fe-10Ni alloys were found to be less than 30 nm. In comparison, the reported grain size of pure ball-milled iron at 700 °C was 6000 nm [12].
Figure 4.6 shows that further increase in annealing temperature causes hardness to decrease dramatically and eventually the hardness for the all alloys drops to less than 3 GPa at the 1000 °C annealing temperature. Figure 4.9 shows optical micrographs of polished and etched Fe-Ni alloys annealed at 800 °C and 1000 °C. Observed microstructures reveal that micron-scale grains could be distinguished from the micrographs, as well as some microporosity present within particles. The initial grain sizes for the all alloys were approximately 10 nm. Annealing at high temperatures results in extensive grain growth and the grain sizes have already reached an average value of about 3000-3500 nm at 800 °C.
(T/T_M=0.60) and 6500-8000 nm at 1000 °C (T/T_M=0.70) for different Fe-Ni alloys, estimated using light microscopy. At 1000 °C, average grain size of pure iron was found to be around 15000 nm, suggesting that Fe-Ni alloys appear to be only marginally more stable than pure Fe. The estimated volume average grain size using optical micrographs does not give the exact grain size because features or grains are not discernable. It provides a general idea about microstructure and grain size distribution. An abnormally grown grain is present in the micrograph b in Figure 4.9 (marked by black arrows), whereas no grain structure could be resolved in the regions of micrographs c and d marked by white arrows. The latter were assumed to be submicrometer and/or nanoscale regions, where the high density of etched grain boundaries produced unresolvable contrast. This was confirmed by Darling et al. [12] in focused ion beam contrast images. They showed using low and high magnification FIB images that 30% of the microstructure of Fe-1Ni annealed at 700 °C is still nanocrystalline, and annealing at 870 °C results in complete grain growth of the microstructure, confirming our results.
Figure 4.10 FIBCCI micrographs for Fe–8Ni alloy after 1 h annealing at (a) 900 °C and (b) 1000 °C.

We also utilized focused ion beam (FIB) images to analyze the microstructures that were obtained using light microscopy. Figure 4.10 shows low magnification focused ion beam channeling contrast images (FIBCCI) of Fe-8Ni alloy annealed (a) at 900 °C and (b) at 1000 °C. The images were obtained using backscattered electrons produced by the ion beam from one powder particle. The contrast in the images is due to the changes in the grain orientations that cause variations in ion channeling efficiency. It is seen from Figure 4.10 that micron size grains are present for the alloy annealed at 900 °C and 1000 °C. No evidence of abnormal grain growth or nanocrystalline grains was observed, consistent with the microstructure obtained using optical images (not shown here) of the same alloy. The large grain captured in Figure 4.10(b) indicates the extensive grain growth at the temperatures where $T/T_m=0.70$. 
4.5. Discussion

In the present work, we changed the nickel content in iron from 0 to 15 at% and prepared nanocrystalline alloys by ball milling. The as-milled powder morphology developed from relatively fine powder for pure iron into large spherical particles with increasing nickel content after 20 h milling. This behavior can be associated with the enhanced cold welding and decreased fracture events during milling as a result of a transition from more brittle to more ductile behavior with increasing nickel in the iron lattice [8].

As discussed earlier, we observed single-phase α-(Fe,Ni) solid solution for every composition and annealing temperature except for the alloys with 8 and 10 nickel content annealed at 600 °C which yield retained austenite. In Fe-Ni [11, 32] and Fe-Mn [29] alloys, retained austenite was intentionally introduced after thermal cycling. It was suggested by those researchers that the presence of retained austenite in ferritic alloys increases cryogenic toughness by lowering the ductile-brittle transition temperature. Retained austenite was also observed for mechanically alloyed Fe-Ni alloys annealed in α + γ region. R. Hamzaoui et al. [33, 34] reported that annealing of as-milled Fe-20Ni at 650 °C lead to the formation of fcc + bcc phases, but no further investigation was carried out.

Given that diffusion is slow in the two-phase region [10], and the austenite grains form preferentially on internal surfaces during annealing [35], such as grain boundary triple junctions, and defects, the fine and defective structure of as-milled alloys greatly enhances the diffusivity. This provides abundant nucleation sites and preferential diffusion paths for austenite formation for the 1 hour annealing time. The effect of cold-work on austenite
formation was described by Miller [10]. He proposed that cold-working prior to annealing in the two-phase region increases the rate of austenite formation and the severity of cold-work extends this effect. However, since appreciable diffusion is required for the formation of austenite in the two-phase region, retained austenite does not form when the alloy is merely heated or cooled at normal rates through the two-phase region (see Figure 4.5). For the same reason, no austenite was determined when we annealed the as-milled powder first at 1000 °C, followed by 600 °C annealing. We believe that annealing at 1000 °C eliminates the majority of defects introduced by ball milling and reduces the grain boundary area, slowing down the kinetics that are necessary for the formation of austenite for the annealing time of 1 hour.

We also investigated grain growth and hardness of pure iron and Fe-Ni alloys as a function of annealing temperatures up to 1000 °C. Annealing of the as-milled powders results in reduced hardness, indicating that the nanostructure developed by ball milling is not retained during annealing due to the extreme levels of cold work introduced during mechanical alloying. Thermal stability of these nanostructures is limited to annealing at 400 °C for Fe-xNi (x≤6) alloys that have a single phase α solid solution upon cooling, and annealing at 600 °C for Fe-xNi (x=8 and x=10) which have ferrite and austenite (α + γ) phases upon cooling to room temperature. Atomic sizes of iron and nickel are very close, suggesting that significant grain boundary segregation and thermodynamic stabilization due to elastic strain energy does not occur [12]. Thermal stabilization of Fe-Ni alloys with zirconium segregation to the grain boundaries is under investigation and will be reported later.
In the current study, the relationship between hardness and grain size is summarized using the Hall-Petch plot in Figure 4.11. Grain sizes used in Figure 4.11 are X-ray grain size in the as-milled state and at the lower annealing temperatures where grain size is less than 30 nm, or grain sizes determined from micrographs at higher annealing temperatures. For comparison, data from different researchers [36-40,42] for nano and coarse grained iron is also displayed together with the present data. It is clearly evident that while there is some scatter in the data in Figure 4.11, our values match quite closely to the nanocrystalline and coarse-grained regime data points reported by previous researchers. In the study reported by
Jang and Koch [40] the hardness of nanocrystalline iron was measured as a function of milling time and increased hardness and decreased grain size were obtained with longer milling times. The data from their study on the as-milled powders shows smaller grain size and higher hardness than the results found in our investigation. It is worth noting that Jang and Koch [40] did not take the instrumental broadening of the diffraction peaks into account in the grain size analysis which could shift their results toward larger grain sizes. They also reported oxygen and nitrogen as impurities, which possibly lead to an additional strengthening effect and, therefore, higher hardness values at a given grain size [41]. Shen et al. [42] investigated the grain size and hardness of ball-milled iron with subsequent annealing. They started with 99.9% pure iron and reported increased grain size and reduced hardness with increasing annealing temperatures, following a Hall-Petch relation. In the current investigation, initial annealing did not cause any increase in hardness, suggesting that no impurity segregation had occurred to the grain boundaries since the starting powders had high purity [42]. We did not see a negative slope in the Hall-Petch plot meaning that no softening of the alloys with decreasing grain size was observed for grain sizes as small as 9.5 nm. However, we found that the Hall-Petch slope for nano grains is smaller than for coarse-grained samples. A similar trend, that is an increase of the Hall-Petch slope of course-grained iron, was reported and discussed by Malow and Koch [39]. Hardness and grain size of retained austenite alloy appears to fit the Hall-Petch relations, suggesting that ultrafine grains with retained austenite can be developed by milling followed by annealing in the ferrite +
austenite region. It was proposed by Miller [10] that since the annealing temperature is relatively low and the recrystallized structure is two-phase, grain growth is restricted.

4.6. Conclusions

Fe-Ni alloys with Ni content from 0 to 15 at% were prepared by mechanical alloying. The composition range of the bcc single phase region was greatly extended with respect to the equilibrium state. Using mechanical milling, iron-nickel powders were hardened to 9.5 GPa by the mechanism of grain refinement strengthening. Subsequent annealing lead to reduced hardness and extensive grain growth, suggesting that the nanostructure developed by ball milling is not retained during annealing. Retained austenite was observed for Fe-8Ni and Fe-10Ni alloys annealed in the two-phase region. Our experiments and analysis suggest that as-milled grain size and defective structure play an important role on the formation of austenite in the two-phase region. The Vickers hardness as a function of the grain size was found to exhibit a Hall-Petch slope that was smaller for nanocrystalline grains compared to coarse-grained powders annealed at high temperatures.

4.7. References


5. EFFECT OF ZIRCONIUM ON GRAIN GROWTH AND MECHANICAL PROPERTIES OF A BALL-MILLED NANOCRYSTALLIN FeNi ALLOY

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5.1. Abstract

Grain growth of ball-milled pure Fe, Fe$_{92}$Ni$_{8}$ and Fe$_{91}$Ni$_{8}$Zr$_1$ alloys has been studied using X-ray diffractometry (XRD), focused ion beam microscopy (FIB) and transmission electron microscopy (TEM). Mechanical properties with respect to compositional changes and annealing temperatures have been investigated using microhardness and shear punch tests. We found the rate of grain growth of the Fe$_{91}$Ni$_{8}$Zr$_1$ alloy to be much less than that of pure Fe and the Fe$_{92}$Ni$_{8}$ alloy at elevated temperatures. The microstructure of the ternary Fe$_{91}$Ni$_{8}$Zr$_1$ alloy remains nanoscale up to 700 °C where only a few grains grow abnormally whereas annealing of pure iron and the Fe$_{92}$Ni$_{8}$ alloy leads to extensive grain growth. The grain growth of the ternary alloy at high annealing temperatures is coupled with precipitation of Fe$_2$Zr. A fine dispersion of precipitated second phase is found to promote the microstructural stability at high annealing temperatures and to increase the hardness and ultimate shear strength of ternary Fe$_{91}$Ni$_{8}$Zr$_1$ alloy drastically when the grain size is above nanoscale.
5.2. Introduction

Improvement of properties in nanostructured materials is attributed to refining the grain size [1, 2]. However, the nanoscale microstructure is unstable due to the thermodynamic driving force for reduction of the total grain boundary area [3, 4]. This unstable microstructure and high tendency for grain growth are key obstacles faced by nanostructured materials and cause a significant problem for improved processing methods and for potential high temperature structural applications [4, 5].

Grain growth in nanostructured materials has been reviewed by many authors [6-9]. The stabilization of nanoscale grain size has been attributed to thermodynamic and kinetic effects on grain boundaries. Kinetic stabilization of grain size is based on grain boundary pinning, which occurs as a result of a reduction in grain boundary mobility [10-14]. Thermodynamic stabilization of nanostructures has been proposed both theoretically [15-18] and experimentally [19-24] based on the elimination of the thermodynamic driving force, that is grain boundary free energy, for grain growth due to solute atoms that preferentially segregate to the grain boundaries. Solute segregation to grain boundaries occurs if there is an attractive grain boundary-solute interaction that decreases the energy of the system [16]. Weissmuller [25] explained this interaction (1) by the elastic strain energy due to atomic mismatch between the solute and solvent atoms which is released when solute segregates to the grain.
boundaries and (2) by the total defect energy of the grain boundaries in nanostructure materials which is reduced with solute segregation.

Recently, Darling et al. [21] studied the influence of solute Zr atoms on the stability of the grain size of nanocrystalline pure Fe produced by ball milling. It was reported that 1 and 4 at. % Zr additions to nanocrystalline Fe resulted in significant stabilization of the grains with little difference between the 1 and 4 at. % Zr alloys. The purpose of this paper is to investigate the influence of Zr solute on grain growth in the nanocrystalline FeNi based system. The Fe-Ni based system has attracted considerable attention for the understanding of steels and other ferrous alloys. In addition, Ni in Fe is a γ-stabilizer and it alters the fcc to bcc transition temperature offering an ideal model to study processes in commercial austenitic steels. Therefore, several studies were performed to investigate the structure and properties of Fe-Ni alloys [26, 27]. As suggested by [22, 28] the addition of Ni to Fe did very little to stabilize the Fe-Ni system against grain growth.

5.3. Experiments

Pure Fe, Fe$_{92}$Ni$_{8}$, and Fe$_{91}$Ni$_{8}$Zr$_{1}$ alloys were prepared by mechanical alloying. As starting materials, appropriate masses of elemental Fe (99.9 %), Ni (99.9 %), and Zr (99.7 %) powders were mixed with 440C stainless steel balls and sealed in a hardened steel vial under an argon atmosphere (O$_2$ < 2 ppm) prior to milling. The weight of the mixed powders was 5.1g and the ball-to-powder weight ratio was 10:1. Ball milling was performed with a SPEX 8000 model mixer-mill for 20h. The temperature of the vial was kept below about 50 °C for
the duration of milling by forced air cooling. Following the milling processing, powders were isochronally annealed at 400 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C in a 98 % Ar + 2 % H₂ gas atmosphere for 1h with subsequent cooling in the furnace where the cooling rate was less than 2-3 °C per second. The as-milled powder was used as the starting material for annealing at each temperature.

X-ray diffraction analysis of the as-milled and heat treated powders was performed using a Rigaku X-ray diffractometer with CuKα (λ = 0.1542) radiation. The room temperature lattice parameter was calculated using Cohen’s method [29]. The instrumental broadening was removed as a function of 2θ using a standard alumina sample and assuming a Gaussian peak shape. The grain sizes of the as-milled and heat treated samples were estimated using the Scherrer formula [30]. Microstructure of the samples is characterized by transmission electron microscopy (TEM) and focused ion beam (FIB) imaging. The ion beam was used for ion channeling contrast imaging (FIB-CCI) and to prepare electron transparent samples for TEM. FIB-CCI images were obtained using backscattered electrons produced by the ion beam from a single powder particle. The contrast in the images is due to the changes in the grain orientations that cause variations in ion channeling efficiency. ImageJ software was used to estimate the volume average grain size.

Microhardness and shear punch tests were carried out to investigate the mechanical properties of the samples. For the microhardness measurements, annealed powders were cold-compacted into 3mm discs under a uniaxial pressure of 3GPa. Compaction of the as-milled powder was not successful and the powder particles were fixed into epoxy resin. All
samples were mechanically polished and microhardness was measured using a Vickers hardness tester with a 50g load. The standard deviation was taken as the error after 8-10 measurements. Shear punch tests samples were compacted into 7mm diameter compacts under an applied uniaxial pressure of 2.5GPa and at a temperature of 500 °C in tungsten carbide dies. Samples were not exposed to any reduction in hardness after hot compaction as no significant grain growth had occurred. Densities varied between 92 and 95 % of the theoretical values. Compacted samples were polished to ~400nm thickness and shear punch tests were run with an MTS Alliance RT/10 tensile frame at a speed of 0.01 mm/min. The punch and sample are 1.00 and 3.00mm in diameter, respectively. Details of the experimental setups for shear punch tests were described elsewhere [31].

5.4. Results

5.4.1 Microstructure evolution during annealing

X-ray diffraction patterns from as-milled powders of pure Fe, Fe$_{92}$Ni$_8$ and Fe$_{91}$Ni$_8$Zr$_1$ alloys (not shown here) revealed fundamental reflections to be consistent with that of bcc phase only with no other phases present. The calculated grain sizes for the as-milled pure Fe, Fe$_{92}$Ni$_8$, and Fe$_{91}$Ni$_8$Zr$_1$ alloys were found to be 10.5 (±2) nm, 9.9 (±2) nm, and 9 (±1.5) nm, respectively. Upon further analysis of the x-ray spectra the fundamental reflections were found to be shifted to lower angles indicating the possible formation of a binary Fe-Ni and ternary Fe-Ni-Zr solid solution between the respective elements. Measurements of the
respective lattice parameters also support the idea of solid solution formation as a systematic increase due to alloy addition (nickel and zirconium) is apparent. Figure 5.1 shows the change in the lattice parameter for all systems undergoing isochronal heat treating. The room temperature values are the as-milled lattice parameters and they include internal lattice strain due to point defects, dislocations, and grain boundary structure introduced by mechanical alloying. Internal lattice strain appears to be enhanced in Fe$_{92}$Ni$_8$ compared to pure Fe [28]. It is also reported that the lattice parameter in Fe-Ni alloys is increased even though Ni is a smaller atom compared to Fe [32]. At annealing temperature of 400°C and above, the elastic strains are relaxed and the continuing drop of lattice parameter for Fe$_{91}$Ni$_8$Zr$_1$ is a clear indication that Zr is being removed from the initial as-milled non-equilibrium solid solution of Zr in the Fe$_{91}$Ni$_8$Zr$_1$ alloy.
Figure 5.1 Variation in lattice parameter as a function of annealing temperature in pure Fe, Fe$_{92}$Ni$_{8}$, and Fe$_{91}$Ni$_{8}$Zr$_{1}$ alloys. The room temperature values are the as-milled lattice parameter.
Figure 5.2 (a, c) Bright Field (BF) and (b) Dark Field (DF) TEM micrographs of the asmilled Fe$_91$Ni$_{8}$Zr$_1$ alloy showing the initial microstructure consists of nanocrystalline grains, some of which are elongated. (d) Indexed Diffraction pattern (DP) confirms the formation of a ternary solid solution.

Figure 5.2 shows the as-milled microstructure of nanocrystalline Fe$_91$Ni$_{8}$Zr$_1$ which consists of nanocrystalline grains, some of which are 10nm wide with an elongation of about 40nm in a given direction. Elongated grains such as these have been reported before, and appear to occur in banded regions throughout the microstructure along with regions where the microstructure appears to be more equiaxed [33, 34]. The x-ray diffraction patterns and
the TEM diffraction patterns from various regions did not show the presence of secondary phases within the microstructure, confirming the formation of a ternary solid solution.

Figure 5.3 Channeling contrast images of Fe$_{91}$Ni$_8$Zr$_1$ as-milled, annealed at 600 °C, 700 °C, and 800 °C. Nanocrystalline microstructure remains stable at 600 °C. A certain fraction of grains grows abnormally into the nanocrystalline matrix, resulting in a bimodal microstructure at 700 °C. At increased annealing temperatures, nanocrystalline state is lost.

Figure 5.3 shows the microstructural evolution of Fe$_{91}$Ni$_8$Zr$_1$ as a function of annealing temperature using focused ion beam channeling contrast images. In the given images, the contrast differences arise due to the ion channeling effect. The effect allows for a semi-
quantitative analysis of grain size below 100nm and quantitative identification of grain size evolution above 100nm. Upon comparison of the as-milled microstructure with samples annealed isochronally, we see that a nanocrystalline microstructure remains stable after one hour annealing at 600 °C. Above this temperature, at 700 °C, a fraction of the grains grow abnormally into the nanocrystalline matrix, resulting in a bimodal microstructure where a few grains grow above 100nm, while the majority of the microstructure remains nanoscale. These abnormal grains exhibit a range of sizes, all of which are less than 1µm and are surrounded by grains of approximately 100nm or less in diameter. The approximate temperature of 700 °C is given by the equilibrium Fe-Ni-Zr ternary phase diagram [34] to be the point at which the bcc-to-fcc transition occurs. The extent of abnormal grain growth continues to increase at 800 °C, consuming the majority of the microstructure, and leaving only a very small fraction of the microstructure nanocrystalline.

Further increases in annealing temperature above 800 °C caused the complete consumption of the smaller grains (nano and ultrafine) in Fe$_{91}$Ni$_8$Zr$_1$, which leads to the formation of a more uniform large grain assembly. Figure 5.4 shows that large grains, having an average diameter of approximately 1µm are now present throughout the microstructure of Fe$_{91}$Ni$_8$Zr$_1$ for both 900 °C and 1000 °C. In comparison, the Fe$_{92}$Ni$_8$ alloy (Figure 5.4) shows more grain growth, which is most dramatic at 1000 °C. Extended isochronal heat treatments at 900 and 1000 °C were also performed on both Fe$_{91}$Ni$_8$Zr$_1$ and Fe$_{92}$Ni$_8$ up to 24 hours. The hardness tests and grain growth investigations revealed that 90 % of the microstructural coarsening for both alloys occurred within the first 15mins of annealing, with negligible
coarsening occurring from 1hr to 24hrs. These isothermal annealing studies suggest that the reported grain size given in Figure 5.4 is the limiting grain size for both Fe$_{91}$Ni$_{8}$Zr$_{1}$ and Fe$_{92}$Ni$_{8}$. Figure 5.4 demonstrates that the grain size of Fe$_{91}$Ni$_{8}$Zr$_{1}$ after annealing at 1000 °C is significantly smaller than that for Fe$_{92}$Ni$_{8}$ annealed under the same conditions as was also reported for pure Fe [28].

**Figure 5.4** Channeling contrast images of Fe$_{92}$Ni$_{8}$ annealed at a) 900 °C and b) 1000 °C and of Fe$_{91}$Ni$_{8}$Zr$_{1}$ annealed at c) 900 °C and d) 1000 °C. Average grain size is smaller in the ternary alloy than that of the binary alloy indicating better high temperature stability.
Figure 5.5 TEM images of Fe$_{91}$Ni$_8$Zr$_1$ alloy annealed at 1000 °C. It shows that micron size grains are present as shown in (a) bright field (BF) and (b) dark field (DF) images. (c) Diffraction pattern (DP) from large view of the sample shows bcc and intermetallic rings. Extra rings (indicated by arrows) were used to image the intermetallics shown in (d).

Additional microscopy studies revealed that the grain growth at higher annealing temperature was coupled with second phase precipitation. Figure 5.5 shows TEM images of Fe$_{91}$Ni$_8$Zr$_1$ alloy annealed at 1000 °C. It reveals that micron size grains are present as shown in bright field (a) and dark field (b) images. The TEM diffraction pattern also confirms the
formation of second phases (Figure 5.5(c)). Fe₂Zr was identified as the second phase, based on the TEM diffraction pattern, energy dispersive spectroscopy studies and the reported phase diagram for the Fe-Ni-Zr system [35, 36]. Further investigation was carried out to image the second phase particles by selecting the extra ring in the diffraction pattern as indicated by arrows in Figure 5.5(c). It can be seen from Figure 5.5(d) that precipitates are mostly less than 20nm and located within the matrix of the grains and around the grain boundaries. HRTEM micrographs in Figure 5.6 confirm that the precipitates can be as small as a few nm in diameter.
Figure 5.6 High resolution transmission electron microscopy images (HRTEM) of Fe$_{91}$Ni$_8$Zr$_1$ alloy annealed at 1000 °C showing second phase particles as small as a few nanometers in diameter.

5.4.2 Mechanical Properties

The mechanical behavior of the samples has been studied with respect to the effect of composition variation, that is, nickel and zirconium addition, and microstructure development during annealing. The important features based on microhardness and shear punch tests, respectively are illustrated in Figures 5.7 and 5.8.
Figure 5.7 shows the indentation hardness and grain size vs. isochronal (1h) annealing temperature for pure Fe, $\text{Fe}_{92}\text{Ni}_{8}$, and $\text{Fe}_{91}\text{Ni}_{8}\text{Zr}_{1}$ alloys annealed at different temperatures up to 1000 °C. The room temperature values are the as-milled hardness. In the as-milled state, the microhardness of $\text{Fe}_{91}\text{Ni}_{8}\text{Zr}_{1}$ is 10GPa while it is 8.8GPa and 9.1GPa for pure Fe and $\text{Fe}_{92}\text{Ni}_{8}$ alloy, respectively (error bars are smaller than ±0.3GPa). The as-milled hardness of $\text{Fe}_{91}\text{Ni}_{8}\text{Zr}_{1}$ is higher than pure Fe and $\text{Fe}_{92}\text{Ni}_{8}$; this is due to grain refinement strengthening and solid solution hardening as confirmed by x-ray and TEM/diffraction analysis.
Figure 5.8 Shear punch test curves for pure Fe, Fe$_{92}$Ni$_8$ and Fe$_{91}$Ni$_8$Zr$_1$ alloys at 900 °C and for Fe$_{91}$Ni$_8$Zr$_1$ at 1000 °C.

The annealing of pure Fe and Fe$_{92}$Ni$_8$ leads to a small reduction in hardness at 400 °C, whereas the hardness decreases dramatically between 400 – 700 °C as a result of rapid grain growth [22, 28, 37]. Moreover, the initial annealing of Fe$_{91}$Ni$_8$Zr$_1$ at 400 °C and 600 °C causes a small decrease in hardness and the grain size does not increase significantly, remaining approximately constant below 15nm as measured by x-ray analysis. The decrease in hardness at low temperatures without significant grain growth was attributed to grain boundary relaxation and the annihilation of the statistically stored dislocations that were generated by the plastic deformation during milling [37, 38]. Further increases in annealing temperature for Fe$_{91}$Ni$_8$Zr$_1$ caused a gradual decrease in hardness up to 800 °C, after which
the hardness drops to about 6.44 and 5.85GPa at 900 and 1000 °C, respectively, due to the formation of micron scale grains. However, the hardness values for Fe$_{91}$Ni$_8$Zr$_1$ remains elevated with respect to Fe and Fe$_{92}$Ni$_8$.

Shear punch tests were conducted to validate the hardness values versus grain size for higher annealing temperatures. Figure 5.8 shows the shear stress versus displacement plot from shear punch tests performed on pure Fe, Fe$_{92}$Ni$_8$ and Fe$_{91}$Ni$_8$Zr$_1$ annealed at 900 °C and for Fe$_{91}$Ni$_8$Zr$_1$ alloy annealed at 1000 °C. The shape of the stress - displacement curve varies significantly with the composition of alloys, that is, ultimate shear stress increases and displacement decreases with nickel and zirconium addition. It is clear from Figure 5.8 that the shear stresses of pure Fe and Fe$_{92}$Ni$_8$ alloy reach to 450MPa and 500MPa, respectively, after 1h annealing at 900 °C. A drastic increase in the ultimate shear stress is obvious for the ternary alloy which is close to 1000MPa for annealing at 1000 °C while it becomes even more impressive and ascends above 1120MPa after 1h annealing at 900 °C.

The ultimate shear stresses correlate with the hardness values (H≈6τ), indicating that the alloys have reached the full strengthening after annealing at 900 °C and 1000 °C followed by compaction at 500 °C. Better ductility might be expected from ternary alloys considering the large grain sizes, however, a major difficulty in the study of the mechanical properties of mechanically alloyed materials has been the problem of consolidating the powders free from artifacts and porosity [39] that can mask the inherent mechanical properties and reduce the ductility. It was also reported that the inability of the hard Fe$_2$Zr second phase particles to deform during compression decreases the ductility [40].
5.5. Discussion

In the present work, we investigated the grain growth and mechanical properties of a ternary nanocrystalline alloy (Fe$_{91}$Ni$_8$Zr$_1$), as a function of annealing temperature. The results were compared to pure nanocrystalline Fe and the parent binary nanocrystalline alloy Fe$_{92}$Ni$_8$. Annealing of the as-milled nanostructured for pure Fe and Fe$_{92}$Ni$_8$ alloyed powders resulted in a rapid reduction in hardness, indicating the overall coarsening of the microstructures to the micron scale. This is in agreement with the previous findings [22, 28, 37, 41] where nanocrystalline Fe shows drastic grain growth at temperatures in excess of 0.4 to 0.45 of its melting temperature (450 °C – 500 °C) and Fe–Ni alloys appear to be only marginally more stable than pure Fe. The addition of 1at% Zr to nanocrystalline Fe$_{92}$Ni$_8$ as reported in the present study has a moderate effect on stabilizing the microstructure. The following discussion will address the apparent modes operating to stabilize the microstructure against growth and to increase strength and hardness despite the loss of the nanocrystalline grain size.

The lattice parameter results shown in Figure 5.1 reveal that there is a rapid decrease in the lattice parameter of Fe$_{91}$Ni$_8$Zr$_1$ with increasing temperature while the decrease is notably smaller for pure Fe and Fe$_{92}$Ni$_8$. Electron diffraction patterns and x-ray diffraction patterns did not reveal the presence of secondary phases in as milled powders. It has been reported by different authors that as-milled alloys have lattice parameters larger than those of equilibrium alloys, due to vacancy complexes and dislocations induced by plastic deformation [42]. Elimination of stored strain energy (due to grain boundary relaxation and the annihilation of
the statistically stored dislocations and excess vacancy complexes that were generated by the plastic deformation during milling) in Fe based nanocrystalline alloys was reported to occur well below the onset temperature for grain growth, generally expected to be approximately 400 to 450 °C [28, 37, 41, 43]. Thus it can be expected that the majority of the as-milled strain will be released at temperatures between 100 and 300 °C. The monotonic decrease in lattice parameter observed for the Fe$_{91}$Ni$_8$Zr$_1$ alloy at temperatures well above 300 °C can therefore be explained by the diffusion of Zr solute out of the FeNi lattice. The segregated Zr solute can either reside in the grain boundaries or in intermetallic phases with Fe and or Ni. If it resides within the grain boundaries it can have a two-fold effect; from a thermodynamic perspective it can lower the interfacial energy while, kinetically it can cause solute drag, particularly at low temperatures and/or driving forces. Despite the possibility that thermodynamic effects may contribute to the observed stability, thermal stability observed below 700 °C may be entirely consistent with kinetic stabilization of the grain size and no appeal to thermodynamic stabilization is necessary.

Above 700 °C, a certain fraction of grains grow abnormally into the nanocrystalline matrix. In thermally stabilized Fe based alloys, namely Fe-Ti [44], Fe-Ta [22] and Fe-Zr [21], the development of abnormal grain growth was also observed. Dake et al. [44] attributed abnormal grain growth during annealing in Fe-Ti alloys to reduced free energy with the appearance of the fcc phase which has a lower free energy than a bcc solid solution of the same composition. Thus, any fcc grain nucleated at this temperature range (above 700 °C) in the Fe$_{91}$Ni$_8$Zr$_1$ alloy will grow into a matrix of bcc grains and reduce both the total
area of grain boundaries and the overall stored energy in the sample. This gives the fcc grains a significant growth advantage over bcc grains, resulting in abnormal grain growth and ultimately loss of nanostructure at higher annealing temperatures. This phenomenon and its impact on microstructure evolution of Fe$_{91}$Ni$_8$Zr$_1$ are evaluated by in situ TEM and XRD studies and discussed in detail in [45].

We detected second phases after conducting TEM investigations for the sample annealed at 1000 °C. The precipitation of these intermetallics can be nucleated either in the grain boundaries caused by increased grain boundary diffusion, or in the grain interiors resulting from the entropy driven dissolution of the solutes upon phase transformation [46]. Precipitation of a second phase is an important competing reaction in thermally stabilized systems by solute segregation to grain boundaries since it will consume the solute atoms at the grain boundaries and will allow extensive grain growth [47] if not kinetically hindered. The microstructure of Fe$_{91}$Ni$_8$Zr$_1$ at 900 °C and at 1000 °C exhibits smaller grain sizes than the Fe$_{92}$Ni$_8$ alloy as shown in Figure 5.4. The most likely mechanism for the increased microstructural stability is the particle - pinning effect on grain boundaries by formation of nanoscale intermetallics, effectively reducing the grain boundary mobility. When a grain boundary is moving through a matrix with second phase particles, the pinning force depends on the volume fraction of particles and particle sizes [13, 48]. The potential effectiveness of the second phase particles as grain boundary pinning points can be evaluated using Zener pinning theory [49]:

\[ D_p \alpha = 0.75d \]  

(5.1)
$D_p$ is the diameter of the pinning particles that stabilize the grain size $d$, and $f$ is the particle volume fraction. $\alpha$ is a factor that can vary from 0.25 to 0.5 [49]. Based on the results in Figure 5.5(d) and Figure 5.6 10nm is used as the average particle size, and 1500nm is used as the stable grain size for the specimen annealed at 1000 °C. The volume fraction of particles would be between 0.22 vol. % - 0.44 vol. % for the lower and upper bound of $\alpha$ for Zener pinning to be the sole source of stabilization. Although the volume fraction of precipitates could not be quantitatively determined from Figure 5.5(d), as we will show below it is estimated to be about 3.8pct, which would stabilize the grain size at 87-175nm according to Eq. (5.1). However, the grain size may have already reached 1500nm at 1000 °C annealing by the time enough precipitates are formed to pin the grain boundaries and restrict further coarsening. In addition, Eq. (5.1) was derived for samples in which boundary curvature is the only driving force for grain boundary migration. If coarsening is driven by fcc grains growing into bcc grains, the boundaries experience an additional driving force (the difference in specific free energies of the bcc and fcc phases), and Eq. (5.1) would represent a lower bound for the limiting grain size. In this case the bcc-to-fcc transition contributes to the discrepancy and explains why stagnation of grain growth occurs at significantly larger grain size than those estimated from the conventional Zener pinning model. It is also important to bear in mind that the effectiveness of solute drag as a stabilization mechanism is expected to decrease when the diffusion rate of the Zr atoms approaches that for grain boundary self-diffusion (i.e. at high temperatures) and the stabilization would be controlled by Zener
pinning rather than solute drag for the microstructures obtained at high annealing temperatures.

**Figure 5.9** Hall-Petch plot of the hardness of as-milled and annealed Fe$_{91}$Ni$_8$Zr$_1$ alloy. Pure iron, Fe$_{100-x}$Ni$_x$ (x=0-10) and Fe$_{100-x}$Pb$_x$ (x=1-5) alloys reported by different authors are also displayed.

Hardness data obtained above 800 °C for the ternary alloy correspond to much higher hardness values than estimated based on the Hall-Petch plot in **Figure 5.9** [28, 37, 43]. This suggests that there is another contribution to hardness in addition to grain size. It has been reported that precipitated Fe$_2$Zr second phase is extremely hard, 9.5GPa, [50] and can influence mechanical properties [51]. The strengthening effects of hard second phase
particles are well established for conventional grain size metals with regard to particle size and distribution [52, 53].

The hardness can be divided into three categories based on different sources of the strengthening mechanism [54]:

\[ H = H_{SS} + H_{Oro} + H_{HP} \] (5.2)

\( H \) is the overall hardness, \( H_{SS} \) is the solid-solution strengthening, \( H_{Oro} \) is the Orowan mechanism strengthening and \( H_{HP} \) is the grain size strengthening. Ni in an Fe matrix does not promote significant solid solution hardening due to the similar atomic radii. However, solid solution strengthening can be expected for Zr in the as-milled FeNi matrix due to the large atomic misfit. The lattice parameter data in Figure 5.1 showed that there is a rapid decrease in the lattice parameter of the ternary alloy from 0.28772 nm in the as-milled state to 0.28695 nm for the anneals up to 800 °C, indicating the loss of zirconium solute from solid solution. The lattice parameter remains at 0.28695 nm for higher annealing temperatures as shown in Figure 5.1. This implies that zirconium either segregated to grain boundaries or formed intermetallics for the specimen annealed at high temperatures > 700 °C. Thus, solid solution hardening can be neglected in Eq. (5.2), leaving two possible strengthening mechanisms to be considered: Orowan and Hall-Petch strengthening.

\[ H = H_{Oro} + H_{HP} \] (5.3)
The contribution of the grain size on estimated overall hardness is shown in Figure 5.9 and can be calculated by the Hall-Petch equation [55]:

\[ H_{HP} = H_0 + k d^{-1/2} \] (5.4)

\( H_0 \) (2.5 GPa) and \( k \) (20.4 GPa nm\(^{1/2}\)) are the constants determined from the intercept and the slope, respectively, of the dashed line in Figure 5.9 and \( d \) is grain size.

The flow stress increase due to a random distribution of impenetrable particles can be estimated using the Orowan-Ashby equation where \( r_o = 2b \) is taken as the core radius [56]:

\[ \sigma_{Oro} = \frac{2MGb}{(1.18)4\pi(\lambda-D_P)} \ln \frac{D_P}{2b} \] (5)

\( \sigma_{Oro} \) is the flow stress due to precipitation strengthening, \( M \) is the Taylor factor, taken as 2.5 for the bcc crystal structure [52], \( G \) is the shear modulus, equal to 83 GPa [57], \( b \) is the Burger’s vector, equal to 0.248 nm [57], and \( \lambda \) is the mean interparticle spacing on the slip plane. \( \lambda \), \( D_p \) and the volume fraction of precipitates, \( f \) are related by [58]:

\[ f = \left(\frac{4}{3}\right)\pi\left(\frac{D_p}{\lambda}\right)^2 \] (5.6)

Eq. (5.5) can be rewritten in terms of hardness by applying Tabor’s relationship (\( H \approx 3\sigma \)) [59]:

\[ H_{Oro} = 3 \sigma_{Oro} = 3 \frac{2MGb}{(1.18)4\pi(\lambda-D_P)} \ln \frac{D_P}{2b} \] (5.7)
The combination of Eq. (5.3), Eq. (5.4) and Eq. (5.7) results in Eq. (5.8), which shows the dependence of the overall hardness on the Orowan and grain size strengthening effects.

\[ H = H_0 + 3 \frac{2^{MGb}}{(1.18)\lambda} \ln \frac{D_p}{2b} + k\lambda^{-1/2} \]  

Grain size strengthening \((H_{HP})\) was calculated from Eq. (5.4) (also confirmed by the Fe-Ni data points on the plot) and subtracted from the overall hardness to obtain the Orowan strengthening \((H_{Oro})\). It was found that hardness due to the Orowan strengthening indicated by arrows in Figure 5.9 is 3.5GPa, 3GPa and 2.4GPa for the samples annealed at 800 °C, 900 °C and 1000 °C, respectively. We can estimate the interparticle spacing from Eq. (5.7) and the precipitate volume fraction from Eq. (5.6) as approximately 37nm and 3.8pct, respectively for the sample annealed at 1000 °C. As stated previously this would stabilize the grain size at 87-175nm at 1000 °C. It is worth noting that the contribution from Orowan strengthening to overall hardness decreases with increasing annealing temperature. This suggests that second phase particles coarsened and yielded larger interparticle spacing and less hardening according to Eq. (5.7).

5.6. Conclusions

Pure Fe, Fe\(_{92}\)Ni\(_8\), and Fe\(_{91}\)Ni\(_8\)Zr\(_1\) alloys have been investigated with respect to their microstructure and mechanical properties for annealing temperatures up to 1000 °C. From the results the following conclusions are drawn:

- Using mechanical milling, Fe-Ni-Zr powders were hardened up to 10GPa by the mechanism of grain refinement strengthening and solid solution hardening.
• Subsequent annealing of pure Fe and Fe$_{92}$Ni$_8$ alloy leads to reduced hardness and extensive grain growth, indicating that the nanostructure developed by ball milling is not retained during annealing.

• Annealing studies showed that up to 600 °C, the microstructure of Fe$_{91}$Ni$_8$Zr$_1$ alloy remains nanoscale (below 15nm). At 700 °C annealing, grain growth of the ternary alloy occurs in an abnormal manner. However, the average grain size is still nanoscale, that is, smaller than 100 nm. This remarkable thermal stability of the microstructure, in comparison to pure Fe and Fe$_{92}$Ni$_8$ alloy, is attributed to solute drag with possible some reduction in the total grain boundary energy due to solute segregation.

• At higher annealing temperatures, Zener pinning of the grain boundaries by Fe$_2$Zr second phase particles contributed to the stabilization of the microstructure.

• The results from the microhardness and shear punch tests show that Orowan particle strengthening is an important contributor to strengthening in Fe$_{91}$Ni$_8$Zr$_1$ at high temperatures.

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6. AN IN SITU EXPERIMENTAL STUDY OF GRAIN GROWTH IN A NANOCRYSTALLINE Fe$_{91}$Ni$_8$Zr$_1$ ALLOY

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6.1. Abstract

Grain growth and microstructural evolution of thermally stabilized Fe$_{91}$Ni$_8$Zr$_1$ were investigated by in situ and ex situ studies. Our investigations suggest that the microstructural evolution is fairly slow and the microstructure shows stabilization up to about 700 °C. Above this temperature, a certain fraction of grains grow abnormally into the nanocrystalline matrix, resulting in a bimodal microstructure and causing the complete loss of thermal stability. The reason for abnormal grain growth and the loss of thermal stability is identified as the appearance of the fcc $\gamma$-phase and consequent reduction in the total area of grain boundaries and the overall stored energy.

Keywords: Nanocrystalline materials; Thermal stability; Abnormal grain growth; in situ transmission electron microscopy (TEM); in situ X-ray diffraction (XRD); Phase transformation

6.2. Introduction

Nanostructured materials are promising for structural applications [1]. However, their widespread application is limited by an inherently high driving force for thermally induced
grain growth, even at low temperatures [2-4]. Accordingly, the understanding of and control over grain growth in nanoscale materials is of great technological and scientific importance [5] as many physical properties (i.e. mechanical properties) are functions of the average grain size and the grain size distribution within the microstructure [6,7].

In the last decade, extensive investigations into the stabilization of metallic nanocrystalline microstructures have been carried out to improve their stability. In spite of a high driving force for grain growth, significant stabilization has been reported [8-13]. This stabilization and resistance to grain growth has been attributed to reducing the energy of the grain boundaries with solute segregation (i.e. thermodynamic stabilization) [14] or reducing the mobility of the grain boundaries by grain boundary pinning (kinetic stabilization) [15]. Nevertheless, the reported works have, for the majority, been based on analysis of evolved microstructures post thermal processing, and not by direct observation at temperature. This is of fundamental importance as it is unclear how grain coarsening occurs in systems stabilized against growth. The advantage of in situ microstructural evolution studies comes from directly observing this phenomenon and its kinetics such that the respective mechanism and driving force can be understood in detail.

In this work, we used in situ transmission electron microscopy (TEM) with video imaging and in situ X-ray diffractometry (XRD) to directly follow grain growth and microstructural evolution in such a system as a function of temperature. Ex situ experiments are also reported giving a broader perspective of the microstructure at longer annealing times. The information obtained from these experiments enables the real time observation of
microstructural evolution and phase transformation and provides a unique view of dynamic reactions as they occur.

6.3. Experiments

A ternary Fe$_{91}$Ni$_{8}$Zr$_{1}$ alloy was chosen as the stabilized Fe-based nanocrystalline alloy for this study. As starting materials, appropriate masses of elemental Fe (99.9%), Ni (99.9%), and Zr (99.7%) powders were mixed with 440C stainless steel balls and sealed in a hardened steel vial under an argon atmosphere ($O_2 < 2$ ppm) prior to milling. Ball milling was performed with a SPEX 8000 model mixer-mill for 20 h. After milling, powders were isochronally annealed at 600 °C, 700 °C, 800 °C, and 900 °C in a 98% Ar + 2% H$_2$ gas atmosphere for 1 h with subsequent cooling in the furnace where the cooling rate was less than 2-3 °C per second. The as-milled powder was used as the starting material for annealing at each temperature. Microstructure of the samples is characterized by focused ion beam channeling contrast imaging (FIB-CCI). FIB-CCI images were obtained using backscattered electrons produced by the ion beam from one powder particle.

The ion beam was also used to prepare an electron transparent sample from as-milled powder for the in situ transmission electron microscopy (TEM) annealing experiments. The sample was mounted in the Aduro holder [16] and imaged in a Hitachi HF-2000 TEM. The Aduro system uses a flat, ceramic membrane as the active specimen support to enable fast, stable and accurate thermal analysis. The membrane has a small thermal mass, which allows for extremely fast heating rates up to $10^6$ °C/sec with virtually instantaneous temperature
stabilization and accuracy of ± 0.5-3 °C. The whole experiment was recorded with a video imaging in bright field (BF) mode to directly observe grain growth in the initially nanocrystalline sample. The increment of the temperature was 50 °C during in situ annealing. High temperature XRD analysis was carried out using an Anton Paar HTK 2000. Samples consisted of a thin layer of powder place onto a Pt strip. A given sample was then brought into alignment on the optical axis of the diffractometer. The heating chamber was pumped down, under a vacuum of approximately 10^{-3} Torr and backfilled with a He 3% hydrogen forming gas to prevent oxidation of the powders during examination. The sample was then resistively heated to temperature at a rate of 60 °C/min, at which point it endured a 10 min isothermal anneal, before performing a 17 min long diffraction scan at the respective temperature. The sample temperature was increased to the next desired set point and the isothermal/scanning process repeated as done previously. This process was repeated to cover the following temperature range of 30 °C, 500 °C, 600 °C, 700 °C, 750 °C, 800 °C, 900 °C and again at 31 °C to complete the test. The grain size at temperature was calculated using the Scherrer Method.

6.4. Results and Discussion

Figure 6.1 illustrates the morphological evolution of nanocrystalline Fe_{91}Ni_{8}Zr_{1} subjected to the in situ thermal annealing in the TEM up to 900 °C. The snapshots were taken from the video and, in general, the majority of the observed grain growth ceased within the time frame given in Figure 6.1. The real time monitoring of the microstructure during in situ
thermal treatments revealed negligible grain growth until 500 °C. Grain growth became discernible at 500 °C and all visible grains in the view remained smaller than 50 nm up to annealing to 600 °C. Gradual increase of the average grain size (i.e. average grain diameter) is observed with the increase in temperature and a few grains reached the size of 100 nm after 15 s at 700 °C. Above this temperature, a certain fraction of grains grew rapidly into the nanocrystalline matrix within the first few seconds of annealing, resulting in a bimodal microstructure at 750 °C. Abnormal grain growth continued at the expense of their neighbors with the increase in temperature to 800 and 850 °C. Further increase in annealing temperature to 900 °C caused the complete consumption of the smaller grains in the microstructure and led to normal grain growth where the microstructure exhibits a uniform increase in size. The last micrograph in Figure 6.1 shows that grains in the viewing area are fairly uniform and reached the size of 400 nm after 25 s at 900 °C, and the nanocrystalline microstructure is lost.
Figure 6.1 Sequence of plan-view bright field TEM micrographs showing the morphological evolution of nanocrystalline Fe$_{91}$Ni$_8$Zr$_1$ alloy during in situ thermal treatments. Below 700°C, the nanocrystalline microstructure remains stable. Above this temperature, a sudden abnormal grain growth is observed resulting in loss of thermal stability. All images are recorded at the same magnification. Temperature and the time at given temperature are displayed at the upper left corner of each micrograph.
Figure 6.2 Channeling contrast images of Fe$_{91}$Ni$_8$Zr$_1$ as-milled, annealed at 600°C, 700°C, 800°C, and 900°C. There is not significant grain growth after one hour annealing at 600°C. Above 700°C, a certain fraction of grains grow abnormally into temperatures, nanocrystalline state is lost and sudden grain growth is observed.
In addition to rapid and abnormal grain growth above 700 °C, we also observed a loss of contrast between neighboring grains with the eventual disappearance of the grains or the boundary between them. The orientation of two grains has to be within a few degrees in order to appear in the same image. The fact that neighboring regions appear/disappear suggests that these regions represent grains that have rotated into alignment with their neighbors to attain the orientation of one of its neighbors. The driving force for the grain rotation might arise from the tendency of the grains to reduce their overall grain boundary energy due to misorientations. This rotation of the adjoining grains is presumably required for crystallographic alignment before the subsequent merging of the two grains to attain the minimum crystallographic energy state [17].

*In situ* TEM observation indicated that microstructural changes and grain growth are fairly slow as the nanocrystalline state remains stable until 700 °C. However, they become extremely fast especially for the first few seconds of annealing at above 750 °C, resulting in sudden abnormal grain growth and loss of thermal stability. The view of the microstructure was limited in the *in situ* TEM experiment and the annealing time was rather short. We took advantage of *ex situ* annealing to investigate the microstructure subjected to longer annealing time and to eliminate the possible influences to grain growth by the free surfaces of the TEM sample. Figure 6.2 reveals low magnification FIB images of the as-milled specimen and annealed at 600 °C, 700 °C, 800 °C, and 900 °C for 1 h. Upon comparison of the as-milled microstructure with samples annealed isochronally, we see that there is not a significant grain growth after one hour annealing at 600 °C. Above this temperature, at 700 °C, a certain
fraction of grains grow abnormally into the nanocrystalline matrix, resulting in a bimodal microstructure. That is, a few grains grew to above the nanoscale, greater than 100 nm, while the majority of the microstructure remained nanoscale. The extent of abnormal grain growth continues to increase at 800 °C, consuming the majority of the microstructure and leaving only a very small fraction of the microstructure nanocrystalline. Further increases in annealing temperature to 900 °C caused the complete consumption of the smaller grains (nano and ultrafine) in Fe\textsubscript{91}Ni\textsubscript{8}Zr\textsubscript{1}, which leads to the formation of a more uniform large grain assembly.
Figure 6.3 In situ XRD scans of a Fe$_{91}$Ni$_8$Zr$_1$ alloy during isochoric annealing from room temperature to 900°C. The first scan 30°C is the initial microstructure showing broad bcc Fe peak. As indicated, fcc Fe peak appears around 650°C and bcc Fe peak remains stable up to 900°C. The last scan 31°C is after heat treatment showing the disappearance of the fcc Fe peaks and the reappearance of the bcc Fe.

Consistent observation from *ex situ* FIB and *in situ* TEM results demonstrates that the majority of the nanocrystalline microstructure of the ternary alloy remains stable up to about 700 °C showing excellent thermal stabilization compared to reported examples of pure iron and Fe-Ni alloys [18-21]. It is postulated that the grain growth in Fe-Ni-Zr alloy below 700 °C was blocked by the interaction between the grain boundaries and zirconium solute by the
solute drag affect and reduction in the grain boundary energy [22]. Above 700 °C, the
development of abnormal grain growth and consequent loss of thermal stability was observed
by the in situ and ex situ studies. Dake and Krill [23] reported that the abnormal grain growth
in binary Fe-Ti alloy is due to the α-to-γ transformation above 900 °C. This phenomenon and
its impact on microstructure evolution and abnormal grain growth were investigated by in
situ X-ray diffractometry for identification of the phases present during thermal annealing.

Figure 6.3 shows diffraction patterns obtained for Fe$_{91}$Ni$_8$Zr$_1$ during isochoric annealing
up to 900 °C for a total duration of 4 hrs, such that analysis at each temperature took
approximately 30 mins. A slight horizontal shift as a function of temperature was noticed in
the peak positions due to thermal expansion of the lattice with increase in temperature [24].
The XRD results reveal that the microstructure remains pure bcc up to annealing to 650 °C
where an fcc peak was first observed. The intensity of the fcc peak at 650 °C is substantially
lower suggesting that the volume fraction of the fcc phase is very small and it is just
beginning to nucleate and grow. It is worth noting that the fcc peak is much narrower than
the bcc peak at and above 700 °C. While the bcc peak narrows with temperature it remains
fairly wide even at 800 – 900 °C. It indicates that even at small volume fractions the fcc
grains are much larger on average than the bcc grains, implying that the large grains formed
above 700 °C are fcc while small grains detected in the microstructure are still bcc.
Comparison of Figures 6.1 and 6.2 with the data obtain from Figure 6.3 suggests that the bcc
to fcc phase transformation is, indeed, responsible for the rapid formation of large (fcc)
grains in (bcc) nanocrystalline matrix above 700 °C and caused the loss of thermal stability.
To evaluate this effect, we can estimate the driving pressure $P$ for grain growth, which determines the velocity $v$.

$$v = M \cdot P = M_0 e^{-Q/RT} \cdot P$$  \hspace{1cm} (6.1)

$M$ is the grain boundary mobility and $Q$ is the activation energy. If we assume the grains in the nanocrystalline TEM specimen (Figure 6.1) are hexagonal prisms (as in thin films) of width $D$ and thickness $h$, and define the driving force for grain boundary migration as the total free energy reduction for incremental growth $\delta D$, then the driving force for an fcc $\gamma$-Fe grain growing in a surrounding bcc $\alpha$-Fe grain matrix is due to the change in volume free energy $(\delta G)$, surface energy $(\delta \Gamma_s)$, and interphase energy-grain boundary energy $(\delta \Gamma_{i/gb})$.

$$\delta G = (g^\gamma - g^\alpha) \delta V = (g^\gamma - g^\alpha) \frac{3\sqrt{3}}{2} D h \delta D$$  \hspace{1cm} (6.2)

$$\delta \Gamma_s = (\Gamma^\gamma_s - \Gamma_s^\alpha) \delta A_s = (\Gamma^\gamma_s - \Gamma_s^\alpha) \frac{3\sqrt{3}}{2} D \delta D$$  \hspace{1cm} (6.3)

$$\delta \Gamma_{i/gb} = \left( \Gamma_{i}^{\gamma/\alpha} \delta A_i - 3h \Gamma_{gb}^\alpha \delta D \right) = \left( \Gamma_{i}^{\gamma/\alpha} - \Gamma_{gb}^\alpha \right) 3h \delta D$$  \hspace{1cm} (6.4)

$A_s$ is the free surface area, $A_i$ is the grain interface area, $V$ is the volume of grains, $g$ is the bulk free energy per volume, $\Gamma_s$ is the surface energy per area, $\Gamma_i$ is the $\alpha$-to-$\gamma$ interface energy per area, and $\Gamma_{gb}$ is the grain boundary energy per area. The pressure acting on the grain interfaces will be;

$$P = \frac{1}{A_i} \left[ \frac{\delta G}{\delta D} + \frac{\delta \Gamma_s}{\delta D} + \frac{\delta \Gamma_{i/gb}}{\delta D} \right]$$  \hspace{1cm} (6.5)
Combination of Eq. (6.2-6.5) will give Eq. (6.6) where \( P > 0 \) will be outward and will drive grain growth.

\[
P = \left[ \frac{1}{3Dh} \right] \left[ \frac{3\sqrt{3}}{2} Dh \left( g^\gamma - g^\alpha \right) + \frac{3\sqrt{3}}{2} D \left( \Gamma^\gamma_s - \Gamma^\alpha_s \right) + 3h \left( \Gamma^\gamma_{\ell} - \Gamma^\alpha_{\ell} \right) - \Gamma^\alpha_{gb} \right]
\] (6.6)

\[
P = \left[ \frac{\sqrt{3}}{2} \left( g^\gamma - g^\alpha \right) + \frac{\sqrt{3}}{2h} \left( \Gamma^\gamma_s - \Gamma^\alpha_s \right) + \frac{1}{D} \left( \Gamma^\gamma_{\ell} - \Gamma^\alpha_{\ell} \right) \right]
\] (6.7)

The grain boundary energy, interphase boundary energy, \( \alpha \)-to-\( \gamma \) volume free energy change, and \( \alpha \)-to-\( \gamma \) surface energy change are reported to be 0.70 J/m\(^2\) [25], 0.8 J/m\(^2\) [26], 1230 J/mol at 727\(^\circ\)C [27], and 0.053 J/m\(^2\) [26] respectively. If \( \gamma = \alpha \) (before phase transformation) then the driving pressure \( P = 0 \). If \( \gamma \) grain forms in \( \alpha \) matrix, it will change the pressure on grain boundaries and there will be a driving force to grow the \( \gamma \) grains in the \( \alpha \)-grain surroundings.

If we use 150 nm as the film thickness, the pressure for grain growth \( P = +150 \) MPa. By comparison of \textit{in situ} TEM and \textit{ex situ} FIB images, it appears that surface energy in the \textit{in situ} TEM sample does not affect the abnormal grain growth significantly. Moreover, the calculations for \( P \) indicate that crucial contributions to grain growth come from the reduction in the grain boundary energy and, mostly, from the volume free energy change for \( \alpha \)-to-\( \gamma \).

This change is large (1230 J/mol) which gives the \( \gamma \) grains a significant growth advantage over \( \alpha \) grains, thereby triggering sudden grain growth in abnormal manner and eventually causing loss of thermal stability. The last XRD scan at 31 \(^\circ\)C is after heat treatment and shows the disappearance of the fcc \( \gamma \) peaks and the reappearance of the bcc \( \alpha \) peaks.
The bcc phase remains up to 900 °C (see Figure 6.3) even though it is expected to vanish according to the Fe-Ni-Zr phase diagram [28]. It is well-known that the austenite phase nucleates at GBs, triple points or near regions in Fe-based alloys [29] and that alloying elements, such as nickel, are redistributed during the nucleation and growth of the austenite phase [30] enriching the solute atoms at some regions and depleting it in others. We propose that the initial solute distribution of Ni (an fcc stabilizer), locally high in some regions, will favor the nucleation and growth of austenite at temperatures near the bcc to fcc transition (~700 °C). The growth and formation of these new fcc grains as temperature increases > 700 °C will lead to the incorporation of Ni in higher concentrations than the average global content within or near the fcc grains. Through mass balance the amount of nickel consumed or redistributed during austenite formation and growth must also be removed or redistributed from the surrounding matrix of nano-grains. The resistance to transformation by these newly depleted (lower nickel content) nano-grained regions is now a function of both composition and temperature as prescribed by the α-to-γ equilibrium phase limits. As more austenite grains nucleate and grow the local nickel solute content in some regions may approach zero, thereby pushing the transition temperature up to that of pure iron, 913 °C, locally. The diffusivity (for Fe - 10 at% Ni) and diffusion distance calculated from Eq. (6.8) and Eq. (6.9) were found to be 2.72x10^{-14} cm²/sec (based on Q and D₀ values obtained from ref. [31]) and 70 nm, respectively, after 30 min annealing at 900 °C.

\[
\bar{D} = D₀ \exp \left( -\frac{Q}{RT} \right)
\]  

(6.8)
\[ r = \sqrt{\bar{D} t} \]  

(6.9)

\( \bar{D} \) is the diffusivity, \( D_o \) is the frequency factor, \( Q \) is the activation energy, \( r \) is the diffusion distance, \( t \) is the annealing time, \( T \) is the annealing temperature, and \( R \) is the gas constant.

This suggests that nickel atoms had the opportunity during thermal annealing to be redistributed over length scales approximately equal to or larger than the grain size within the retained nanocrystalline regions. This implies that the small grains observed at 800 – and 900 °C in the FIB images in Figure 6.2 are bcc \( \alpha \) grains that never transformed to or were consumed by fcc \( \gamma \) grains during thermal annealing.

**Figure 6.4** Grain size analyses of the diffraction peaks shown in Figure 6.3, plotted against annealing temperature for the duration of 30min at each temperature. The bcc phase consists of nanoscale grains until 900°C, which grow an initial size of 10nm to a final size of 25nm. The fcc peak was intense enough to calculate grain size at 700°C.
Figure 6.4 shows the Scherrer grain size analysis of the diffraction peaks reported in Figure 6.3. It reveals that the grains of the bcc phase grow from an initial size of 10 nm to a final size of 25 nm after 30 min annealing at 900 °C (for a total duration of 4hrs). The fcc phase appears at 650 °C but the corresponding diffraction peak is not intense enough to allow calculation of the grain size. The estimated grain size of the fcc phase was approximately 105 nm at 700 °C, and proceeded to increase with increasing annealing temperature.

6.5. Conclusions

The observations from in situ and ex situ experiments reported above and the information obtained from these studies enable us to understand the grain growth in stabilized Fe-Ni-based alloys. From our observations it is suggested that the microstructural evolution is fairly slow and the microstructure shows a solid stabilization up to about 700 °C. This is attributed to zirconium segregation to grain boundaries and solute drag effect. Above 700 °C the grain growth kinetics becomes extremely fast, especially for the first few seconds of annealing and causes a sudden grain growth in abnormal manner. The reasons for abnormal grain growth and the loss of thermal stability were identified as the appearance of the fcc γ phase and consequent reduction in the total area of grain boundaries and the overall stored energy in the sample.

Nomenclature

$M$ is the grain boundary mobility
$Q$ is the activation energy
ν is the velocity of grain boundary

D is the grain diameter

h is the specimen thickness

δD is the incremental growth

δG is the change in volume free energy

δГs is the change in surface energy

δГi/Гb is the change in the interphase energy-grain boundary energy

A_s is the free surface area

A_i is the grain interface area

V is the volume of grains

g is the bulk free energy per volume

Гs is the surface energy per area

Γ_i is the α-to-γ interface energy per area

Γ_{gb} is the grain boundary energy per area

P is the pressure acting on the grain interfaces

D̅ is the diffusivity

D_o is the frequency factor

r is the diffusion distance

t is the annealing time

T is the annealing temperature

R is the gas constant

6.6. References


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7. THERMAL STABILITY AND MECHANICAL PROPERTIES OF NANOCRYSTALLINE FE-NI-ZR ALLOYS PREPARED BY MECHANICAL ALLOYING

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Submitted for Publication

7.1. Abstract

The stability of nanostructured Fe_{100-x-y}Ni_xZr_y alloys during post processing at elevated temperatures has been investigated. Emphasis was placed on understanding the effects of composition and microstructural evolution on grain growth and mechanical properties at temperatures near and above the bcc-to-fcc transformation. Results reveal that microstructural stability is lost due to the bcc-to-fcc transformation (occurring at 700°C) by the sudden appearance of abnormally grown fcc grains. However it was determined grain growth can be suppressed kinetically at higher temperatures for high Zr content alloys by precipitation of intermetallic compounds. Eventually at high enough temperatures, and regardless of composition, the retention of nanocrystallinity was lost, leaving behind fine micron grains filled with nanoscale intermetallic precipitates. Despite the increase in grain size, the in-situ formed precipitates were found to induce an Orowan hardening effect rivaling that predicted by Hall Petch hardening for the smallest grain sizes. The overall transition from grain size strengthening to precipitation strengthening is reported for these
alloys. The large grain size and high precipitation hardening result in a material which exhibits high strength and significant deformation properties.

**Keywords:** Nanocrystalline materials; Thermal stabilization; Grain growth; Zener pinning; Mechanical properties; Fe-base alloys

### 7.2. Introduction

Steels with nanocrystalline or ultra-fine grain sizes offer the intriguing properties such as high strength [1-3] and toughness [4, 5]. The Hall-Petch relationship predicts that there is an inverse relationship between the material’s strength and the average grain size, as illustrated in Eq. (7.1) [6, 7] and the largest improvements of which occur at the finest grain size (<100 nm).

\[
\sigma_y = \sigma_0 + kd^{-1/2}
\]  

(7.1)

\(\sigma\) is yield stress, \(\sigma_0\) is the intrinsic yield stress, \(k\) is a constant for a given material, and \(d\) is the grain diameter. However, grain boundaries are sources of internal energy due to the high atomic disorder and such small grain size configurations account for a large increase in the total free energy of the system according to Eq. (7.2), making the nanomaterials unstable [8-11].

\[
dG \approx \gamma dA
\]  

(7.2)
As grain boundaries have a surface energy term $\gamma$, decreasing the grain boundary area can decrease the internal stored energy. Thus, the reduction of this excess free energy $dG$ provides a strong driving force for grain growth during the processing steps (i.e. consolidation) and/or product’s life at potentially at high temperatures. It is therefore critical to determine the grain size evolution of such microstructures, as it can drastically change the mechanical properties.

Here, we describe the microstructural evolution and grain growth in mechanically alloyed nanocrystalline Fe-Ni alloys with Zr addition and differentiate the stabilization mechanisms acting on grain boundaries. Fe-Ni alloys are chosen for stability investigations since they are important for understanding the behavior of many steels and other ferrous alloys. It has been reported [12] that the addition of Ni to Fe did very little to stabilize the Fe-Ni system against grain growth. Zirconium was shown to be an effective grain size stabilizer in pure Fe and Fe-base systems [13-16] and will be investigated in this study. We found that the grain growth process occurs at higher annealing temperatures with increasing zirconium additions. We present experimental evidence that reveal the possible reasons for the microstructural stability and elevated mechanical properties in spite of micron size grains formed in some compositions.

### 7.3. Experiments

Pure Fe, Fe-Ni, and Fe-Ni-Zr alloys were prepared by mechanical alloying. Appropriate masses of Fe (99.9 %), Ni (99.9 %), and Zr (99.7 %) powders were mixed with 440C
stainless steel balls and sealed in a hardened steel vial under an argon atmosphere (O₂ < 2 ppm) prior to milling. A ball-to-powder mass ratio of 10:1 with a powder charge of 5.1g was loaded into the vials and milled for 20 h using a SPEX 8000 model mixer-mill. As-milled powders were isochronally annealed up to 1000 °C in a 98% Ar + 2% H₂ gas atmosphere for one hour with subsequent cooling in the furnace where the cooling rate was less than 2-3 °C per second. X-ray diffraction analysis of the as-milled and heat treated powders was performed with a Rigaku X-ray diffractometer using CuKα (λ = 0.1542) radiation. The lattice parameters and grain sizes were estimated using Cohen’s method [17] and the Scherrer formula [18], respectively. The instrumental broadening was removed as a function of 2θ using a standard alumina sample and assuming a Gaussian peak shape. The lattice strain was estimated from Williamson-Hall analyses [19]. Microstructure of the samples is characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and focused ion beam (FIB) imaging. The ion beam was used for ion channeling contrast imaging (FIB-CCI) and to prepare electron transparent samples for TEM studies. Microhardness tests were carried out using a Vickers hardness tester with a 50 g load. The standard deviation was taken as the error after 8-10 measurements. Shear punch test samples were compacted under an applied uniaxial pressure of 2.5-3GPa and at a temperature of 500 °C in tungsten carbide dies. Hardness measurements confirmed that no significant grain growth had occurred after hot compaction. Densities varied between 93 and 96 % of the theoretical values. Shear punch tests were run with an MTS Alliance RT/10 tensile frame at a
speed of 0.01 mm/min. Details of the experimental setups for shear punch tests were described elsewhere [20].

7.4. Results

7.4.1. Microstructural characterization of as-milled powders

Figure 7.1 shows (a) the as-milled X-ray diffraction patterns and (b) lattice parameter of selected alloys as a function of alloy compositions and annealing temperatures. X-ray diffraction patterns from as-milled powders (Fig. 7.1(a)) reveal only the presence of bcc Fe. Upon further analysis of the x-ray spectra the fundamental reflections were found to be shifted to lower angles indicating the possible formation of binary Fe-Ni and ternary Fe-Ni-Zr solid solution between the respective elements. The peaks of the as-milled alloys exhibit a significant broadening due to the refinement of grain size and the increase of internal lattice strain. The calculated grain size and lattice strain for the as-milled powders were found to be within 8-11 nm and 0.62-0.94 %, respectively, as indicated in Figure 7.1(a). Our results are in good agreement with the reported grain size and lattice strain of as-milled iron [13, 21]. Measurements of the respective lattice parameters (Fig. 7.1(b)) show a systematic increase due to alloy addition (nickel and zirconium) and support the idea of solid solution formation. The room temperature values are the as-milled lattice parameters and they include internal lattice strain due to point defects, dislocations, and grain boundary structure introduced by mechanical alloying [12].
Figure 7.1 (a) As-milled X-ray diffraction patterns as a function of alloy compositions, b) lattice parameters of selected alloys as a function of alloy compositions and annealing temperatures. The room temperature values are the as-milled lattice parameter. Incremental reduction of the lattice parameter at each annealing temperature is given by %.
7.4.2. Structural evolution and grain growth in annealed samples

Figure 7.2 shows the microstructural evolution of Fe-Ni-Zr alloys as a function of annealing temperatures and alloy compositions using focused ion beam channeling contrast images. The contrast differences arise due to the ion channeling effect and the micrographs are presented in a way to make the comparison easier between the respective alloy compositions and annealing temperatures. The microstructure of Fe$_{91}$Ni$_8$Zr$_1$ annealed at 700 °C (Fig. 7.2(a)) shows abnormal grain growth. That is, a few grains grew above 500 nm while most grains remained nanoscale. The extent of abnormal grain growth continues to increase at 800 °C for 1 at% Zr, consuming the majority of the microstructure and leaving only a very small fraction of the microstructure nanocrystalline (Fig. 7.2(b)). Further increase in annealing temperature above 800 °C caused complete consumption of the smaller grains in Fe$_{91}$Ni$_8$Zr$_1$, which leads to the formation of more uniform large grain assembly with an average diameter of 750 nm at 900 °C (Fig. 7.2(c)) and 1500 nm at 1000 °C (Fig. 7.2(d)).

Figures 7.2(g) and (h) show the microstructures of Fe$_{89}$Ni$_8$Zr$_3$ at 800 °C and Fe$_{88}$Ni$_8$Zr$_4$ annealed at 900 °C, respectively, i.e. the effect of increasing Zr content. Upon comparison of Fe$_{91}$Ni$_8$Zr$_1$ annealed at 700 °C (Fig. 7.2(a)) with Fe$_{89}$Ni$_8$Zr$_3$ annealed at 800 °C (Fig. 7.2(g)) and Fe$_{88}$Ni$_8$Zr$_4$ annealed at 900 °C (Fig. 7.2(h)), we see that the grain growth process in Fe-Ni alloys occurs at higher annealing temperatures with higher zirconium additions. It was also found that reducing the nickel amount from 8-to-4 at% does not affect the grain size significantly for 1 at% Zr at 900 °C, comparatively (Figs. 7.2(c and f)) and after annealing at 1000 °C (Figs. 7.2(d and e)). Nevertheless, the micrographs obtained after annealing at 1000
°C reveal that the microstructures consist of large grains having an average diameter of 1.5 microns for 1 at% Zr (Figs. 7.2(d and e)) and a slightly smaller grain size for 4 at% Zr (Fig. 7.2(i)).

Figure 7.2 FIB micrographs versus alloy compositions (at%) and annealing temperatures; a) Fe-8Ni-1Zr at 700 °C, b) Fe-8Ni-1Zr at 800 °C, c) Fe-8Ni-1Zr at 900 °C, d) Fe-8Ni-1Zr at 1000 °C, e) Fe-4Ni-1Zr at 1000 °C, f) Fe-4Ni-1Zr at 900 °C, g) Fe-8Ni-3Zr at 800 °C, h) Fe-8Ni-4Zr at 900 °C, i) Fe-8Ni-4Zr at 1000 °C
Additional microscopy and X-ray studies indicate that grain growth at high annealing temperatures is coupled with second phase precipitation. X-ray diffraction peaks displayed in Figure 7.3 show that the microstructure of Fe$_{91}$Ni$_8$Zr$_1$ annealed at 1000 °C consists of fundamental reflections of alpha bcc Fe only, with no other phases present, while the intermetallic peaks become discernible at the same annealing temperature for Fe$_{90}$Ni$_8$Zr$_2$. Additionally, the temperature at which the intermetallic peaks first appear is shown to decrease to 800 °C with 3 at% Zr and to 700 °C with 4 at% Zr additions. Further microscopy investigations reveal that second phase particles were present in the microstructure of Fe$_{91}$Ni$_8$Zr$_1$ annealed at 1000 °C although they were not detected by X-ray studies, suggesting that second phases occupy only a small portion of the microstructure or are very small in nature. Figure 7.4 shows TEM images of Fe$_{91}$Ni$_8$Zr$_1$ (Figs. 7.4(a-c)) and Fe$_{88}$Ni$_8$Zr$_4$ (Figs. 7.4(d-f)) alloys both annealed at 1000 °C. Micron size grains are present in Fe$_{91}$Ni$_8$Zr$_1$ with small precipitates within grains and along the grain boundaries. In comparison Fe$_{88}$Ni$_8$Zr$_4$ shows a reduced grain size and increased second phase particles size exhibiting a larger volume fraction for the same annealing temperature as Fe$_{91}$Ni$_8$Zr$_1$. The precipitation of these intermetallics may be nucleated either in the grain boundaries caused by increased grain boundary diffusion, or in the grain interiors resulting from the entropy driven dissolution of the solutes from the grain boundaries [11].
Figure 7.3 X-ray diffraction lines as a function of annealing temperatures and alloy compositions. Intermetallics form at lower temperatures with increasing Zr content.
7.4.3. Hardness and shear Punch tests of annealed samples

Figure 7.5 summarizes the changes in (a) hardness and (b) grain size from XRD, TEM and FIB investigations as a function of alloy compositions and annealing temperatures. Grain size estimates above 700 °C were not exact since the obtained microstructures were bimodal, but they are comparative with hardness. Also included for comparison is data for nanocrystalline pure Fe and Fe-Ni alloys. The room temperature values are the as-milled
hardness and grain size. The grain size and hardness for the as-milled powders were found to be within 8-11 nm and 8.7-11.7 GPa, respectively. There is an increase in the as-milled hardness with the addition of Ni and Zr as a result of grain refinement strengthening and solid solution hardening of the Fe matrix by the oversized Zr atoms. The annealing of pure Fe, Fe_{96}Ni_{4}, and Fe_{92}Ni_{8} leads to a small reduction in hardness at 400 °C whereas the hardness decreases dramatically to less than 3.5 GPa between 400 – 700 °C as a result of rapid grain growth. The initial annealing of Fe-Ni-Zr alloys at 400 °C and 600 °C causes a small decrease in hardness and the grain size does not increase significantly, remaining approximately constant below 15 nm as measured by x-ray analysis. In comparison to Fe-Ni alloys, the reduction in hardness was gradual in Fe-Ni-Zr alloys up to 800 °C, after which the hardness drops to about 6 GPa at 900 °C. More importantly, the hardness values for Fe-Ni-Zr alloys appear inversely proportional with Zr amount at and above 900 °C while remaining extremely elevated with respect to Fe and Fe-Ni alloys even at the annealing temperature of 1000 °C which represents a homologous temperature of 0.7.
Figure 7.5 (a) Hardness and (b) grain size (from XRD, FIB, and TEM) versus annealing temperature. Room temperature hardness and grain size are the as-milled values.
Shear punch tests were conducted to validate the elevated hardness values for large grained samples obtained at high annealing temperatures and to check the effect of precipitates on samples’ strength and ductility. Figure 7.6 shows the shear stress versus displacement plot from shear punch tests and SEM shear surface images performed on selected compositions. The shape of the stress - displacement curve varies significantly with the composition of alloys. The ultimate shear stress increases dramatically with the addition of Zr to Fe-8 at%. Ni. However, the ductility is drastically reduced when the Zr addition is increased from 1 to 4 at%. 1at% Zr alloys showed ductility leading to the shear failure whereas an abrupt shear failure with no ductility was observed for the sample containing 4 at% Zr as indicated by the SEM images in Figure 7.6. In addition, the ultimate shear stress is lower for 4 at% Zr although it has smaller grain size compared to 1 at% Zr additions to Fe-Ni alloys (Figs. 7.2(d and i)). The trend observed in the shear punch test results also agrees with the inverse relation observed between zirconium amount and hardness results at high annealing temperatures (~800-1000 °C, Figure 7.5(a)). This trend suggests that formation of second phases increases mechanical properties with 1 at% Zr additions, but this effect is reduced for 4 at% Zr as a result of extensive second phase coarsening. The ultimate shear stresses correlate with the hardness values, indicating that the alloys have reached the full strengthening after annealing at elevated temperatures and followed by compaction at 500 °C.
Figure 7.6 Shear punch test curves and SEM images of shear surfaces for selected alloys. Annealing temperatures are given in the parentheses.

7.5. Discussion

The following discussions will address the apparent modes operating to stabilize the microstructure against grain growth and to increase the mechanical properties despite the complete loss of the nanocrystalline grain size.

7.5.1. Microstructural stability upon annealing

7.5.1.1. Low temperature stabilization

The lattice parameter results shown in Figure 7.1(b) reveal that there is a rapid decrease in the lattice parameter of Fe-Ni-Zr alloys with increasing annealing temperatures while the
decrease is notably smaller for Fe-Ni alloys. Our calculations showed that there is a 0.458 percent total reduction of lattice parameter in Fe$_{88}$Ni$_8$Zr$_4$ after 1 hour annealing at 600 °C. This reduction was smaller for Fe$_{81}$Ni$_8$Zr$_1$ (0.333 percent) and almost negligible for Fe$_{92}$Ni$_8$ (0.114 percent). As-milled alloys have lattice parameters larger than those of equilibrium alloys due to vacancy complexes and dislocations induced by plastic deformation during mechanical milling [12, 22]. The annihilation of these dislocations and excess vacancy complexes along with grain boundary relaxation was reported to occur below the onset temperature for grain growth in Fe based nanocrystalline alloys, which is expected to be about 400 °C or lower [12, 21, 23, 24]. Thus the monotonic decrease in the lattice parameters of Fe-Ni-Zr alloys at 400 °C and above can be attributed to the diffusion of Zr solute out of the Fe-Ni lattice. The zirconium solutes can either segregate to the grain boundaries where they can be better accommodated or form intermetallic phases with Fe and/or Ni. The latter is kinetically less favorable at low temperatures and for small amounts of Zr. If Zr resides within the grain boundaries it can have two-fold effect; from a thermodynamic perspective it can lower the excess free energy of the system, while kinetically it can cause a solute drag effect at lower temperatures and/or driving forces, giving rise to grain size stability.

7.5.1.2. Abnormal grain growth

It was observed that a certain fraction of grains grew abnormally into the nanocrystalline matrix resulting in a bimodal microstructure for Fe$_{91}$Ni$_8$Zr$_1$ at 700 °C (Fig. 7.2(a)) and complete loss of the stability above this temperature. In comparison the observed
microstructural stability was increased to 800 °C with 3 at% Zr (Fig. 7.2(g)) and to 900 °C with 4 at% Zr (Fig. 7.2(h)) additions. Kotan et al. [25] investigated the abnormal grain growth in Fe$_{91}$Ni$_8$Zr$_1$ by in situ TEM and XRD studies and attributed it to the formation of fcc grains which have a lower free energy than surrounding bcc grains. Thus, any fcc grain nucleated at and above 700 °C in the Fe$_{91}$Ni$_8$Zr$_1$ alloy will grow into a matrix of bcc grains and reduce both the total area of grain boundaries and the overall stored energy in the system. This gives the fcc grains a significant growth advantage over bcc grains, resulting in an abnormal grain growth and ultimately loss of nanostructure in Fe$_{91}$Ni$_8$Zr$_1$ as observed in Figures 7.2(a-d).

7.5.1.3. High temperature stabilization

The development of abnormal grain growth in thermally stabilized Fe based alloys was previously observed for Fe-Ti [26], Fe-Ta [14] and Fe-Zr [13]. Dake et al. [26] reported that addition of more solute atoms (Ti) into the (Fe) matrix negates abnormal grain growth and provides microstructural stability to higher annealing temperatures due to an increase in the bcc-to-fcc transition temperature shown on the Fe-Ti phase diagram [27]. We see the same trend in the current study when the appreciable grain growth is suppressed up to 700 °C with 1 at% Zr (Fig. 2(a)) and this suppression is increased to 800 °C (Fig. 7.2(g)) and 900 °C (Fig. 7.2(h)) with 3 and 4 at% Zr additions, respectively. However, Zr additions do not affect the bcc-to-fcc transformation temperature in Fe-Ni alloys according to the Fe-Ni-Zr ternary phase diagram [28]. In this regard it is also important to bear in mind that the effectiveness of
solute drag as a grain-size stabilization mechanism is expected to decrease when the diffusion rate of the Zr atoms approaches that of an undecorated boundary at higher temperatures, leaving two possible stabilization mechanisms; (1) thermodynamic stabilization by solute segregation to grain boundaries, and (2) kinetic stabilization by Zener pinning of the grain boundaries through the second phase formation. Precipitation of a second phase is expected to be an important competing reaction to thermodynamically stabilized systems. In a closed system the total solute is conserved, therefore, the formation of secondary stoichiometric phases involving the stabilizing agent will compete for the available solute, ultimately lowering the thermodynamic stability and allowing extensive grain growth to ensue. Thus, considering the extensive second phase formation, it can be anticipated that Zener pinning could be the dominant source of the stabilization of the grain size at higher annealing temperatures.

It has been predicted theoretically that when a grain boundary is moving through a matrix with second phase particles, the pinning force depends on the volume fraction of particles and particle sizes [29, 30]. The potential effectiveness of the second phase particles as grain boundary pinning agents is known to increase with small particle sizes and large volume fractions and is evaluated using the Zener pinning equation [31]:

$$D_P \alpha = 0.75d f$$

(7.3)

$D_P$ is the diameter of the pinning particles that stabilize the grain size $d$, and $f$ is the particle volume fraction. $\alpha$ is a factor that can vary from 0.25 to 0.5 [31]. Although X-ray diffraction
studies did not show any intermetallic peaks in Figure 7.3, TEM investigations revealed second phases for Fe$_{91}$Ni$_8$Zr$_1$ alloy annealed at 1000 °C as shown in Figure 7.4(c). The authors previously performed a back-calculation of the critically pinned grain size for 1at% Zr [16] and found that at 700 °C the available precipitated second phases were of insufficient volume fraction (3.8 pct) to pin the grain boundaries, due to the high driving force for grain growth resulting from the bcc-to-fcc phase transformation. Therefore rapid coarsening to the micron scale takes place in nanocrystalline Fe$_{91}$Ni$_8$Zr$_1$ as soon as the transformation occurs. In comparison x-ray diffraction results for 4 at% Zr as shown in Figure 7.3 prove that intermetallics are already present at 700 °C. Unlike in 1 at% Zr these second phases are able to pin the grain boundaries when the bcc-to-fcc transformation occurs and restrict the grain growth. In addition, new precipitates are likely to continue forming until all the solute atoms are consumed, which is approximately at 800 °C, according to lattice parameter results shown in Figure 7.1 for 4at% Zr. These pin the grain boundaries and maintain the grain stability up to 900 °C, as seen in Figure 7.2(h). This microstructural stability was maintained up to 800 °C for 3 at% Zr as seen in Figure 7.2(g), but was lost at 900 °C as micron size grains appear (figure not shown here) presumably due to a lower volume fraction of pinning precipitate.

In conclusion the most likely mechanisms for the increased microstructural stability below 700 °C appear to be; (1) thermodynamic stabilization of grain boundaries by zirconium solute segregation, and (2) solute drag effects. The stability above 700°C can be
attributed solely to the kinetic pinning of grain boundaries by formation of second phase particles (Zener pinning).

Eventually at high enough temperatures the precipitated second phases increased in diameter (assuming all the solute atoms are consumed above 800 °C based on the reduction in the lattice parameter) resulting in a reduced Zener pinning effect according to Eq. (7.3), and leaving behind fine micron grains filled with nanoscale intermetallic precipitates. We see in Figures 7.2(d, e, and i) that the microstructures consist of submicron and micron scale grains at 1000 °C regardless of the Ni and Zr amount, indicating that the microstructures are not stable above 900 °C. It should also be noted that Fe$_{91}$Ni$_8$Zr$_1$ and Fe$_{95}$Ni$_4$Zr$_1$, both annealed at 900 (Figs. 7.2(c) and (f)) and 1000 °C (Figs. 7.2(d) and (e)), have very similar grain sizes at the same annealing temperatures. Considering the hardness and shear punch results along with the microstructure images, it can be concluded that the Ni amount does not affect the stabilization of Fe-Ni-Zr alloys significantly for 4 and 8 at% Ni compositions.

7.5.2. Mechanical properties of Fe-Ni-Zr alloys

In this section we discuss the possible mechanistic contributions to strength in Fe-Ni-Zr alloys. As shown in Figure 7.7, hardness data for the ternary alloys correspond to much higher hardness values than estimated purely from grain size alone (see dotted line Hall-Petch plot). This suggests that with Zr additions there is another contribution to hardness beyond the grain size effect, both at low temperatures and at high temperatures. This is displayed in Figure 7.8(a-b) as a function of alloy compositions and annealing temperatures.
Figure 7.7 Hall-Petch plot of the hardness of as-milled and annealed pure Fe, Fe-Ni and Fe-Ni-Zr alloys. Pure Fe data was taken from [23]. The dotted line was fit to the pure Fe and Fe\textsubscript{92}Ni\textsubscript{8} data points.

The hardness can be divided into four contributions based on different strengthening mechanisms:

\[ H = H_0 + \Delta H_{GB} + \Delta H_{SS} + \Delta H_{Or} \]  

(7.4)

\( H \) is the overall hardness, \( H_0 \) is the intrinsic hardness of high purity single crystal Fe, \( \Delta H_{GB} \) is the additional hardness due to grain refinement, \( \Delta H_{SS} \) is the increment of hardness resulting from solid-solution strengthening, and \( \Delta H_{Or} \) is the Orowan mechanism strengthening. The
contribution of the grain size on estimated overall hardness can be calculated from Eq. (5) and can be distinguished by comparing the ternary alloys with pure Fe and Fe-Ni alloys as shown by the dashed line in Figure 7.7.

\[ \Delta H_{GB} = (constant) \ d^{-1/2} \]  

Figure 7.8(a) displays solid solution hardening of selected elements in an Fe matrix reported by [24], and (b) additional hardening vs. temperature where the hardness is due to sources other than grain size (\(H_0 + \Delta H_{GB}\) was subtracted from overall hardness). This is to differentiate the contribution of grain size from other hardening effects such as solid solution or second phase particles.

7.5.2.1. **Solid solution strengthening in as-milled samples**

It was reported that the atomic radius ratio of solute-to-iron is the primary factor in controlling low temperature hardness (solid solution hardening) of the iron alloys [32]. Ni in an Fe matrix does not promote significant solid solution hardening due to the similar atomic radii (5.8%). However, the addition of Zr to Fe-Ni matrix produces very large misfit strain (26%), also revealed by the lattice parameter data in Figure 1. To provide further insight on the nature of solute solution hardening in Fe-Ni-Zr, we adopt an approach that was detailed by [24] to calculate the solid solution hardening in Fe matrix using the Labusch model [33]. Guduru and co-workers [24] reported that for a given matrix, model predictions of the solid solution hardening effect have the form, \(\Delta H = k \varepsilon^p c^q\) where \(k\) is a pre-factor containing the
shear modulus and the Burgers vector for a given matrix element [33], and $p$ and $q$ are exponents given as $4/3$ and $2/3$, respectively, for the Labusch model. We calculated the solid solution hardening contribution at room temperature using $\Delta H_{SS} = H - (H_0 + \Delta H_{GB})$. These values can be compared with solid solution hardening data for V, Mo, W and Pb addition to pure Fe reported in [24], noting that V, Mo and W are equilibrium solid solutions whereas Pb is a nonequilibrium solute produced by SPEX ball milling. It is evident that our results are in good agreement with these data and match our room temperature data in Figure 7.8(b). Zr therefore produces solid solution hardening in the Fe-Ni matrix and the increased as-milled hardness with zirconium addition can be explained by solid solution hardening [34]. Further comparison in Figure 7.8(a) shows that our data is shifted somewhat to the right. We can identify three possibilities to explain this. First, there can be solute segregation to grain boundaries in Fe-Ni-Zr resulting from high energy ball milling that removes solutes from the grain interiors. Second, the comparison is based on a pure Fe matrix and our matrix is Fe-Ni which can produce additional misfit. Third, there can be clustering of the Zr atoms within grains. High resolution transmission electron microscopy and Z-contrast techniques are needed to confirm the atomic distribution of Zr in the Fe-Ni-Zr alloys. This was beyond the scope of the present investigation.
Figure 7.8 a) Solid solution hardening of selected elements in an Fe matrix, b) Contribution to hardness, other than grain size, as a function of annealing temperature.
7.5.2.2. Grain boundary relaxation strengthening at low temperatures

There is an increase in the additional hardness after annealing at low temperatures as shown in Figure 7.8(b). It has been reported that nanocrystalline metals contain nonequilibrium grain boundaries with excess dislocations, misfit region, and excess free volume [2, 35, 36]. These boundaries evolve during low temperature annealing by the annihilation of dislocations and excess vacancy complexes [37], which occurs about 400 °C or lower for Fe base alloys [12, 14, 35], and can cause grain boundary relaxation and restructuring without a significant grain growth [35, 37]. Jang and Atzmon [35] observed grain boundary relaxation by high resolution transmission electron microscopy upon annealing in nanocrystalline Fe prepared by high energy ball milling. They suggested that grain boundaries evolve gradually during low temperature annealing from an initial discontinuous structure into more equilibrium structures with regularly spaced grain boundary dislocations. Grain boundaries are expected to control plasticity in nanocrystalline metals by grain boundary sliding, and/or acting as additional sources and sinks for dislocations. Thus, it is expected that the relaxation of nonequilibrium boundaries should impact mechanical properties in nanocrystalline materials. Rupert et al. [37] reported 20% increases in hardness in Ni-W upon annealing due to grain boundary relaxation. It was proposed [38] that the relaxation process is dominated by the diffusion of excess vacancies along grain boundaries and climbing to a triple junction where they can be accommodated. Excess vacancies and defects in the microstructure will facilitate the diffusion of some Zr atoms to dislocations which will also increase the hardness as a result of the interaction
between dislocations and solute Zr atoms. This will reduce the dislocation sources for the same or similar grain size causing higher hardness.

**7.5.2.3. Precipitation strengthening at high temperatures**

At higher annealing temperatures the precipitation of intermetallics occurs and will consume the zirconium solute atoms. This will reduce the effect of solid solution hardening and eventually will transition to Orowan strengthening. The strengthening effects of second phase particles are well established for conventional grain size metals with regard to particle size and its distribution [39, 40]. The flow stress increase due to a random distribution of impenetrable particles can be estimated using the Orowan-Ashby equation, and can be rewritten in terms of hardness by applying Tabor’s relationship \((H = 3\sigma)\) [41] where \(r_o = 2b\) is taken as the core radius [42]:

\[
H_{Oro} = 3 \sigma_{Oro} = 3 \frac{2MGb}{(1.18)4\pi(\lambda - D_p)} \ln \frac{D_p}{2b}
\]  

(7.6)

\(\sigma_{Oro}\) is the flow stress due to precipitation strengthening, \(M\) is the Taylor factor, \(G\) is the shear modulus, \(b\) is the Burger’s vector, and \(\lambda\) is the mean interparticle spacing on the slip plane. \(\lambda, D_p\) and the volume fraction of precipitates, \(f\) are related by [43]:

\[
f = \left(\frac{4}{3}\right) \pi \left(\frac{D_p^2}{8\lambda^2}\right)
\]  

(7.7)
Based on Eq. (7.6-7)), the hardening effect depends on the interparticle spacing which is determined by the second phase particle size and volume fraction of particles. At the early stage of the precipitation, the volume fraction and size of the precipitates will increase. It has been reported that precipitated second phases containing Zr can be extremely hard (i.e., $H_{Fe_2Zr}=9.5\text{GPa}$ [44]) and can influence mechanical properties at very early stages of the precipitation [45] by the onset of Orowan strengthening. This causes higher hardness for the alloys with higher Zr content as seen in Figure 7.8(b) which forms intermetallics at lower annealing temperatures (see Figure 7.3). The maximum amount of hardening observed in Figure 7.8(b) exhibits a temperature and composition dependence, i.e. higher Zr content reaches the plateau hardness at lower temperature relative to lower Zr content. Intermetallics form at or before 700 °C for 4 at% Zr and they will coarsen more rapidly lowering the peak temperature for the specified alloy. In comparison, 1 at% Zr, intermetallics will form later and since there is less of Zr in the microstructure, coarsening kinetics will be slower. Higher hardness can result with lower Zr content due to the retention of coherency with lack of precipitate growth, causing higher peak hardness at higher temperatures for 1at% Zr. Figure 7.1(b) shows that the lattice parameters of all alloys are within the range of the error bars around 800 °C, meaning that all solute atoms should be consumed. Hence the volume fraction of the second phases is assumed to remain constant for the higher annealing temperatures. Precipitates will coarsen and this coarsening will be more dramatic for the compositions with more Zr, therefore intermetallics should begin forming at lower and lower temperatures. At higher annealing temperatures, coarsening kinetics will be such that we can
achieve microstructures with a large volume fraction of second phases, but the interparticle spacings are in fact larger than we would observe for the alloys with less Zr content. According to Eq. (7.5), this will reduce the effectiveness of the Orowan strengthening, as is observed at and above 900 °C in Figure 7.5(a) and Figure 7.8(b). Larger second phase particles will lose their coherency with the matrix which can also reduce hardness. This explains both the downward trend and the inverse relation observed at high temperatures between the hardness (Fig. 7.5(a)), ultimate shear stress (Fig. 7.6) and the zirconium content. Hard and brittle second phases that are large in diameter and in volume fraction will also reduce the ductility as is observed for Fe$_{88}$Ni$_{8}$Zr$_{4}$ in Figure 7.6.

7.6. Conclusion

The thermal stability and mechanical properties of nanocrystalline Fe-Ni alloys as a function of Zr amount and annealing temperature was examined. Investigations revealed that annealing of Fe-Ni alloys leads to reduced hardness and extensive grain growth at low temperatures, indicating that the nanostructure developed by ball milling is not retained during annealing. However, microstructural stability was maintained up to 700 °C with the addition of 1 at% Zr and increased to 800 and 900 °C with 3 and 4 at% Zr additions, respectively. Despite the possibility that thermodynamic stabilization may contribute to the observed stability for some alloys below 700°C, the microstructural stability observed at high annealing temperatures can be attributed entirely to kinetic stabilization, by Zener pinning above 800 °C. The results from the microhardness and shear punch tests show that Orowan
particle strengthening can be as effective as Hall Petch hardening at the smallest grain sizes. This is significant since the processing method is relatively simple and does not require a complex heat treating schedule to achieve impressive strength values. Secondly, since the mechanical property enhancement does not require nanocrystalline grain size higher temperatures can be used which facilitate bulk consolidation. This opens a new approach for the synthesis of high strength steels with the potential for high ductility.

7.7. References


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8. THERMAL STABILITY OF NANOCRYSTALLINE ALLOYS

8.1. Thermal stability of nanocrystalline Fe–Cr alloys with Zr additions

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Abstract

The primary objective of this work was to determine the influence of 1–4 at% Zr additions on the thermal stability of mechanically alloyed nanocrystalline Fe–Cr alloys containing 10 and 18 at% Cr. Grain sizes based on XRD, along with microhardness changes, are reported for isochronal annealing treatments up to 1000 °C. Microstructure investigations were done using optical microscopy, channeling contrast FIB imaging, and TEM. Grain size stabilization in the nanoscale range was maintained up to 900 °C by adding 2 at% Zr. Kinetic pinning by nanoscale intermetallic particles was identified as one source of high temperature grain size stabilization. Intermetallic particles also contribute to strengthening in addition to the Hall–Petch effect. The analysis of microhardness, XRD data, and measured values from the TEM image for Fe-10 at% Cr with 2 at% Zr suggested that both thermodynamic and kinetic mechanisms would contribute to grain size stabilization. There was no significant difference in the results for the 10 and 18 at% Cr alloys, which indicates that the α→γ transformation does not influence the grain size stabilization.
8.2. Thermodynamic Stabilization of Nanocrystalline Binary Alloys

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**Abstract**

The work presented here was motivated by the need to develop a predictive model for thermodynamic stabilization of binary alloys that is applicable to strongly segregating size-misfit solutes, and that can use available input data for a wide range of solvent-solute combinations. This will serve as a benchmark for selecting solutes and assessing the possible contribution of thermodynamic stabilization for development of high-temperature nanocrystalline alloys. Following a regular solution model that distinguishes the grain boundary and grain interior volume fractions by a transitional interface in a closed system, we include both the chemical and elastic strain energy contributions to the mixing enthalpy $\Delta H_{\text{mix}}$ using an appropriately scaled linear superposition. The total Gibbs mixing free energy $\Delta G_{\text{mix}}$ is minimized with respect to simultaneous variations in the grain-boundary volume fraction and the solute contents in the grain boundary and grain interior. The Lagrange multiplier method was used to obtain numerical solutions with the constraint of fixed total solute content. The model predictions are presented using a parametric variation of the required input parameters. Applications are then given for the dependence of the nanocrystalline grain size on temperature and total solute content for selected binary systems where experimental results suggest that thermodynamic stabilization could be effective.
8.3. A Predictive Model for Thermodynamic Stability of Grain Size in Ternary Alloys

Mostafa Saber, Hasan Kotan, Carl C. Koch, Ronald O. Scattergood

Submitted for publication

Abstract

This work presents a new model for thermodynamic stabilization of ternary nanocrystalline alloys. It is applicable to strongly segregating size-misfit solutes and uses input data available in the literature. The model is based on a regular solution approach such that the chemical and elastic strain energy contributions are incorporated into the mixing enthalpy $\Delta H_{\text{mix}}$, and the mixing entropy $\Delta S_{\text{mix}}$ is obtained using the ideal solution approximation. The Gibbs mixing free energy $\Delta G_{\text{mix}}$ is minimized with respect to simultaneous variations in the grain size and solute segregation parameters. The Lagrange multiplier method is used to obtain numerical solutions for the minimum $\Delta G_{\text{mix}}$ corresponding to grain size stabilization for given alloy compositions. The temperature dependence of the nanocrystalline grain size and interfacial solute excess can be evaluated for selected ternary systems. As an example, model predictions are compared to experimental results for Zr additions to base Fe-Cr and Fe-Ni alloys.
8.4. High temperature stabilization of nanocrystalline grain size: Thermodynamic versus kinetic strategies

Carl C. Koch, Ronald O. Scattergood, Mostafa Saber, and Hasan Kotan

Journal of Materials Research

Abstract

Data from the literature and our laboratory have been reviewed regarding the maximum homologous temperatures that can be attained by the addition of solute elements that may induce thermodynamic or kinetic (Zener pinning) stabilization of a nanocrystalline grain size (100 nm) to elevated temperatures. The results of this review suggest that kinetic stabilization by Zener pinning by nanoscale second phases may be the more effective strategy for keeping a nanoscale grain microstructure at the highest homologous temperatures. More research is necessary to confirm this suggestion and to determine the influence of nanoscale grain boundary second phases on the mechanical behavior of the nanocrystalline matrix.
8.5. Thermal Stability of Nanocrystalline Grain Size in Ternary Fe-base Alloys
Carl C. Koch, Ronald O. Scattergood, Hasan Kotan, Mostafa Saber

Recrystallization and Grain Growth (2013)

Abstract

Research to develop strategies for the thermal stabilization of nanocrystalline grain sizes has focused on either thermodynamic stabilization (reducing the grain boundary energy, driving force, for grain growth by solute segregation to the grain boundaries) or kinetic stabilization (reduction of grain boundary mobility by various mechanisms such as Zener pinning and solute drag). Most of these studies have focused on pure nanocrystalline metals. We report recent research in our laboratory involving nanocrystalline binary alloys with ternary additions. The possibilities of thermodynamic or kinetic stabilization will be reported for Fe-base (Fe-Cr and Fe-Ni) alloys. The thermal stability of these nanocrystalline alloys, prepared by mechanical alloying of powders, with ternary additions of Zr, are studied by XRD, TEM and hardness as a function of annealing temperature. The relative importance of thermodynamic or kinetic stabilization in various temperature ranges are discussed for the different alloys. In agreement with our recent model for thermodynamic stabilization, it is found that Zr solute additions are more effective in stabilizing the nanocrystalline grain size in the Fe-Cr than in the Fe-Ni system.
8.6. Thermal Stability and Mechanical Properties of nanocrystalline Fe-Ni-Zr Alloys

Hasan Kotan, Mostafa Saber, Carl C. Koch, and Ronald O. Scattergood

TMS 2013 142nd Annual Meeting and Exhibition

Abstract

Thermal stability of nanostructure materials is crucial for consolidation of nanocrystalline particles and for high temperature structural applications. We investigate the influence of 1 and 4 at% Zr additions to the thermal stability and mechanical properties of a ball milled Fe-Ni alloy consolidated by hot compaction and ECAE. Grain growth and microstructural evolution were investigated by in situ (TEM and XRD) and ex situ studies. Investigations reveal grain growth to be slow up to about 700°C. Above this temperature, rapid grain growth occurs to submicron size and is coupled with precipitation of second phases. A fine dispersion of precipitated second phase is found to contribute to the stabilization at higher annealing temperatures by Zener pinning of the grain boundaries. The results from the microhardness and shear punch tests show that Orowan particle strengthening is an important contributor to total materials strength annealed above 800°C.
8.7. In-situ and ex-situ experimental studies of the bcc-to-fcc phase transformation in Fe-based nanocrystalline alloys
Hasan Kotan, Kris A. Darling, Mostafa Saber, Ronald O. Scattergood, Carl C. Koch

MRS/ASM/AVS 2012

Abstract
Grain growth and microstructural evolution of thermally stabilized Fe$_{91}$Ni$_8$Zr$_1$ were investigated by in situ and ex situ studies. Our investigations suggest that the microstructural evolution is fairly slow and the microstructure shows stabilization up to about 700 °C. Above this temperature, a certain fraction of grains grow abnormally into the nanocrystalline matrix, resulting in a bimodal microstructure and causing the complete loss of thermal stability. The reason for abnormal grain growth and the loss of thermal stability is identified as the appearance of the fcc-phase and consequent reduction in the total area of grain boundaries and the overall stored energy.
8.8. Thermal Stability of Nanoscale Grain Size in Fe-10Cr Alloys with Zr Additions
M. Saber, H. Kotan, C.C. Koch, R.O. Scattergood

2012 MRS Fall Meeting & Exhibit

Abstract

The primary objective of this work was to determine the influence of 1 to 4 at% Zr additions on the thermal stability of mechanically alloyed nanocrystalline Fe-Cr alloys containing 10 at% Cr. Grain sizes based on XRD, along with microhardness changes, are reported for isochronal annealing treatments up to 1000°C. Microstructure investigations were done using optical microscopy, channeling contrast FIB imaging, and TEM. Grain size stabilization in the nanoscale range was maintained up to 900°C by adding 2 at% Zr. Kinetic pinning by nanoscale intermetallic particles was identified as one source of high temperature grain size stabilization. Intermetallic particles also contribute to strengthening in addition to the Hall-Petch effect. The analysis of microhardness and XRD data for Fe-10 at% Cr with 2 at% Zr suggested that both thermodynamic and kinetic mechanisms would contribute to grain size stabilization. Nanoscale grain size stabilization of the Fe-Cr alloys is being extended to the Fe-Cr-Ni alloys in the current research.
8.9. A Predictive Model for Thermodynamic Stabilization of Grain Size
M. Saber, H. Kotan, C.C. Koch, R.O. Scattergood

2012 MRS Fall Meeting & Exhibit

Abstract

Thermodynamic stabilization is achieved when segregation of solute atoms to grain boundaries produces a metastable equilibrium state with respect to grain growth. This has been proposed as a mechanism to stabilize a nanocrystalline grain size at high temperatures. Alternate stabilization mechanisms are based on retarding grain boundary mobility by grain boundary pinning (Zener pinning, etc.). The work presented here was motivated by the need to develop a predictive model for thermodynamic stabilization, applicable to strongly segregating solutes, that uses available input data. This will serve as a benchmark for selecting solutes and assessing the possible contribution of thermodynamic stabilization in the development of high-temperature nanocrystalline alloys. Following a regular solution model recently developed by Trelewicz and Schuh [1], the grain boundary region is distinguished from the grain interior region by a transitional interface. The elastic part of the enthalpy due to the solute atomic size misfit is not taken into account in [1] and we include this using the Wynblatt and Ku approximation [2] for linear superposition of the elastic and chemical contributions to the mixing enthalpy. It is important to recognize that the elastic term always contributes to segregation whereas the chemical term may contribute or detract. The total Gibbs free energy of mixing is minimized with respect to simultaneous variations in
the grain-boundary content and the solute concentrations within the grain boundary and grain
interior regions using the Lagrange multiplier method. The model predictions are presented
as a parametric study of the key input variables. Applications to the temperature dependence
of the grain size and solute segregation will be given for selected systems where
experimental results suggest that thermodynamic stabilization can contribute.
9. SUMMARY AND CONCLUSIONS

The thermal stability and mechanical properties of nanocrystalline pure Fe, Fe-Ni, and Fe-Ni-Zr alloys as a function of annealing temperatures and alloy compositions have been investigated. It was revealed that annealing of pure Fe and Fe-Ni alloys leads to reduced hardness and extensive grain growth at low temperatures, indicating that the nanostructure developed by ball milling is not retained during annealing. It also indicates that nickel has no significant effect on thermal stabilization of iron. Retained austenite was observed for Fe-8Ni and Fe-10Ni alloys annealed in the two-phase region. Our experiments and analysis suggest that as-milled grain size and defective structure play an important role on the formation of austenite in the two-phase region.

The grain growth of Fe-Ni alloys is suppressed by the addition of just 1 at% Zr addition up to annealing to 700 °C where only a few grains grow abnormally. Results revealed that microstructural stability of Fe-Ni alloys with 1 at% Zr addition is lost above 700°C due to the bcc-to-fcc transformation by the sudden appearance of abnormally grown fcc grains. However, it was determined grain growth can be suppressed kinetically at higher temperatures for high Zr containing alloys by precipitation of intermetallic compounds. Eventually at high enough temperatures (at 1000 °C) the retention of nanocrystallinity was lost, leaving behind fine micron grains filled with nanoscale intermetallic precipitates. Despite the possibility that thermodynamic effects may contribute to the observed stability for some alloys below 700°C, the obtained microstructural stability at high annealing
temperatures can purely be attributed to kinetic stabilization, that is Zener pinning above 800 °C for Fe-Ni-Zr alloys.

The observations from *in situ* and *ex situ* experiments reported in this work and the information obtained from these studies enable us to understand the grain growth in stabilized Fe-Ni-Zr alloys. From our *in situ* observations it is suggested that the microstructural evolution is fairly slow and the microstructure shows a solid stabilization up to about 700 °C. Above 700 °C the grain growth kinetics becomes extremely fast, especially for the first few seconds of annealing for 1 at% Zr addition and causes a sudden grain growth in abnormal manner. The reasons for abnormal grain growth and the loss of thermal stability were identified as the appearance of the fcc γ phase and consequent reduction in the total area of grain boundaries and the overall stored energy in the sample.

The grain growth of the ternary alloy at high annealing temperatures is coupled with precipitation of second phases. A fine dispersion of precipitated second phase is found to increase the mechanical properties of Fe-Ni-Zr alloys drastically when the grain size is above nanoscale. The results from the microhardness and shear punch tests show that Orowan particle strengthening in Fe-Ni-Zr alloys can be as significant as Hall Petch hardening is at the smallest grain sizes. In addition, small second phases increase strain hardening of the materials, yielding more plastic deformation and ductility. This realization is significant as the reported method is relatively simple and does not require a complex heat treating schedule to achieve such impressive strength values. The reported microstructures open a
new design space for the synthesis high strength steels with the potential to exhibit high ductility.
10. FUTURE REMARKS

According to the results obtained in this research, the following works are recommended for the future investigations;

We do not know yet how much solute segregates to grain boundary or resides in the grain boundary during annealing and grain growth. Z-contrast imaging and high resolution transmission electron microscopy studies could be powerful tools for analyzing solute segregation and solute distribution at and among the grain boundaries.

Abnormal grain growth and resulting bimodal grain size distribution in nanocrystalline metals and alloys are critical to the properties since they lead to increases in uniform elongation and ductility. Thus, controlling the percent area of abnormally grown grains can be beneficial by adjusting the heat treating schedule and the solute concentration (%Zr).

It was clearly shown that abnormal grain growth occurs for 1 at% Zr addition at around 700 °C due to bcc-to-fcc phase transformation and increasing Zr content would increase microstructural stability by forming second phases before 700 °C. However, at high enough temperatures the material is weaken in terms of mechanical properties due to the extensive second phase coarsening. In this regard, it should be considered to introduce oxide nano second phases, which do not coarsen upon annealing at high temperatures, into the material before the phase transformation occurs (700 °C) and investigate the microstructural stability as well as mechanical properties.
Considering the homogeneous microstructure and good mechanical properties of annealed and consolidated samples, the in situ formed second phases need to be optimized by careful investigation of composition (0-4 at% Zr) and temperature. Further microstructural investigation by high resolution transmission electron microscopy is suggested on the formation of second phases to learn more about their sizes, distributions, and interactions with the matrix.

Further mechanical tests such as tensile test should be performed on consolidated samples to have a better understanding of the mechanical properties (i.e. ductility). In addition, the effect of strain rate on the active deformation mechanism in consolidated Fe-Ni-Zr alloys needs to be investigated.