Abstract

DARLING, KRISTOPHER ALLEN. Thermally Stability of Nanocrystalline Microstructures. (Under the direction of Ron O. Scattergood.)

The objective of the proposed research is to develop the experimental data and scientific basis that can optimize the thermodynamic stabilization of a nanoscale microstructure during consolidation of Fe powder particles through select solute diffusion to grain boundaries.

Fe based alloys were high energy ball milled to produce supersaturated solid solutions with a nominal grain size of ~10nm. Solutes such as Y, W, Ta, Ni and Zr were selected based on their propensity to grain boundary segregated in Fe. Based on preliminary heat treatments Zr was selected as the solute of choice. Upon further heat treating experiments and microstructural analysis it was found that Zr solute additions of < 4at% could stabilize a nanocrystalline microstructure of <100nm at temperatures in excess of 900°C. This is in stark comparison to pure nanocrystalline Fe which shows coarsening to the micron scale after annealing above 600°C. Reduction in grain boundary energy due to Zr segregation and solute drag are proposed as mechanism responsible for the observed thermal stability.

In addition to the work presented on Fe based Zr alloys supplementary research is presented on the following systems: Fe based Ni alloys, Pd 20at%Zr, Cu3Ge and CuGeO3.
The addition of Ni to Fe was selected as a control. Since Ni and Fe have similar atomic radii, the elastic enthalpy of segregation of Ni in Fe is low (+1kJ/mol) and at high temperatures Ni has complete solid solubility in Fe; It is suggested that Ni will have a negligible influence in the thermal stability of nanocrystalline Fe. It was shown that at 700°C the addition of 1at% Ni produce a bimodal microstructure consisting of ~ 70% abnormally grown grains and ~ 30% nanocrystalline grains of 100-200nm. While these results are interesting extensive work is still needed to understand the mechanisms governing the thermal stability in this system. A presentation of the collected data is given.

Pd 20 at% Zr was high energy ball milled to produce an average grain size of ~6nm. Fe contamination was high due to the extensive cold welding exhibited by this system. The as-milled alloy showed an increase in hardness from ~6.5GPa to ~10GPa after heat treating at 1000°C for 1 hour. Based on these hardness measurements this alloy exhibits high thermal stability up to 1000°C. However, after heat treating at 1273°C the formation of Zr oxides were detected. Occurring simultaneously with the secondary phase formation was a rapid decrease in Vickers hardness from ~10GPa to ~ 3GPa. Ion channeling contrast images revealed that a nanocrystalline microstructure was not maintained at 1273°C. While these results are in conflict with what was reported in literature additional work is needed to confirm the results, however a presentation of the collected data is presented.
The intermetallic $\varepsilon_1$ compound Cu$_3$Ge was produced through high energy mechanical alloying that produced a nanocrystalline microstructure. The nanocrystalline microstructure was found to remain stable at temperatures up to 500°C for 5 hours which represents ~76% of the melting temperature. Resistivity measurements showed low resistivity, 8.8$\mu$Ω-cm, which was comparable to that of identical thin films with grain sizes thousands of times larger. Nano-indentation was performed to have an understanding of the mechanical properties.

The combination of cryogenically milled Cu$_3$Ge powders and sono-chemical synthesis produce a prototype of a new class of materials. The prototype was a nanostructured composite composed of 4.5 nm diameter Cu nanocrystals embedded in a 3D amorphous CuGeO$_3$ polyhedron web matrix. A complete structural and compositional characterization was reported.
Thermal Stability of Nanocrystalline Microstructures

by
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DEDICATION

I dedicate this work to my wife Gina Darling my true love and best friend.
Kris Darling was born in 1978 to Earl and Shirley Darling. After moving to Goldsboro North Carolina Kris began Southern Wayne High School in Goldsboro. Upon graduation Kris began Wayne Community College where he met his future wife Gina Palumbo. It was this event which would change his life forever. After completion of community college Kris worked as a dental assistant and was soon engaged. Wanting more for his future family Kris when back to college at NC State University in January 2002. Kris went on to graduate Summa Cum Laude in his undergraduate studies and eventually graduated early with his PhD Feb. 2009.
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In recent years, nanocrystalline metals and alloys have had the attention of the scientific community. This is mainly due to the intriguing mechanical properties to which they are associated. Numerous reports now exist indicating an order of magnitude increase in strength is possible in metals and alloys that exhibit grain sizes approaching the lower limit of nanocrystallinity\(^1\)\(^-\)\(^4\). While achieving high strength has never been a problem the ability to achieve any amount of uniform elongation, the prerequisite for appreciable ductility, was a challenge in the past\(^5\)\(^-\)\(^7\). Recently numerous reports of improved ductility indicate that tens of percent elongation may be possible in nanocrystalline metals\(^8\)\(^-\)\(^10\). The combined possibility of ultra high strength and improved ductility make nanocrystalline metals and alloys the future of advanced metallurgy.

There are several methods for producing nanocrystalline (<100nm grain size) metals and alloys, however none produce samples suitable for bulk mechanical applications. Many methods such as mechanical milling techniques can produce metallic particulates (average diameter 10-100\(\mu\)m) with an internal nanocrystalline microstructure <50nm.

The most convenient way to deal with consolidation of metal particles is through powder metallurgy techniques such as sintering. Sintering is a method which allows for the
production of useful parts having almost limitless geometry. However, since this method involves the application of heat and pressure, the microstructure of nanocrystalline metals which gives rise to the advanced physical properties is in jeopardy of coarsening. Thus, the technological aspects of the thermal stability in nanocrystalline materials must be realized if steps are to be made towards large scale applications.

There are two methods for preventing grain growth: a thermodynamic approach and a kinetic approach. The thermodynamic approach deals with reducing the interfacial energy. Kinetic approaches deal with reducing grain boundary mobility. Since grain boundary mobility follows an Arrhenius behavior kinetic modes of reducing grain boundary mobility will eventual be overcome by temperature 11. Therefore, a better approach is to reduce the interfacial energy, which shows very little temperature dependence 12. It is this approach, the thermodynamic approach, that is undertaken in work presented for this thesis.

Based on this thermodynamic approach, dilute solute additions of Ni, Zr, Y, Ta and W were added to pure Fe. Among these alloys, the addition of Zr to pure Fe led to a group of nanocrystalline alloys extremely resistant to grain growth at elevated temperatures. That is, a grain size of 50nm was maintained over a range of temperatures (24°C to approximately the alloys respective melting points 13. This was a remarkable achievement since the alloys were comprised of only 0.33, 1 and 4 at% Zr in Fe.
A presentation of the collected experimental data and scientific basis for the stabilization in these nanocrystalline Fe-Zr alloys, along with the systems that failed, will be documented. In addition, information on Pd 20 at% Zr will be given as an attempt to validate the former work of Krill et al. the first to report thermal stability up to 95% of the melting temperature $^{14}$. Additionally, the thermal stability, mechanical and electrical properties of nanocrystalline Cu$_3$Ge will be reported. Finally, results on the self assembly of a 3D CuGe nanoweb will be given.
References: Chapter 1

2.1. Grain Growth and Stability of Nanocrystalline Metals

2.1.1. Grain Growth in Nanocrystalline Metals

Conceptually, the perturbation between grains in a polycrystal, also known as grain boundaries, are regions of disturbed lattice only a few atomic diameters wide and generally account for an insignificant fraction of the microstructure. As the grain size decreases below 10nm in a nanocrystalline material, the percent microstructure constituted by grain boundaries increases and can be in excess of 50%. Thus, grain boundaries in nanocrystalline materials can account for a large increase of the total free energy of the system. The reduction of this excess free energy, via the removal of grain boundary area, represents a large driving force for grain growth. The driving force/pressure (P) for grain growth, based on the expansion of a curved interface, is 1:

\[ P = A \gamma_b / r \tag{2.1.1} \]

A is a constant, \( \gamma_b \) is the grain boundary free energy per unit area and r is the radius of curvature of a grain, which is proportional to the grain size. When r is in the range of tens of nanometers the driving pressure for grain growth is large ~ 1GPa. It has been demonstrated that pure nanocrystalline metals (Al, Sn, Pb, Zn and Mg) exhibit extensive grain growth at
room temperature. Metals with higher melting points, such as Co, Ni and Fe, are not exceptions to this phenomenon and show rapid grain growth over moderate temperature ranges (220-450°C), resulting in grain sizes in the micron range at ~50% of their respective melting temperatures.\textsuperscript{5-7}

Figure 2.1.1 shows the effect of a heat treatment on electroplated copper. In the initial condition, the electroplate copper had an average grain size of 60nm and after heat treating under sintering conditions (64% of the Tm for 2 Hrs), the average grain size increased by a 1000X and the microhardness decreased by 10X.

![Microstructures](image)

**Fig 2.1.1.** (a) Gives the microstructure of as deposited electroplated nanocrystalline copper. (b) Gives the microstructure of the as deposited electroplated nanocrystalline copper after sintering at ~600°C for 2 Hrs.
It is this thermal instability which limits the overall processing and applications of nanocrystalline metals and alloys. Therefore, it becomes imperative to create alloys which are resistant to grain growth at elevated temperatures.

### 2.1.2. Stability of Nanocrystalline Metals (Kinetic and Thermodynamic)

The thermal stability of these microstructures is essential for the adoption of nanocrystalline materials in commercial processes and applications. A number of investigations on the thermal stability of nanocrystalline materials have been conducted based on controlling the parameters in Equation 2.1.2, the equation for velocity of a grain boundary undergoing curvature driven grain growth \(^8-^9\).

\[

\nu = M \cdot P = M_o \exp \left( -\frac{Q_m}{RT} \right) \cdot \frac{2\gamma_b}{r} \quad (2.1.2)

\]

M is mobility, \(M_o\) is the pre-exponential factor for the mobility term, and \(Q_m\) is the activation energy for grain boundary mobility. The pressure, P, is entirely curvature driven and therefore related to \(\gamma_b\), the interfacial energy per unit area, and the radius \(r\) of the grain. There are generally two approaches used to reduce the velocity of a moving grain boundary,
those being to modify the kinetic parameter (M) or the driving force (P), which contains the
thermodynamic parameter ($\gamma_b$).

**Kinetic Modes of Stability “Reduction of Mobility”**

Several methods are available for applying a retarding force to a grain boundary
thereby reducing the kinetics of grain growth. Those being: pinning with second phases $^{10}$,
pores $^{11}$ and/or chemical ordering $^{12}$, solute drag-effects $^{13}$.

**Solute Drag Effects**

Solute drag effects are well known for their influence on grain boundary migration $^8$. For grain boundaries undergoing curvature driven growth, the kinetics of such growth
depend on whether the boundary can break away from the solute atmosphere. Two factors affect the ability of a boundary to break away from the solute drag opposing force: the magnitudes of the drag force and the force driving grain growth. There are two distinct regions when comparing the mobility of a grain boundary and solute concentration $^8$. When solute concentration is low, the change in the mobility of the boundary is negligible and grain growth takes place uninhibited. As solute concentration increases, the atmosphere becomes a heavier burden and hence, boundary mobility decreases with continual increase in solute concentration. When the pressure driving grain growth is low, as in large grains or in regions in which the growth rate $dR/dt$ is low, the solute has enough time to diffuse (near and
along the grain boundary) and keep up with the boundary as it expands. As the driving pressure/force continues to increase and growth takes place more rapidly, the solute must now diffuse over longer paths throughout the lattice in shorter times. Therefore, as the driving pressure increases, (as in nanocrystalline alloys) it is expected that the grain boundaries break away from the solute atmosphere and again, normal grain growth takes place. Solute drag can still take place at higher temperature as now diffusion of the solutes is enhanced by thermal expansion of the lattice, but the exact magnitude of the pinning pressure will depend heavily on solute-solvent interactions. Michels et al. showed a grain size dependence on grain growth due to the influence of grain boundary solutes in nanocrystalline Pd 19 at% Zr alloy 13. This alloy was annealed at 600°C. As a result, the average grain size increased from 5nm to 16nm. While simultaneously the average solute concentration on the grain boundaries as measured by lattice parameter measurement was shown to increase from 19 at% Zr to 27 at% Zr. Two mechanisms were possible for grain boundary uptake of Zr solute: diffusion of solute through the lattice or solute entrapment during boundary expansion. A temperature of 600°C represents 47% of the respective melting temperature of Pd 19 at% Zr, and it is expected that lattice diffusion could not explain the amount of solute on the grain boundaries. Solute entrapment via moving boundaries was therefore suggested as the most likely mechanism. Knauth et al. used solute drag effects in nanocrystalline Ni and Ni 1 at% Si to explain difference in grain growth kinetics 14. While both systems exhibit initial grain growth at the same starting temperature, the rate of growth in the Ni 1at% Si
slowed at higher temperatures. Through calculations, it was shown that appreciable lattice diffusion was not warranted at the temperatures and times allowed, thus grain boundary uptake of Si was attributed to its incorporation during boundary expansion. The difference in interfacial energy reduction between the pure Ni and the Ni 1 at% Si in the segregated state was negligible, indicating that thermal modes of grain size stability were not contributing factors in grain growth reduction.

**Chemical Ordering**

It has been shown with chemically disordered alloys that grain growth kinetics increase; however, once ordering takes place or develops, grain growth can be reduced. Gao and Fultz have shown that through high energy mechanical alloying, it was possible to disorder (Fe₃Si)₉₅Nb₀₅₁₂,₁⁵. This ternary alloy had greater thermal stability against grain growth than did the binary alloy (Fe₃Si), over the temperature range of 350 to 500°C. Initially it was shown that grain growth took place governed only by the forces experienced by the expansion of a curved interface (uninhibited). Next, Nb segregation to the grain boundaries took place, while simultaneously, the formation of Fe₃Si DO3 ordered domains appeared. The appearance of these domains did not occur homogeneously but rather through nucleation and growth. It was suggested that these two processes were interrelated. That is the segregation of the Nb atoms out of the lattice to the grain boundaries facilitated ordering, since the associated kinetics with ordering in the binary FeSi are simpler than in (Fe₃Si)₉₅Nb₀₅. Bansal et al. suggested that the addition of Mn occurs in place of Nb. Grain
boundary segregation of Mn was not expected, since Mn directly substitutes for Fe in the ordered binary Fe₃Si system. It was shown that Mn additions to Fe₃Si accelerate the ordering kinetics and that these ordering kinetics were strongly related to reduced grain growth in the ordered alloy. That is, the grain boundary mobility was the highest in the disordered state and lowest once chemical ordering occurred. This may be due to low diffusion kinetics exhibited by ordered structures as compared to their disordered counterparts.

2nd Phase Pinning

For a long time it has been known that secondary phases will impede the movement of interfaces/dislocations. The traditional method of reducing/stopping grain boundary mobility can be expressed in terms of a pinning pressure Equation 2.1.3.

\[ P_z = \frac{3F\gamma}{2r} \]  (2.1.3)

Where \( P_z \) is the pinning pressure exerted by the precipitates or dispersoids, \( F \) is the volume fraction of distributed particles of radius \( r \), and \( \gamma \) is the specific grain boundary energy.

Thus, for successful pinning of grain boundaries, the pinning pressure must be larger than the pressure driving grain growth Equation 2.1.1.

\[ P = A\gamma_b/r \]  (2.1.1)
As stated earlier, when \( r \) is in the range of tens of nanometers the driving pressure for grain growth is large (~ 1GPa). If \( P_z \) is to be greater than \( P \), then the radius of the secondary particle must be very small and/or a very high volume fraction of the secondary phase is needed. Currently, there are several experimental examples exhibiting successful grain boundary pinning in a nanocrystalline metal/alloy by nanoscale secondary phases. The work by Perez et al. on nanocrystalline Fe-Al\(_x\), where \( x = 0, 2.6 \) or 10 wt\%, showed that after annealing at 650°C for one hour a grain size of ~ 20nm was maintained in the samples containing 10 wt% Al, even after heating above 1100°C a grain size of 60nm or less was maintained for the 10 at% Al alloys. The authors attributed the thermal stability to the dispersion of FeAl\(_2\)O\(_4\) at low temperatures and at high temperatures to AlN and Al\(_2\)O\(_3\). Using inert gas fusion, authors determined the amount of O and N (due to contamination) available to combine with the 10 wt% Al. This equated to 2.3 wt% leaving a total of 7.3 wt% in solution. Though this falls within the equilibrium solubility limit, lattice parameter measurements determined the leftover 7.3 wt% Al was not dissolved. This indicates a large amount of Al solute may have resided in the grain boundaries, leading to other mechanisms responsible for the thermal stability. Shaw et al. studied the thermal stability of a nanostructured Al\(_{93}\)Fe\(_3\)Ti\(_2\)Cr\(_2\) alloy prepared by ball-milling of elemental powders. Initially, in the as-milled state, the FCC Al grains were supersaturated solid solutions. Upon heating the precipitation of several intermetallic phases occurred. Al\(_6\)Fe was the first to appear, followed by Al\(_3\)Ti, Al\(_{13}\)Fe\(_4\) and Al\(_{13}\)Cr\(_2\). It was found that the onset temperature for grain
growth occurred at the same temperature as the precipitation of the Al₆Fe phase. The authors stated that grain growth inhibition below temperatures at which precipitation occurred was due to solute drag effects. At temperatures higher than 450°C, second phase Zener drag effects were responsible for the thermal stability. The result being the retention of Al grains with an ~ average diameter 20nm after post annealing at 77% of the alloys melting temperature for 1hr.

There exists several works on grain boundary pinning in nanocrystalline electroplated samples. Due to the complex nature of the bathing solutions required to refine the microstructure to the nanoscale, it is typical to induce the formation of secondary phase from the bath additives during annealing. These secondary phases can then pin the grain boundaries in place preventing further grain growth. Examples of this scenario can be seen in the works of Boylan et al. and El-Sherik et al. on Ni 1.2% P and Ni 0.12%S. Both observed grain growth up to the point of precipitation of nickel phosphides and sulfides⁠¹⁰,¹⁹.
**Thermodynamic Stability “Reduction of Interfacial Energy”**

Reduction in grain boundary mobility has experimentally been successful, however, because mobility follows the Arrhenius law, the pinning pressure on grain boundaries by any obstacles will eventually be overcome with the application of enough thermal energy \(^1\). A more promising approach could be to modify the thermodynamic parameter in the pressure term (\(\gamma_b\)), which shows only a slight temperature dependence \(^20\).

The driving force for grain growth is proportional to the interfacial energy, therefore reducing the interfacial energy should, have a large effect on reducing grain growth. It has been shown that the interfacial energy (\(\gamma_b\)) varies with the overall solute concentration, according to the Gibbs adsorption equation: equation 2.1.4.

\[
\frac{\partial \gamma_b}{\partial \ln c_s} = -RT \Gamma_s
\]

\(\Gamma_s\) is the interfacial solute excess and \(c_s\) is the solute concentration, T and R have their usual meanings. For grain boundary segregation (\(\Gamma_s > 0\)), \(\gamma\), the interfacial grain boundary energy should decrease with increase in \(c_s\). Based on the work of Hondros and Seah, the plots of \(\gamma_b\)
versus $c_s$ show a more negative trend for solutes which have a much larger atomic radius than
the element in which they are dissolved $^{21}$. This suggests that large atomic differences
between solute and solvent induce grain boundary segregation of the solute and
consequently, a reduction in the grain boundary interfacial energy may be realized. This
reduction is possible because the excess free volume provided by the broken atomic
periodicity within the grain boundaries allows for large misfit solutes to relieve the elastic
misfit strain associated with being in the lattice. In addition, the segregated state at the grain
boundary, the over-sized solute atoms can take on a bonding state closer to their native
environment. Figure 2.1.2, taken from the work of Seah, gives the propensity of select
solute to grain boundary segregate in specific solvents $^{22}$. The interpretation of the graphs is
simple. The solvent and the solute are selected, the propensity of the solute to segregate in
the selected solvent is given by the magnitude of separation of the two along the x-axis. The
magnitude of separation of the solute along the y-axis, either above or below, the solvent
indicates the likelyhood that either grain boundary embrittlement or strengthening will occur
upon segregation.
Fig 2.1.2. Gives the propensity of select solutes to grain boundary segregate.

If a solvent solute combination is selected in which the propensity to grain boundary segregate is high, then the solute excess at the grain boundaries upon annealing will increase and the interfacial energy could potentially be driven to zero and result in an effective grain boundary energy \( = 0 \). This result would imply that grain boundaries represent no penalty to
the stability of a polycrystalline system at any temperature and the thermodynamic driving
force for grain growth would be absent. The ideology and extensive derivations of this
theory can be seen in the works of Weissmuller 23-24, Liu and Kirchheim 25, Kirchheim 26,
Millett et al 27 and Beke et al 28. A general consensus was found in the aforementioned
works that a metastable thermodynamic equilibrium grain size could exist in some systems
due to solvent-solute interactions at grain boundaries with respect to interactions in the
lattice. This concept was based on the grain boundary interfacial energy, the enthalpy change
of segregation by the system and the solute excess in the form of a grain boundary
monolayer. Slight differences in the metastability arise when considering solute-solute
interactions in the absorbate layer. This is ignored when using the Langmuir-McLean
theories to extrapolate solute effects on reducing interfacial energy and includes such
deviations not predicted by Weissmuller (compositional dependence on the enthalpy change
of segregation, multiple surface coverages and temperatures for any particular metastable
state) 29. In addition, solute-solute interactions predict that below certain surface fractions,
the minimum of the system may only be possible at low surface coverages 29.

Examples of Thermodynamic Stability of Nanocrystalline Metals

Based on the aforementioned theories there exist several experimental examples that
suggest the reduction of interfacial energy as a means of stabilizing nanocrystalline
microstructures. It has been shown in Nb-Cu 30, Ni-P 31, RuAl-Fe 32, Ti-Cu 33, Y-Fe 34 and
In many of these systems, a reduction in grain growth was observed at modest temperatures with eventual precipitation of equilibrium intermetallic phases at higher temperatures. When solute is lost to the formation of a secondary phase rapid and/or abnormal grain growth were routinely observed. Solute segregation to grain boundaries was suggested as the mechanism for interfacial energy reduction in all metastable systems produced via non-equilibrium processing. Although it is unclear whether kinetic modes of stability (solute drag forces and/or mobility activation energy increases associated with solutes on the grain boundaries, particle/second phase pinning and chemical ordering may have played a role in grain size stability of the above mentioned systems.

Krill et al. performed a more extensive analysis into interfacial energy reduction by solute segregation in nanocrystalline Pd with Zr impurities. Krill derived an expression for how segregated grain boundary solute reduced the intrinsic grain boundary energy for a given system Equation 2.1.5.

\[
\gamma = \gamma_o - \Delta H_{\text{seg}} \frac{n_{b\text{seg}}}{A} \tag{2.1.5}
\]

\(\gamma_o\) is the intrinsic interfacial grain boundary energy,

\(\Delta H_{\text{seg}}\) is the enthalpy change of B solute atoms to the grain boundary,

\(n_{b\text{seg}}\) is the number of moles of B solute at the grain boundary of area A.
Inserting typical values for high and low angle grain boundaries (0.5 and 0.2 J/m²) into equation 4 shows that for solid solutions in which $\Delta H_{\text{seg}}$ is in excess of 25-10kJ/mol, an effective value for $\gamma$ of $\sim$0 can be reached.

The Pd-Zr system is interesting in that the $\Delta H_{\text{seg}}$ is 31kJ/mol suggests a high propensity towards grain boundary solute segregation \textsuperscript{37}. However, the system exhibits extensive room temperature solubility of $< 12$ at\% which increases up to $\sim 17$ at\% at elevated temperatures \textsuperscript{38}. The enthalpy of mixing for Pd-Zr is -364kJ/mol \textsuperscript{37} and suggests that once segregated, solute will resist the formation of secondary phases. In order to maximize solute segregation effects, the room temperature solubility limit was increased to 21 at\% with mechanical alloying. With alloy concentrations above 21 at\%, room temperature precipitation of the intermetallic phase Pd$_3$Zr occurred. The lattice parameters of the milled alloys retaining solid solution showed an increasing linear relationship with Zr content \textsuperscript{9}. Upon isothermal annealing at a temperature range of 1125 to 1500°C (T/TM > 0.90 where TM is melting temperature in Kelvin), the grain size remained stable at less than 100nm. ZrO$_2$ was found to form in high content Zr alloys when annealed under poor vacuum conditions. Samples that exhibited oxidation induced loss of solute also showed an increased grain growth rate over non-oxidized samples. This observation absolved particle pinning as a means for thermal stability in this system. Samples that resisted the formation of secondary phases showed that the density of solute at the grain boundaries increased linearly with grain
size/temperature. At the same time, the lattice parameter of the alloys dropped and approached that of pure Pd. This would imply loss of solute from the lattice. It was suggested that the mechanism for segregation was one of entrapment of the solute during boundary expansion and not bulk lattice diffusion. Krill et al. showed that, with an increase in solute content at the grain boundaries, there was also an associated decrease in the interfacial grain boundary energy of the alloys by using equation 4\textsuperscript{9}. It was reported that increasing the bulk Zr solute concentration increased the onset temperature for grain growth while suppressing the rate of grain growth. This effect was maximized with a bulk Zr concentration of 20 at\%. Krill et al. then suggested that stability in this system at low temperatures was attributed to solute drag effects and that only a reduction in interfacial energy could result in stability at higher temperatures\textsuperscript{9}. Extensive analysis and data was not collected for high temperature microstructure evolution.

Additional extensive studies on nanocrystalline electroplated Ni with W additions by C.A. Schuh et al. have recently been reported\textsuperscript{36,39,40,41}. The estimated elastic enthalpy for W atoms dissolved in Ni is 60kJ/mol\textsuperscript{37}. The room temperature solubility of W in Ni is ~ 12 at\%\textsuperscript{38}. Various compositions were produced between 1 at % and 20 at%.

It was found that Ni-W alloys exhibit a monotonic trend of decreasing grain size with alloying additions. Through annealing studies and peak broadening analysis, it was determined that all compositions exhibited exceptional thermal stability below 500\degree C. At
higher temperatures, grain growth took place and resulted in grain sizes in excess of 100nm. At the higher temperatures and concentrations > 20 at% W, precipitation of the equilibrium intermetallic phase Ni₄W took place. Precipitation of this equilibrium phase was not observed at lower concentration over the temperature range tested. Grain size evolution was monitored with TEM and was found to correlate well with Scherrer analysis of the grain size from XRD measurements. Abnormal grain growth was not found for any of their samples.

Though computer simulations and atom-probe tomography, it was determined that the segregation of W to Ni grain boundaries was weak. As a result, grain boundary interfacial energy of the system decreased 60% but did not reach a value of zero for any composition tested. Grain boundary segregation was most pronounced for low atomic % W and decreases with increasing atomic % W. It was found that short range ordering was suppressed more for smaller grain sizes due to a grain boundary disordering affect. By considering solute-solute interactions, the compositional dependence of $\Delta H_{\text{seg}}$ was found to influence segregation behavior in Ni W alloys more than the computed grain size effect. It was reported that the most dramatic effect on decreasing $\gamma_b$ occurred in the dilute limit where segregation was greatest. Formation energy calculations predicted that Ni W alloy became more stable as the grain size increased. Further computer simulations indicated that the onset temperatures for both grain growth and grain boundary relaxation decrease with decreasing grain size. In conjunction, there exists a crossover point at the smallest grain sizes in
which grain boundary relaxation occurs before grain growth. More importantly, a connection in that thermodynamic effects (reduction in interfacial energy due to solute diffusion) may enter into both the pressure and mobility terms in the generally expected equation for the velocity of a grain boundary undergoing curvature driven growth was shown 36. This interfacial energy/mobility connection is paralleled on the relationships between grain boundary disorientation angle, energy and mobility in pure metals 42,8. As the disorientation of low angle boundaries decrease a subsequent decrease in interfacial energy as well as in increase in the activation energy for boundary mobility has been reported 8. It is therefore expected that mobility should decrease because diffusion becomes more restricted within the boundary. It was shown in the Ni W systems that the onset temperature for grain growth can be doubled by increasing the activation energy of grain boundary mobility, while a 60% reduction in interfacial grain boundary energy has only a minimal effect 36.

Work using TAP analyses (tomographic atom probe) done by Farber et al. on Ni P showed P enriched zones around the grain boundaries of annealed samples 31. After heating at 400°C, it was determined that a continuous 0.8nm thick zone of composition ~ 14at% P occurred at the Ni grain boundaries and that the precipitation of the equilibrium phase Ni3P occurred. At lower temperatures, the composition of the grain boundary layer decreased in % P. By using a mass balance, Farber was able to predict the grain size of select Ni P alloys at temperatures below which precipitation occurred 31. For high concentration of P,
annealing had little effect on increasing the grain size. The lack of grain growth was attributed to the formation of a metastable grain size as predicted by reduction in interfacial energy. At lower P concentration annealing had a large effect on increasing grain size. The authors attributed this effect to kinetic stability factors.

The work by Botcharova et al. on Cu Nb alloys prepared and consolidated by mechanical alloying have shown high thermal stability. Seah’s plot Figure 2.1.2 suggest a strong likely hood that Nb will grain boundary segregate in Cu. Through mechanical alloying, Botcharova was able to produce Cu Nb solid solutions with a nominal Nb content of 0, 5, 7 and 10 at% and <15nm grain size. Heat treating these samples at 600, 700, 800, 900 and 1000°C led to the precipitation of a Nb rich phase. The size of the Nb rich phase was found to increase with annealing temperature and time up to a size of ~500nm. The copper grain size was found to increase from the as milled grain size. However, even at 1000°C (~94% of pure copper TM), a microstructure of less than 50nm, consisting of equiaxed grains, was maintained. This is counter intuitive since, the general consensus is that the formation of precipitates is highly correlated with extensive grain growth in systems that show thermodynamic stability. No explanation was proposed for the thermal stability of the alloys at such high temperatures by Botcharova et al.
2.2. Synthesis of Nanocrystalline Metals

Nanocrystalline metals were originally produced by Gleiter and coworkers at the University of Saarlandes Germany, in 1981, by employing inert gas condensation. Since then several other techniques have been developed to produce such microstructures.

1. Electro-Deposition
2. Controlled Crystallization of Amorphous Precursors
3. Physical Vapor Deposition
4. Pulse Laser Ablation
5. Sever Plastic Deformation

These techniques can be divided into one step processes and two step process based on the product type.

2.2.1. One Step Methods

The one step methods involve the production of bulk materials with an internal microstructure <250 nm. The one step methods involve techniques such as electro-deposition, severe plastic deformation, crystallization of bulk metallic glasses, and vapor/lazer deposition/ablation. These processes are costly and they each have limitations. Electroplating of nanostructured metals has been accomplished. However, the
material produced is normally left with microscopic pores. In addition samples are contaminated with organic bath additives necessary for grain refinement. As such electroplated samples are generally suitable only for thin plates and coatings. Some severe plastic deformation techniques, such as high pressure torsion and equal channel angular pressing, can produce nanostructures but have difficulties in the ability to reach the most limiting grain sizes possible within a system. Crystallization of bulk metallic glasses can lead to embrittlement of the material due to the formation of intermetallics. Vapor deposition is most suitable for the production of coating and films.

2.2.2. Two Step Methods

The two step methods involve the production of particulates with an internal microstructure <100nm.

Inert Gas Condensation

Inert Gas Condensation can produce metallic powders with an internal nanocrystalline microstructure, however, this process can be complicated and expensive equipment is required to produce the powder product.\[^2,4^4\].

Mechanical alloying (MA) Mechanical Milling (MM).

One of the most commonly used methods is high energy ball milling or (High Energy MA/MM). Mechanical Milling/Alloying is a very versatile method for producing
nanocrystalline metals and alloys. This method has been employed in the production of such materials for over the past 10 years. In general, mechanical milling/alloying produces nanostructured materials with grain sizes $\ll 100$ nm by mechanical attrition of coarser-grained materials. This process includes repeated welding and fracturing of powders, typically in a high energy ball mill. As in MA, this re-welding and fracturing continues until the elemental powders making up the initial charge are blended on the atomic level, such that either a solid solution and/or phase change results. The chemistry of the resulting alloy is comparable to the percentages of the initial elemental powders. With continued milling time, grain size reduction occurs, which eventually saturates at a minimum value that has been shown to scale inversely with melting temperature of the compound. In literature there exists a large body of work dedicated to understanding the mechanisms governing the production nanocrystalline materials by this method, as well as the mechanical and other physical properties of materials produced in this manner.

2.3. Advantages of Mechanical Alloying

In general, there are three reasons that mechanical alloying was selected for production of the alloys tested in this thesis.

2.3.1. The Production of Particulates

Most metals/alloys can be prepared through mechanical-alloying with the product being in particulate form. Generally, most high melting metals can be directly ball milled to
produce powder. In instances where materials are too ductile to be directly milled into powder such as (low melting metals, and many face center cubic structured metals), surfactants and/or cryogenic milling can be employed to induce to production of powder. Fine particulates offer greater versatility when considering up scaling to industrial manufacturing. This is due to the ability for these particulates to be sintered into almost any shape or size given the proper conditions (high temperatures and pressures) and is already a very long existing practice in the manufacturing scheme.

2.3.2. Increased Solubility Limit

High energy ball milling has been shown to vastly increase the limit of solid solubility in many metallic systems in which equilibrium room temperature solubility does not otherwise exist. In general, many solvent-solute systems that exhibit large changes in elastic enthalpy upon segregation (a prerequisite for a large reduction in interfacial energy) are systems which exhibit very little solid solubility in each other. Thus, high energy ball milling has the ability to create super saturated solid solutions\textsuperscript{63-67}. As with other techniques, such as ECAP and HPT, this is not possible. The result of having a super saturated solution which resist the formation of secondary phases (via having a large negative enthalpy of mixing) is also important. As the basis for interfacial energy reduction is to maximize the diffusion of large misfit (insoluble) solutes from solid solution to the grain boundaries and once there resist the formation of secondary phases.
2.3.3. Production of the Smallest Possible Grain Size

High energy ball milling has been shown to dramatically reduce the grain size in metallic systems. Decreasing the grain size greatly influences the mechanical properties and several reports now exist detailing these mechanical advancements in the limits of nanocrystallinity. Decreasing the grain size not only improves the mechanical strength and properties but it also increases the amount of grain boundary area present in the sample. It has been theorized by the above mentioned authors that complete monolayer coverage may be required to reduce the interfacial energy to zero. Given this, a large amount of solute would then be required to saturate the grain boundaries in a nanocrystalline material. Figure 2.3.1 below gives the atomic percent Zr required to form a complete monolayer in an Fe matrix having cubic shaped grains verses the fixed grain size of the matrix. In a system in which the average grain size is 50nm, an alloy composition of approximately 1 at% Zr in Fe would be required to produce monolayer coverage in all the grain boundaries of the system. As the average grain size decreases, the Zr content need in the alloy to produce monolayer coverage dramatically increases.
Fig 2.3.1. Gives the atomic % Zr required to produce monolayer coverage in nanocrystalline Fe verse the grain size of the matrix.

### 2.4. Current Limitations of Nanocrystalline Fe

Through high energy ball milling, it is possible to refine the grain size in pure Fe to ~10nm ± 2nm, as can be seen in Figure 2.4.1a \(^6^8\). The grain size distribution is narrow with approximately 25% of the number fraction of the microstructure above 10nm. Figure 2.4.1b gives a Hall Petch Plot for several literature values for ball milled Fe compiled in the work of R.K. Guduru et al \(^6^9\). The initial part of the graph is steep, with an eventual leveling off at the limiting grains sizes. The graph extends over 1000X decrease in grain size, resulting in a 30X increase in hardness (~4.7GPa yield strength). Taken from the thesis work of Mallow,
it can be seen through grain growth studies of pure Fe, Figure 2.4.1c, that grain growth initially takes place rapidly with an eventual leveling off at longer times \(^{68}\). Additionally, it can be seen that a large change in grain size occurs at 552\(^{\circ}\)C. Figure 2.4.1d are literature values compiled in Figure 4 of reference \(^{70}\) giving the as measured grains size as a function of the homologous temperature at which they were annealed. Literature values agree well with the work of Malow, that is the onset for rapid grain growth in pure nanocrystalline Fe occurs at about 45\% (552\(^{\circ}\)C) of its melting temperature. Thus it appears that this temperature is a threshold temperature and is the baseline for the improvement of thermal stability in Nanocrystalline Fe alloys.
Fig 2.4.1 (a-d), (a) gives grain size for pure Fe produced through high energy ball milling. (b) is a Hall-Petch plot of nanocrystalline iron complied from literature values. (c) is the isothermal grain size evolution of pure Fe produce through high energy ball milling taken from literature. (d) is a plot of grain size versus percent melting temperature for nanocrystalline Fe compiled from literature.
2.5. Motivation of Current Work

Based on a thermodynamic approach, it will be shown in the data presented in this thesis that dilute solute additions of Ni, Zr, Y, Ta and W were added to pure Fe. Of these alloys, the addition of Zr to pure Fe led to a group of nanocrystalline alloys extremely resistant to grain growth at elevated temperatures. That is, a grain size of 50 nm was maintained over a range of temperatures (24°C to ~ the respective melting points \(^70\)). This was a remarkable achievement, since the alloys were comprised of only 0.33, 1 and 4 at% Zr in Fe. The motivation for this work followed from the stabilization effect of Zr in Pd system (1). As such, Zr in Fe has a size misfit of +28% and an estimated elastic enthalpy change \(H_{\text{seg}} = 92\text{kJ/mol} \(^{37}\), compared to +11% and 31kJ/mol for Zr in Pd \(^{37}\). The interfacial enthalpy of mixing for Zr in Fe is -118kJ/mol while for Zr in Pd it is -364kJ/mol \(^{37}\). The large negative enthalpy of mixing for Zr in Fe indicates that the alloys should resist the formation of a secondary equilibrium intermetallic phase predicted by the phase diagram. Figures 2.5.1 and 2.5.2 give the thermodynamic parameters (elastic enthalpy change for segregation and the enthalpy of mixing) for select solutes in Fe \(^{37}\).
Fig 2.5.1 gives the enthalpy of mixing for select solutes in Fe.

### Table Fe - IV

Calculated values in kJ (mole of atoms)$^{-1}$ for both limiting partial enthalpies of solution, $\Delta H^\text{solute}_{\text{Fe} X}$ and $\Delta H^\text{solute}_{\text{X} Fe}$, and the heat of mixing, $\Delta H^\text{mix}$, for liquid binary iron alloys. The reference states are those of (Fe) and (X).

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<th>$\Delta H^\text{solute}_{\text{X} Fe}$</th>
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There is an extra uncertainty in a value marked by * since it is not known whether the assumption is justified to take the same $\Delta H^\text{mix}$ in both the solid phase and the liquid phase for this element.
Fig 2.5.2. gives the elastic enthalpy change for select solutes in Fe (i.e. solute A in solvent B).
References: Chapter 2


Experimental: CHAPTER (3)

3.1. Milling of Alloys

3.1.1. Fe-Based Alloys

Fe based alloys were investigated. The solute concentrations selected for comparison were 0 to 10 atomic percent and included such solutes as W, Ta, Y, Zr and Ni. Hardened steel vials and 440C stainless steel balls were used for mechanical alloying in a Spex 8000 shaker mill. Milling was accomplished by loading the hardened steel vials with the correct weight ratio of Alpha Aesar Fe and solute powders (~-325 mesh, 99.95 to 98.5% purity) to produce the desired compositions. A 5g charge was used. The ball to powder mass ratio was maintained at 10:1. The vial was sealed in an argon atmosphere (O₂<1 ppm) prior to milling. Milling took place for 20 hrs at an approximate temperature of 24 to 40°C (room temperature). The mechanical milling resulted in powders with a particle range of 20-100µm and a nanocrystalline microstructure of approximately 5-10nm.

3.1.2. Pd 20 at% Zr

Pd based alloys were investigated. The solute concentration selected for analysis was 20 atomic percent Zr. Hardened steel vials and 440C stainless steel balls were used for mechanical alloying in a Spex 8000 shaker mill. Milling was accomplished by loading the
hardened steel vials with the correct weight ratio of 99.95% pure palladium sponge and 99.95% pure zirconium powder. A 2.5g charge was used due to material cost. A ball-to-powder weight ratio of 1.6:1 was used. Initially the charge was milled for 24 hours in vacuum. This resulted in complete welding of the charge to the inside of the vial. In an attempt to create usable yield, the vial was then filled with Ar and milled for another 24 hours. This process gave a small powder yield and attempts to reproduce powder samples using this method were not successful.

3.1.3. Cu₃Ge

Ge powder was first produced by placing high purity cleaved Ge wafers in a polished hardened tool steel vial loaded with a 10:1 mass ratio of 440 stainless steel ball bearings to Ge. The vial was then sealed in an Ar atmosphere (O₂<1 ppm) prior to mechanical milling. Milling occurred at room temperature for ~15 min in a SPEX 8000 high-energy shaker mill. The resultant Ge powder was sifted through a 2500 mesh screen, which yielded average particle sizes <5µm. X-ray diffraction (XRD) analysis confirmed that neither oxidation nor amorphization of the powder occurred during the milling process. The mechanically milled Ge powder was always stored in a sealed glass vial in an argon environment.

The ε₁ compound Cu₃Ge was prepared by loading the milled Ge powder with the correct weight ratio of Alpha Aesar Cu powder (170+425 mesh, 99.9%) into a hardened and
cleaned steel vial to produce the desired Cu-25 atomic percent Ge. The ball to powder mass ratio was maintained at 10:1 and the vial was sealed under a vacuum of 10^{-4} Torr prior to milling. Mechanical alloying in the SPEX 8000 shaker mill was then performed at room and liquid nitrogen temperatures for various times. Liquid nitrogen milling was accomplished by placing the sealed vial in a thick nylon sleeve modified to allow placement into the high energy mill, as well as to allow an inflow and outflow of liquid nitrogen. After the ball milling procedure was completed, the Cu$_3$Ge powder was removed from the steel vial in an Ar atmosphere glove box and stored in a glass vial. The milled nanocrystalline grain size Cu$_3$Ge powder consisted of agglomerated particles that ranged in size from 1-100µm.

3.2. Bulk Sample Preparation

3.2.1. Uniaxial Pressing, Heat Treating and Mounting of Powders

Thin, disk-shaped specimens were prepared through uniaxial cold pressing of the asmilled powders at 3.5GPa in a tungsten carbide 6.35mm diameter die. These tablets were subsequently heat treated over a temperature range of 24-1373°C for up to 60mins under an Ar/2%H atmosphere. All compositions for one data point i.e. (1/3, 1 and 4 at 500°C) were heat treated together at the same time. This was done to remove issues of repeatability with different heating treatments. The heat treated samples were then grouped and mounted in Epothin, a room temperature cureable resin, (available through Buhler), which polymerizes with no increase in temperature.
3.3. Experimental Techniques for Microstructural Characterization:

3.3.1. Indentation

For the body of work given, the Vickers hardness tests were performed using a Buehler Micromet II retrofitted with a 100X objective lens, this was combined with an ocular lens of 10X, giving a total magnification of ~1000X. The lens system was calibrated with an Olympus objective micrometer with a grating spacing of 0.005mm. The automated loading system was checked using a digital pocket balance and calibrated to the correct load. The automated loading time was checked with a digital stop watch, and then calibrated to give the correct time. Hardness tests were then performed on individual particles within the compacts with loads appropriate to avoid influences of the plastic zone with particle boundaries. The dwell time of 15 seconds for each indent was concurrent with ASTM standards (ASTM Standard Test Method for Vickers Hardness of Metallic Materials (1)).

Nanoindentation was also performed on limited samples. Indentation was performed with a Hysitron IT 900 TriboIndenter. This system is completely automated and was used for measuring hardness and elastic modulus of sample materials.

3.3.2. X-ray Diffraction

X-ray diffraction techniques are routinely used by investigators of nanocrystalline materials in order to gain an understanding of their microstructures. Broadening of peaks
within a spectrum occurs because of three factors: 1 a decrease in the crystallite size, 2 the stored strain in a material and 3 instrumental factors (2). In order to accurately estimate the grain size of a nanocrystalline material, the instrumental broadening must first be subtracted from the total broadening. Thus it is important to have a good understanding of what the instrumental broadening is attributed to and how to accurately determine its magnitude. For the work completed in this thesis, x-ray diffraction analysis of the ball milled powders was performed with a Rigaku x-ray diffractometer using CuKα (\(\lambda = 0.1542 \text{ nm}\)) radiation, with a diffracted beam graphite monochromator having instrumental broadening \(\approx 0.1^\circ\) at an angle of 69.13°. The instrumental broadening was measured as a function of 2theta, and both the Gaussian and Lorentzian integral breath values are given in Figure 3.3.1. below for a high temperature annealed Fe standard and from a (100) single crystal Si peak.
Correct alignment of the diffractometer’s optical axis is crucial for minimization in broadening and as such alignment should be checked frequently to insure optimum performance. The correct tube voltage and current setting for a 2kW CuKα tube are 40kV and 40mA (3). Due to tube cooling issues, these values were never used. Settings of 25kV and 30mA were used to avoid over heating issues. These settings, in combination with the high absorption of CuKα radiation in sample with Fe, led to low signal to noise issues which were most pronounced in the as milled cases. To compensate, much longer count times of approximately 5-10sec, with a step size of 0.04°, were required to attain adequate data.
Samples were prepared by sprinkling approximately 200mg of ball-milled powder onto a glass slide coated with amorphous double sided adhesive tape. This sample was then mounted in a standardized x-ray holder.

CuKα2 peak stripping and background subtraction was accomplished by using Xpowder software which can be found via http://www.xpowder.com/. Peak fitting was accomplished by using the Origin 5.0 built-in fitting function for Gaussian and Lorentzian profiles. By design, the output of the Gaussian function gives a value equal to only 0.85% of the true full width at half maximum. Therefore, a correction must be applied to get correct width value. These full width values were then converted to integral breaths using the standard conversion equations. Once the integral breaths are known, a number of techniques can be used to determine the crystallite size and stored strain in the samples.

For the body of work presented here, the crystallite size was estimated using the Scherrer formula Equation 3.3.1 (2):

$$\beta = \frac{0.9\lambda}{d \cos(\theta_o)}$$

(3.3.1)

where $\beta$ is the peak broadening, $\lambda$ is the wave length of the incident radiation, $\theta_o$ is the center of the peak and $d$ is the volume average coherent length normal to the diffracting plane. As
with the Scherrer equation, $\beta$ is the sum of the broadening due to the crystallite size and stored strain. Therefore, the estimated grain size can be smaller than the actual grain size. For this work, the grain size was then calculated from the Scherrer equation for each fundamental peak and the values averaged.

For the body of work presented here, the internal lattice strain was estimated using the Stokes Wilson formula Equation 3.3.2 (4):

$$\eta = \frac{\beta \cot(\theta_o)}{2}$$  \hspace{1cm} (3.3.2)

Where $\eta$ is the micro strain, $\beta$ is the peak broadening and $\theta_o$ is the center of the peak. As with the Scherrer equation, $\beta$ is the sum of the broadening due to the crystallite size and stored strain. Therefore, the estimated strain can be larger than the actual strain. It should be mentioned that there exists other methods that extract the different portions of the broadening separately, such as the Williamson-Hall and the Warren-Averbach methods. For this work the strain was then calculated from the Stokes-Wilson equation for each fundamental peak and the values averaged.
3.3.3. **Optical Microscopy**

For the Work presented here, Fe base alloys were polished first with tungsten carbide sanding papers in the following sequence of: 240, 400, 800, 1200, 2400 and 4000 grit. The samples were polished unidirectionally and then rotated 90° after each polishing stage. This was done as a check to insure that all scratches from the previous grit size had been removed before proceeding to the next lowest grit size.

Samples were then polished with a suspension of alumina particles in water in the following sequence 1, .3 and .05 μm particles sizes. At each of these stages, the samples were thoroughly rinsed with water and placed in a sonicator to avoid contamination of the finer grit polishing stages. A mirror finish should be seen on the sample after all polishing stages are complete. The samples were then etched for approximately 15sec at room temperature in a Nitol solution containing 98% ethonal and 2% nitric acid. Once the etching was complete, the samples were quickly transferred to water to rinse away any remaining etchant. The samples were then washed and dried with acetone, followed by ethanol. Samples were imaged using a Zeiss inverted microscope and Axio Vision LE software. Image J software was used to analyze optical images for average grain size and percent area abnormal grain growth due to high temperature annealing.
3.3.4. Scanning Electron Microscope

For the work present here, a Hitachi S3200 Variable Pessure Scanning Electron Microscope was used. This SEM operates as a conventional high resolution thermionic microscope that allows the operator to back fill the chamber with an inert gas such as N\textsubscript{2}. Thus, samples which are poorly conducting, such as metallic samples embedded in resin, can be inserted directly in the scope chamber without applying a metallic coating. The SEM was equipped with an Oxford Isis EDS system which allows for semi-quantitative elemental analysis of element with an atomic number equal to or greater than 5. The given software also allows for x-ray line scans and mapping of elements.

3.3.5. Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM)

X-ray inherently gives no information on grain size/precipitate distributions such as volume and number fractions and is especially insensitive to indicating abnormal grain growth (secondary recrystallization). It is therefore, necessary to utilize TEM imaging techniques to gain a direct measurement of these microstructural relations as they pertain to understanding modes of grain growth stability. As the production of all samples reported in this work were of particulate form, TEM sample preparation was problematic due to the high hardness and low inter particle bonding. As such several methods and attempts were conducted in order to produce adequate samples for such analysis.
3.3.5.1. **TEM Sample Preparation**

**Bulk Sample Preparation**

*Uni-axial Pressing*

Thin disk specimens were then prepared by uniaxial cold pressing the as-milled powders at 3.5GPa in a tungsten carbide 6.3 mm diameter die. These tablets were subsequently heat treated over a temperature range of 24-1373°C for 60mins under an Ar/2%H atmosphere. Resultant samples had inadequate density and particle bonding to allow for mechanical thinning to below 100 μm, the prerequisite for electro jet and ion milling procedures.

*Explosive Compaction*

Nanocrystalline Fe based powders were produced by mechanical milling. These powders were then loaded into Cu tubes and sealed under argon. Consolidation was accomplished by explosive compaction at the University of Utah, Salt Lake City, USA. The sample attained a high density, approximately 99.9%, though some sections of the sample contained blow holes due to the propagation of the shock wave during compaction. The compaction procedure is described in more detail by Guruswamy et al. (5). Samples were then cross sectioned using a diamond saw and thinned below 100 μm by mechanical polishing. Electro jet thinning resulted in preferential etching at the particle bond sites and
led to premature failure of the overall samples integrity. Adequate samples could not be produced by this method.

_Powder Dispersion Methods: (In Chronological Order)_

**Desired Results:**

Fe based metal powders were to be dispersed into a matrix for TEM analysis. The principle of cold welding was to create a matrix-powder-matrix “sandwich”. The resulting sandwich was to be less than 100µm, so that further thinning could be done efficiently using jet polishing techniques. Because of the jet polishing technique, the matrix used for holding the metal powders must be a conducting material. Also, due to the jet polishing technique, it was required that the final sandwiches were to be 3mm disks or that it was feasible to punch 3mm disks from the sandwiches. This was done in order to fit the requirements of the jet polishing sample holder.

**Procedure 1 – Cold welding using pressing of multiple Cu “strips”**

Sheets of annealed copper, ultra high purity Cu and Al cut to various dimensions (4cm² and below), were pressed together in a press with the intentions of achieving cold welding. Loads of 5 to 40 tons were used to press the disks together. It was found that smaller sample sizes bonded better due to higher stresses upon pressing. However, upon the application of any significant forces to pull apart the strips, it was determined that practical bonding could not be achieved using this technique.
Procedure 2 – Cold welding using rolling of multiple Cu “strips”

Procedure 2 employed the same techniques as procedure 1, except cold rolling techniques were employed to deform the strips. Very similar results were found from this technique.

Procedure 3 – Cold welding using pressing of multiple 3mm Cu disks

A 3mm punch and die were used to punch 3mm disks out of a sheet of annealed copper. It was intended that the small surface area of the disks would provide a necessary stress for cold welding. Disks were found to have a convex face and a concave face. Disks were placed in a press with the concave face of one sample in contact with the convex face of another sample. Loads of 5 to 40 tons were used to press the disks together. It was found that loads of over 10 tons were sufficient for “bonding” of the two disks.

A solution of ethanol and metal powders was placed in the concave face of a copper disk and the ethanol was allowed to evaporate. Next, another disk was placed on top of the first in a “sandwich” format and pressed at loads over 10 tons. The powder concentration within the sandwich was varied. It was found that less lead to better bonding. 3mm disks were punched out of the flattened samples to be used in jet polishing. The aforementioned “bonding” was later determined to be only mechanical locking i.e. an overlap of the samples over one another during pressing, as opposed to being actual cold welding.
Procedure 4 – Cold welding using rolling of multiple 3mm Cu disks

Procedure 4 employed the same techniques as procedure 3, except the copper disks were pressed together in a cold roller, as opposed to in a press. This procedure separated the disks upon entering the roller, and also, sandwiches had to be rolled multiple times to achieve desired thicknesses. The bonding of the disks was poor due to the disks separating or shearing apart at the interface.

Procedure 5 – Cold welding using rolling of folded Cu strips

Procedure 5 employed the same techniques as procedures 1 and 2, however only one strip of copper was used as the matrix. The strip was folded in half over itself and it was intended that the folded corner would provide an area of stress concentration as well as prevent the sliding apart of the interface during the rolling procedure. Direction of rolling was varied as well as the location of the fold (horizontal as opposed to vertical folding). It was found that a small degree of cold welding was achieved at the folded portion of the sample. Powder was placed in the fold of the copper and the corner end of the sample was fed through the cold roller. Samples were rolled to the lower thickness limit of the machine (approximately 80-90µm). The powder charge prevented the interface from welding.
Procedure 6 – Direct pressing of powders into single Cu strips

Procedure 6 employed similar techniques to procedure 5. However, to increase the efficiency of sample production, a large amount of powder was pressed directly into single strips of copper using direct uniaxial pressing and high loads. Next, the strip was fed through the rolling mill several times to reduce the starting thickness from 1mm to ~100 μm. This helped both the bonding of the Fe powder into the matrix of copper, as well as dispersed the initial powder, pressed uniaxially, over a larger area. Using this technique, strips of copper could be cut proportionally to the desired number of TEM samples. Since the powder to be examined comes directly in contact with pressing surfaces, it was important that pressing surfaces be cleaned well prior to pressing. Numerous 3mm disks could be punched from these samples. This process produced lots of samples with particles very well bonded to the matrix copper with a uniform thickness (100 μm), already appropriate for jet polishing.

Jet Polishing Procedure

The 3mm disks were placed into the sample holder. A solution of 5% nitric acid in ethanol was used as the jet polishing solution. This solution was suitable for etching Fe and Cu evenly. Samples were jet polished until a very small hole could be seen using the proper voltage, current and temperature settings. It was intended that the material surrounding the small hole would be electron transparent for TEM analysis. It was found that 6v and 200mA with the 5% nitric acid solution would produce a pin sized hole in approximately 2 minutes.
However in many case preferential etching took place between the weld interface of the Fe particle and copper matrix. TEM samples were produce by this method but were of low quality.

*Focused Ion Beam (FIB) Preparation*

Samples were prepared using FEI Quanta 200 3D focused ion beam system. This instrument allows for milling and deposition on the submicron scale. The electron optics are 200V to 30kV and ion optics are 5-30kV with an 800,000X max magnification. Samples were prepared for both institute imaging under the ion beam for ion channeling contrast imaging and for H bar lift out samples for TEM imaging. Extensive elaboration on the FIB processing of nanocrystalline samples for TEM and ion channeling contrast imaging is given in the following chapter (Chpt. 4).
References: Chapter 3


Application of Focused Ion Beam (FIB) to Nanocrystalline Metals: CHAPTER (4)

Submitted to Materials Characterization

Application of Focused Ion Beam Microscopy to Nano-Crystalline and Ultra-Fine Grained Metals

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4.1. Introduction

Producing electron transparent specimens can be the most difficult aspect of microscopy for some materials due to a wide range of problems from difficult to process specimen geometries such as powders (1) to the need for site specific analysis (2). Up to the development of the Focused Ion Beam (FIB) (3) the most common preparation techniques were mechanical thinning followed by either electro-jet-polishing (4) or ion-milling. In both cases specimens are mechanically thinned to 100µm or less and then selectively thinned further in certain regions. The goal of each technique is to obtain as large of an electron transparent region as possible from a bulk specimen while not changing the microstructure of interest in the process. At the same time suitable electron transparency requires a final thickness of less than 100 nm (5) with even thinner requirements for advanced TEM methods such as Z-contrast imaging and high resolution TEM. In some materials this can prove problematic since the largest thin regions will be possible at the very onset of perforation of a hole though the dimple produced by either technique. If the material exhibits poor inter-particle bonding or a large difference in chemical etching rates the onset of perforation can be difficult or impossible to achieve.

The submerged double-jet electropolishing technique was developed by Schoone and Fischione (6) in 1966 which allowed for automatic termination of the polishing operation when a perforation was detected. In this system the specimen is setup as the anode and the
voltage, current density, temperature, time, and fluid flow rates all affect the polishing process (7). In addition to these system parameters the mechanical properties (8) and even physical dimensions of the specimen must also be considered for ideal conditions to be obtained. Due to the complexity of these interactions significant personal experience along with literature research on similar materials must be performed to obtain acceptable results with any consistency. In our research nanocrystalline (NC) and ultra-fine-grained (UFG) metal alloys were electro-polished both in the mechanically consolidated bulk state and also by embedding the hard powder particles into a softer matrix of annealed copper (9). In all three cases poor inter-particle bonding and/or chemical etch rate differences prevented suitable electron transparent specimens from being obtained.

Gaseous source ion beams are commonly used in TEM sample preparation in a similar fashion to electropolishing as a “final step” to electron transparency. Argon is typically used as the ion source with beam energies ranging from several eV to tens of eV. The energy of the beam as well as the angle of the beam to the specimen surface are each important in minimizing surface damage (10). It was reported in the study that low energies and low angles produce the minimum amount of surface damage with the Ar ion beam. In our research UFG Zn-Al alloys were Ar ion milled at both low and high beam energy and at both low and high angles. The films deteriorated prior to suitable electron transparency. Due to the highly non-radial symmetric appearance of the perforations (more resembling
cracks than holes) it is thought that poor particle bonding limited the ability of the ion mill to produce acceptable electron transparent specimens.

Ion emission from a liquid metal source (LMIS) was also first developed in the 1960’s by Krohn (11) who was researching thrusters for use in space flight. Several years later he used the concept to develop an ion probe for high resolution mass spectroscopy (12). Gallium was proposed as a high brightness, low energy spread liquid metal ion source in 1975 (13) and has since been the dominant LMIS for use in FIB instruments. The development and advancement of FIB technology was initially driven by the semiconductor industry (14) where it has been put to a wide array of uses from device fabrication and lithography to circuit diagnostics and failure analysis. There are many advantages in using a FIB for specimen preparation. Perhaps the most important advantage is the precise site selection and milling control enabling high-quality surface finish of the final specimen. General FIB instrumentation and application are discussed in detail in literature (15) (16). In summary, the FIB microscope operates along the same principle as the scanning electron microscope (SEM) in that a beam of charged particles is rastered across a specimen. However, in a FIB microscope the charged particle beam consists of positively charged ions rather than electrons. The resultant signals at each raster position are used to form an ion induced secondary electron image that exhibits a wide range of useful information (16). The most important information for determining grain sizes in polycrystalline metals is ion channeling contrast where lattice planes can steer ions through small angular changes (17).
In secondary electron mode crystals which are able to channel more effectively due to their orientation produce fewer detectable electrons since secondary electron production is a near-surface phenomenon. The crystals close to the ideal channeling directions therefore show up darker than those which channel less. This effect shows a cyclical repetition through varying tilt angles with varying widths and distances between troughs depending on relative crystal orientation (18). In addition to imaging, the FIB can be used for micromachining such as selective materials deposition and local material removal by milling and polishing.

During the last 25 years, the FIB instrumentation has become an important technology for a wide array of materials science applications (18). Metal research with submicron features, such as interface, grain size, grain boundary, and precipitate distribution, are of specific interest in recent years (19). Analysis of such features is essential to understand their structural and functional properties. Due to its micromachining and imaging capability the FIB has great prospect in the characterization of these submicron and nanometer scale features. Decreasing costs, increasing performance, and perhaps most importantly the increased availability of the FIB machines has exposed more scientists to the flexibility of this technology for all sorts of microscopy. The goal of this paper is to examine and discuss the use of the focused ion beam to UFG and NC metals and its benefits over traditional two-step processing techniques.
4.2. Experimental

Ball Milling – Heat Treatments

Two nanocrystalline iron (1at% nickel and 1at% zirconium) and one zinc (9at% aluminum) based alloy were investigated. For both the iron and zinc based alloys hardened steel vials and 440C stainless steel balls were used for mechanical alloying in a Spex 8000 shaker mill. Milling was accomplished by loading the hardened steel vials with the correct weight ratio of high purity elemental powders to produce the desired compositions. The ball to powder mass ratio was maintained at 10:1. The vial was sealed in an argon atmosphere (O₂<1 ppm) prior to milling. Milling took place for up to 20 hrs at room temperature for the iron alloys and up to 10 hours at cryogenic temperatures for the zinc alloys. Cryogenic temperatures were necessary for the zinc alloys to maintain the mechanically alloyed material in powder form during processing. Cryogenic temperatures were maintained throughout the milling process using a specially designed capsule which enveloped the steel vial in a continuously fed liquid nitrogen bath. The resulting iron and zinc alloys were subsequently heat treated at approximately 40-70% of the homologous melting temperature for 60 minutes under an Ar/2%H atmosphere to study grain growth and stability of the microstructures. X-ray diffraction analysis of the ball milled powders was performed with a Rigaku x-ray diffractometer using CuKα (λ=0.1542 nm) radiation with a diffracted beam graphite monochromator having instrumental broadening ≈ .1°. Nanoscale microstructures were confirmed for the iron based alloys from diffraction line broadening measurements using the
Scherrer equation and TEM analysis. All zinc alloys were too coarse for x-ray line broadening studies with average grain sizes always above 100nm. Their ultra-fine-grained structure was confirmed with TEM analysis.

**Electropolishing**

Milled powders were uniaxially cold pressed at 1GPa for zinc alloys and 4GPa for iron alloys in a tungsten carbide die. The thin disk specimens were then heat treated at the previously described temperatures to increase bonding and density. Samples were mechanically thinned and polished to the correct dimensions required for electrojet polishing (3mm diameter and approximately 80µm thick). Samples were subsequently electrochemically thinned (8% nitric acid, 92% ethanol) using a Fischione Model 120-230 electrojet polisher. Inadequacies with particle bonding and preferential etching led to overall sample deterioration for both the iron and zinc based alloys. Similar experiences have been reported in other systems (20). As a second electropolishing method samples of iron alloy powder were prepared by embedding the milled powders into 1.5mm thick strips of annealed copper by uniaxial pressure. These strips were then thinned to 100µm by cold rolling. Cold rolling allowed for particle dispersion as well as increased particle bonding with the matrix. TEM samples 3mm in diameter were subsequently electrochemically thinned (8% nitric acid, 92% ethanol) from the backside. While Nitol is universal etchant for copper alloys with iron
dispersoids preferential etching at the particle matrix interface occurred leading to particle pullout even under weak magnetic fields.

**Dimpling – Ion Milling**

As with the electropolishing preparation method milled powders were uniaxially cold pressed and mechanically thinned to a 3mm diameter and thickness of approximately 80 µm. The samples were then dimpled until the bottom of the dimple was less than 10µm thick. An argon ion mill was used for final thinning. The dimple was ion-milled until a perforation formed the bottom of the mechanically thinned area. The resulting specimens deteriorated in the thinnest regions before they became electron transparent. A range of incident angles and beam energies was used with little improvement in the resulting samples.

**Focused Ion Beam**

The FIB has unique advantages in cases where mechanical preparation is difficult or impossible (21) as in the case of TEM specimen from as-milled particles. Extensive reviews of FIB micromachining capabilities for cross sectional TEM specimen preparation can be found in literatures (22). The conventional FIB TEM lift-out (LO) process (23) used in this study consists of four major steps:
1. Creating lift-out thin section;
2. In situ lift-out of thin section;
3. Thin-section attachment onto TEM grid;
4. Final thinning.

This conventional lift-out procedure was followed for the TEM sample preparation of as-milled powder particles and powder pressed into pellet form in Fe based alloys. In the case of particles pressed in pellet form for Zn based alloys a novel method combining the advantages of traditional TEM specimen forming technique and the FIB thinning technique was devised. The following sections describe the FIB TEM specimen preparation processes in detail. All FIB related work was performed using an FEI Quanta 200 3D DualBeam system with a 30keV Ga\(^+\) ion beam. Bulk samples for lift-out work were coated with approximately 100 nm of palladium-gold using a Denton sputter coater. Images in this paper were taken with a 30keV/90pA electron beam at a working distance of 15mm. Images were also taken in “snap shot” mode using the ion beam as a direct imaging tool with contrast resulting from ion channeling.

As-milled particles and bulk consolidated Fe samples

The conventional FIB TEM lift-out process was followed to prepare TEM specimens from the as-milled particles and mechanically consolidated samples. Prior to any milling a
platinum layer was deposited to serve as a protective cap to the final cross-section face. This protected the final surface from ion beam tail damage during the milling procedure. This platinum strip was deposited using an ion beam current of 500pA. Cross section cuts were done with a beam current of 20nA and a subsequent cleaning of the cut face was carried out with a beam current of 5nA. These cross section cuts were done on both sides of the platinum strip to create the thin lift-out section. The in-situ lift-out of the thin section was performed with an Omni-probe micro-manipulator system. Platinum deposition was used to fasten the micro-manipulator to the thin section and also for attachment of the thin section to a copper TEM grid. All attachments were done by using a 100pA beam whereas the detachments were done with a 1nA beam. Final polishing was performed with ion beam currents of 1nA, 300pA, and 100pA in series to create the final smooth electron transparent window surface. The final transparent windows had a thickness of 50-70nm. Surfaces prepared for ion-channeling imaging were polished with the same procedure but only on a single surface.

The “Wedge” Technique

The Wedge technique was devised to allow the bulk specimen to act directly as the film support and specimen grid to place into the TEM. The UFG/NC powder was pressure consolidated into a 3mm diameter disc. The diameter was chosen to fit into standard TEM specimen holders. It was thinned to approximately 100µm and then halved using typical
metallographic techniques then a tripod polisher was used to polish a slope into the surface until the knife-like edge could be observed across the center of the 3mm diameter (Figure 4.1). The tip of the knife edge was polished perpendicular to the original flat face to present a very thin (~10µmx3mm) flat surface to the ion beam. The thinned edge was used to produce the final electron transparent film. A platinum cap layer was deposited onto the leading edge using a 500pA ion beam. A 5nA ion beam was first used to thin the face to ~2µm. Final polishing was then carried out with an ion beam current of 1nA, 300pA, and 100pA to create the electron transparent window. The final transparent window had a thickness of 50-70nm.

Figure 4.1: Procedure for producing wedge.
4.3. Results Section

As-milled particles and consolidated Fe samples

Figure 4.2 shows the procedure for a TEM film lift out. Figure 4.2a shows an isolated unstressed metallic particle with a diameter of ~30µm. The alloy’s composition was 99at% Fe and 1at% Ni. The particle had been heat treated at 900°C for 1 hour. The region of interest was masked with a 3µm thick Pd layer. This layer protects and prevents the carry down of surface topography as well as premature milling due to the beam divergence (beam tail) during cross-sectional preparation. Electrical contact to the stage and particle isolation was made possible by particle dispersion on to carbon tape. Figure 4.2b shows a top down view after completion of the initial hog out (the beginnings of the H bar lift out). The film was approximately 6 µm thick. Figure 4.2c shows an oblique view of the same stage of preparation. Figure 4.2d shows film attached to the copper supporting grid after being progressively thinned using a decreasing beam current as described in the experimental section. The final film thickness was well below the 100nm threshold for acceptable transparency and produced this transparency over a 100+ µm² area. Figure 4.2e shows a bright field image of an isolated region of the nanostructure within the sample. The results proved that nanostructures did in fact exist, but alongside a much coarser surrounding microstructure.
This supports the results predicted by x-ray line broadening which was the motivator for this microscopy study. The remaining nanostructured regions after annealing at such a high homologous temperature comprised a very small volume fraction of the material.

Figure 4.2: (a-d) shows the procedure for a TEM film lift out from an un-stress metallic particle. (e) shows a bright field micrograph of the samples microstructure.
Figure 4.3 shows the procedure for an ion channeling/SEM cross-section. Figure 3a again shows a region within an isolated metallic particle of identical Fe-Ni composition as the aforementioned particle, this time heat treated at 700°C for 1 hour. Again the region of interest was masked with the Pd. Figure 3b shows a higher magnification view of the cross-sectional area of the undeformed and stress free particle. In these images the observable contrast is generated via channeling of the ions through regions of varying crystallographic orientations which emit secondary electrons proportional to the lattice orientation. Immediately apparent is the microstructure consisting of large irregular polycrystalline grains of various orientations with an average diameter of 10 µm. Layered between these larger grains are regions of UFG/NC grains with an average grain size of ~ 150 nm. Other areas of interest in the image are the rough outer surface layer of the particle as well as the micro porosity associated with incomplete particle bonding.
Figure 4.3: (a) as-milled Fe-Ni alloy heat treated at 700°C for 1 hour. (b) higher magnification view of fine structures
Figure 4.4 shows the final cross-section of a pellet which had been uniaxially cold pressed from Fe-1 at% Zr as-milled powder and then heat treated at 913°C for an hour. The field of view is within a single powder particle within the pellet (Figure 4a). The low density of the final pellet allowed for clear distinction of individual particles on the surface due to the 20-30 vol% porosity seen. The ion-channeling image contrast shows the as-annealed microstructure consisting of nanostructured grains over a very wide area with a slight asymmetry to the grain dimensions in one direction. The preferred orientation of this asymmetry in some regions (Figure 4b) of the image could be due to the pre-anneal deformation although similar characteristics have been seen in free-standing powders subject to no mechanical deformation after milling. No significant abnormal grain growth behavior was observed although very small volume fractions of individual grains in the ultra-fine grain regime were seen.
Figure 4.4 (a) shows the final cross-section of a pellet which had been uniaxially cold pressed. Figure 4(b) shows a higher magnification of the above cross section.
Wedge technique

Significant difficulties in creating an electron transparent section and the attachment of this thin section to TEM grids was experienced using the conventional FIB TEM lift-out specimen preparation procedure with the Zn-Al based UFG and NC alloys in this study. This is likely a result of the residual stress from processing and the very low hardness of Zn-Al leading to bending and coiling of the film. The so called wedge technique presents a small volume, easy to thin edge to the ion beam while at the same time serving as mechanical support to the film and also as the specimen grid to be placed in the TEM column (Figure 4.5a). Using this geometry with concepts from the traditional H-bar polishing technique high quality electron transparent sections were able to be produced (Figure 4.5b) using significantly less time on the FIB with large areas showing excellent electron transparency. The UFG microstructures were characterized to have an average grain size of 175 – 400nm depending on the annealing conditions (Figures 4.5c, d).
Figure 4.5 (a) shows the wedge polished sample. (b) shows TEM sample FIBed to electron transparency. Images (c-d) show bright and dark field images of the samples microstructure.
4.4. Discussion Section

Production of high quality and large area electron transparent specimens through traditional TEM specimen preparation techniques such as electropolishing and ion-milling has proven difficult and in some cases impossible in the UFG and NC alloys studied. For some of the annealed Fe based microstructures very limited volumes fractions of nano-crystalline material were found within a coarser matrix. X-ray diffraction line broadening results along with elevated hardness measurements suggested nanostructures existed within the specimens; the challenge was to find and image them. Random site selection as would occur with traditional two-step transparent specimen preparation methods would be unlikely to reveal this type of microstructure easily if at all. The site-specific thinning ability along with the in-situ imaging of the FIB allowed for TEM films to be produced directly in regions which initially showed the fine contrast of the nanostructures using the ion channeling effect of the ion beam. For the Zn base alloys studied the FIB allowed for production of a self supporting electron transparent film directly into a bulk specimen which could also serve as the specimen grid for insertion into the TEM. This prevented the premature failures seen in both traditional two step preparation techniques as well as film lift-outs using the FIB while at the same time reducing sample preparation costs.
4.5. Conclusion

The focused ion beam has allowed for highly reliable TEM specimen preparation with the ability to prepare samples from difficult to process specimens as well as site specific selection where needed. These abilities along with the relative ease and speed in which samples can be produced has led to the FIB becoming the primary TEM specimen preparation technique for our research group and increased the quality and quantity of images obtained. Future advancements as well as the continued spread of the availability of FIB technology will only help scientists who seek to understand and characterize the microstructures of the materials they are studying.
References: Chapter 4


8. Influence of material properties of TEM specimen preparation of thin films.


Results: Fe Based Zr Alloys: CHAPTER (5)

For this study, Fe based alloys were investigated. The expected thermally stabilizing solutes selected for comparison were Ta, Y, W and Zr with approximate compositions of 1, 5 and 10 at% in Fe. These solutes were selected for Fe, based on their propensity to grain boundary segregate, that is, the elastic enthalpy of segregation and their ability to resist the formation of secondary grain boundary phases from segregated solute, i.e. the enthalpy of mixing. These values can be seen in Table 5.1.

Table 5.1 Thermodynamic parameters for select solutes in Fe

<table>
<thead>
<tr>
<th>Solute Addition</th>
<th>Elastic Enthalpy (kJ/mol)</th>
<th>Enthalpy Mixing (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>+1</td>
<td>-6</td>
</tr>
<tr>
<td>Ta</td>
<td>+61</td>
<td>-67</td>
</tr>
<tr>
<td>Y</td>
<td>+95</td>
<td>-6</td>
</tr>
<tr>
<td>W</td>
<td>+35</td>
<td>0</td>
</tr>
<tr>
<td>Zr</td>
<td>+92</td>
<td>-118</td>
</tr>
</tbody>
</table>

The addition of Ni to Fe was selected as a control. Since Ni and Fe have similar atomic radii, the elastic enthalpy of segregation of Ni in Fe is (+1kJ/mol) is low. At high temperatures, Ni enjoys complete solid solubility in Fe. It is suggested that Ni will have a negligible influence in the thermal stability of nanocrystalline Fe. The results for Ta, Y, W
and Zr are given below. While some preliminary data on Ni in Fe is given here, a separate chapter on the in-depth experimental results for Ni in Fe is given in addition to this chapter.

Figure 5.1 gives the initial grain size for all room temperature milled samples (20 Hrs.) Ni initially has an effect of reducing the grain size of nanocrystalline Fe. However after the addition of more than 1 at% Ni, further reduction in grain size is not observed. As intuition suggests, increasing the atomic misfit between solvent and solute should lead to a greater reduction in the grain size. As observed, elements with the largest atomic radii (Y and Zr) have the most influence on reducing the grain size.

![Grain Size vs Solute Composition](image)

Figure 5.1. the as milled grain size for Fe versus at% Ni, Y, Ta, W and Zr
Figure 5.2 gives the internal lattice strain induced by room temperature milling, and the atomic size misfit between the solutes and Fe. Ni has an initial influence of increasing the lattice strain. However after the addition of 1 at% Ni, further increases in lattice strain are not observed. Again, Y and Zr have the largest effect, and that is to increase the lattice strain with increased solute content.

![Lattice Strain vs Solute Composition](image)

Figure 5.2 the as milled lattice strain for Fe versus at% Ni, Y, Ta, W and Zr

Solutes having ideal elastic enthalpies (a prerequisite for large interfacial energy reduction) and tendencies for grain boundary segregation, showed precipitation in the initial un-heat treated as-milled states. Based on X-ray analysis (Figures 5.3-5.6), it can be seen that the formation of secondary phases occurred. The precipitating compositions include Y and Ta (5 and 10 at%). Ni, W and Zr showed no initial precipitation at any compositions.
milled. In the remaining compositions, a meta-stable solid solution was induced and maintained throughout the milling process. Based on these observations, i.e. the ability of a solid solution to resist secondary phase formation, the additions of Zr and W to Fe appeared to be the solutes of choice. Additions of W to Fe gives an enthalpy of mixing of 0kJ/mol and an elastic enthalpy of +35kJ/mol, while Zr in Fe has an interfacial enthalpy of mixing of -118 kJ/mol and an elastic enthalpy of +92kJ/mol. Based on thermodynamic parameters, the solid solution of W in Fe should form secondary phases before the solution of Zr in Fe. It is also suggested that Zr has a higher propensity to grain boundary segregate in Fe compared to W.

Figure 5.3 the as milled diffraction patterns for (Fe, Fe 1, 5 and 10at% Y)
Figure 5.4 the as milled diffraction patterns for (Fe, Fe 1, 5 and 10at% Ta)

Figure 5.5 the as milled diffraction patterns for (Fe, Fe 1, 5 and 10at% W)
To further test the ability of certain alloys to resist secondary phase formation, the additions of W and Zr to Fe were tested through isothermal annealing at elevated temperatures. The addition of 5 and 10 at% W to Fe were tested and both showed the dramatic formation of secondary intermetallic phases at 700°C. The extent of precipitation was greater in the 10at%W alloy than that of the 5 at%. However extensive phase formation still occurred in the 5 at% W alloy. The x-ray diffraction of 5 at% W in Fe is given in Figure 5.7.
Figure 5.7 the Fe 4 at% W heat treated at 700°C for 1 hour

The solubility of Zr in Fe was maintained at room temperature up to 10 atomic percent, as given by the lack of extra visible peaks in the x-ray spectrums. Also a decrease in the intensity and an increase in the width of the diffraction peaks occurred with an increase in Zr concentration, indicating a decrease in grain size and increase in strain with Zr concentration. By comparing Figures 5.8-5.10, the effect of time and temperature on loss of solubility, or rather precipitation of what was determined to be the intermetallic phase Fe₂Zr can be observed. Figure 5.10 shows that solubility was maintained for 10 at% Zr at 500°C
for all times up to 60min. However, at 700°C, immediate precipitation occurred. The compositions of 1 and 4 at% Zr maintained solubility at 500 and 700°C for all times 5, 15, 30 and 60 mins (Figures 5.8 and 5.9). Based on these results, in combination with the thermodynamic parameters, the compositions of 0 to 4 at% Zr were determined to be best alloys for resisting formation of secondary phases and thus the most likely alloys to exhibit significant thermal stability at even higher temperatures.

![Image of heat treated diffraction patterns](image)

Figure 5.8 the heat treated diffraction patterns for (Fe 1at% Zr)
Figure 5.9 the heat treated diffraction patterns for (Fe 4at% Zr)

Figure 5.10 the heat treated diffraction patterns for (Fe 10at% Zr) at 500°C (60min) and 700°C for (15 and 60min)
To ensure the occurrence of grain boundary segregation of the Zr solute, isothermal annealing studies were undertaken. The results of 4 at% Zr annealed at 800°C are given in Figure 5.11. Figure 5.11 gives the isothermal changes in grain size and lattice parameter in this sample. As indicated, there is a rapid increase in grain size to about 23 nm after 15 min, followed by a slow increase to 27 nm after 60 min. This was mirrored by a corresponding decrease in lattice strain which is not shown. The lattice parameter shows an inverse trend, which is a rapid drop from 0.2882 nm followed by a slow decrease to 0.2871 nm after 60 min. This is still larger than the lattice parameter of pure Fe (horizontal line ~0.2869 nm). Since the x-ray spectra showed no second phase formation and because there exists a ~28% size misfit between Zr and Fe, the lattice parameter of pure Fe will increase linearly with solute content in solution. Taking the drop in lattice parameter due to annealing and dividing it by the total possible change, it can be estimated that approximately 85% of the solute has been removed by annealing at 800°C for 1 hr.
Figure 5.11 shows the change in grain size as a function of time for 4 at% Zr in Fe at 800°C. In addition the simultaneous decrease in lattice parameter is given. The horizontal line at ~0.2867nm represents the theoretical lattice parameter for pure Fe.

The Fe-Zr alloys were re-milled at compositions of 1/3, 1, 4, and 10 atomic percentages. Several microstructural characterization techniques were then carried out on isothermally annealed samples. The reported results are given below.

Figure 5.12 shows the Vickers hardness as a function of annealing time for mechanically alloyed nanocrystalline 0, 1/3, 1 and 4 at% Zr in Fe. As milled, the hardness for the 0, 1/3 and 1 at% Zr samples are between 8 and 10GPa. These values are expected and correspond well with similar reports of nanocrystalline Fe produced by severe-plastic
deformation techniques. However, the 4 %at Zr sample deviates noticeably from the hardness values for pure Fe as given in the literature. This hardness increase in Fe-4 at% Zr is attributed to a combination of solid solution strengthening and decreased grain size to 5.4nm, as estimated by x-ray, compared to 9.5nm for pure Fe. The initial hardness appears to drop with the addition of 1/3 at% Zr and increases again with the addition of more solute into solution. The 1/3 at% Zr is the only sample in this study that shows an initial increase in hardness with annealing to 530°C. The rest of the compositions show either no change or a slight decrease in hardness with annealing to 530°C. The hardness for all compositions shows a negative trend above 530°C. This is most apparent for pure Fe. It has been well documented that nanocrystalline Fe shows dramatic grain growth at temperatures in excess of 0.4 to 0.45 of its melting temperature (450°C-500°C). The hardness in the 1/3, 1 and 4 at% Zr samples are elevated with respect to pure Fe throughout the plotted temperature range. At the higher temperatures, the hardness for all compositions tends to coalesce to the same hardness. The 1/3 at% Zr at 1173°C has large error bars relative to the other samples; the reason for this will be discussed later.
Figure 5.12 shows the Vickers hardness versus annealing temperature (0, 1/3, 1, and 4, at% Zr). The initial slope of the plot is steep with a gradual leveling off at the limiting grain sizes reported. In this study, the hardness of the 4 at% Zr is elevated with respect to that of the lower solute concentrations (1/3 and 1 at% Zr), which both agree well with the other reported values for nanocrystalline, pure Fe. In this plot, 0.1nm⁻¹ corresponds to a grain size of 100nm and an average hardness of 4.75GPa. This indicates that all alloys in Figure 5.12 are predicted to have nanocrystalline microstructures consisting of ≤100nm grains at temperatures ≤913°C.
Figure 5.14 as reported in 3 with additional data, shows the grain size evolution (as measured by x-ray analysis) versus annealing temperature for 1/3, 1, 4 at% Zr and pure Fe. The initial grain sizes of the 0, 1/3, 1 and 4 at% Zr are 9.5, 8.3, 6.7 and 5.4 nm respectively. Figure 5.14 shows that at approximately 700°C (54%Tₘ), the grain size for nanocrystalline Fe has already reached a value of about 6000 nm. For comparison, our ball milled Fe-Zr alloy samples are all still nanocrystalline at temperatures well beyond that. Upon reaching about 800°C, grain growth of 1 and 4 at% Zr alloys ceases altogether at a grain size of about 45nm, while the grain size for 1/3 reaches 100nm. From x-ray measurements, the grain structure of all of the Fe-Zr alloys remains nanocrystalline and stable up to temperatures
approaching their respective melting points. Mechanisms which govern kinetic stabilization such as solute drag, particle pinning, etc. would be overcome at the temperatures over which thermal stability has been observed in these alloys. This supports the idea that the stabilization is due to thermodynamics as opposed to a kinetic mechanism. For comparison, data on Fe 1 at% Ni and Fe 10 at% Cr have been added. Since both Ni and Cr have atomic radii similar in size to Fe, the elastic enthalpy for segregation is small: approximately (+1 kJ/mol and 0 kJ/mol for Ni and Cr in Fe respectively) \(^1\). Therefore the additions of such solutes should have a minimal effect on interfacial energy reduction. As the data suggests, grain growth of these alloys is similar to that of pure Fe.

Figure 5.14 the grain size verse annealing temperature (1/3, 1, 4 and Reference Fe)

6000 nm data point is our work
From Figure 5.14, the grain size of 1/3 at\% Zr at 900ºC corresponds to ~100nm, and from Figure 5.12, the hardness of 1/3 at\% Zr at 900ºC corresponds to ~4.6 GPa. These data points, plotted on Figure 5.13 as (0.1, 4.6), fit well with the given literature data for nanocrystalline Fe. The data from Figure 5.14 suggests that between the temperatures of 800ºC and 1173 ºC, the microstructure of all Zr alloys remains stable with no grain growth. However, Figure 5.12 shows that over the same temperature range, a decrease in hardness occurs for all Zr alloys. Upon etching and optical analysis, it becomes apparent that abnormal grain growth (secondary recrystallization) has occurred in some of the alloys. Additionally, from the work of Seah 4, it is suggested that grain boundary segregation in Fe may led to grain boundary decohesion or embrittlement. This decrease in hardness could be attributed to either or both of the aforementioned mechanisms. Cracking was not observed at the corners of any Vickers indents made.

Figure 5.15 (a-b) shows the effect of solute concentration on grain size stability at 500ºC and 700ºC. In all alloys, there is a rapid increase in grain sizes within the first 5-8 minutes, after which grain growth stagnates in all alloys. The grain stability of the alloys at 500ºC (Fig. 5.15a) are staggered by composition, with 10 at\% Zr being the most stable. The pure Fe sample taken from literature was heat treated at ~50ºC lower than the other samples. However, the pure Fe still shows 40% more grain growth than the 10 at\% Zr sample. At 700ºC (Fig.5.15b), all the samples show a rapid increase in the initial stages of grain growth,
with an eventual leveling off at longer times. The grain growth in the same alloys at 500°C occurs to a much greater extent, with pure Fe being off the chart, 1 and 4 at% Zr samples exhibiting a ~2X increase, and 10 at% Zr having a ~3X increase in grain size. At 700°C, precipitation was observed in the 10at% Zr sample. This observation represents the first evidence for discounting Zener pinning as a kinetic mode of stability in the work presented here on FeZr alloys.

Figure 5.15 (a-b). the effect of solute concentration on grain size stability (10, 4, 1, 1/3 and 0 at% Zr) (Fig(a) 500°C and Fig(b) 700°C)
Figures 5.16-5.18 show optical micrographs of the microstructural evolution of the 0, 1/3 and 1 at% Zr alloys annealed at 530, 700, 913 and 1170°C for one hour. The micrographs are cross-sectional images of the mechanically-etched, alloyed, powder particles containing a nanocrystalline microstructure. The large cracks in the samples are due to incomplete bonding between the particles of the compact.

Figure 5.16(a-d) shows the microstructure for the as-milled nanocrystalline pure Fe. At 530°C, the image is void of any resolvable microstructure. From x-ray, the average grain size is measured to be ~60nm. At 700°C, the average grain size of the nanocrystalline Fe is measured optically to be 6000nm. At the alpha BCC to gamma FCC transition temperature (913°C) \(^5\), the microstructure doubles to an average grain size of 12000nm. However, once crossing 913°C, a large change in the average grain size of the sample takes place at 1173°C and is measured optically to be 40,000nm, suggesting that crystal structure influences the thermal stability of Fe. An Arrhenius plot (not shown) of grain size versus 1/T for the three points (700, 913 and 1173°C) shows curvature, indicating a possible change in mechanism after breaching 913°C.
Figure 5.16(a-d) the microstructural evolution in nanocrystalline Fe vs annealing temperature

Figure 5.17(a-d) shows the microstructure for the as milled nanocrystalline Fe 1/3 at% Zr. At 530°C, the image is void of any resolvable microstructure. The grain size, as measured by x-ray, is ~16.2nm. The following temperatures and grain sizes measurements from x-ray are as follows: 700°C $\rightarrow$ 33.1nm, 913°C $\rightarrow$ 100nm, and 1170°C $\rightarrow$ 90nm. The most noticeable change in microstructure occurs at 700°C, in which the microstructure begins to show abnormal grain growth (light regions). The average grain size of the abnormally grown microstructure was not measured for any temperature. However, the percent area of abnormally grown microstructure, measured optically from several lower magnification
images at 700°C, is estimated to be (~20%). This percentage increases with temperature to (30%) for 913°C. At higher temperatures, an effect of the BCC to FCC transformation on thermal stability of nanocrystalline Fe Zr alloys is not evident.

Figure 5.17(a-d). the microstructural evolution in nanocrystalline Fe .33 at% Zr vs annealing temperature.

Figure 5.18(a-d) is the microstructure for the as-milled, nanocrystalline Fe 1 at% Zr. At 530°C, the image is void of any resolvable microstructure. The average grain size is measured from x-ray to be ~15nm. The grain sizes, with respect to annealing temperature from x-ray measurements, are as follows: 700°C → 21nm, 913°C → 46.0 nm and 1170°C →
45nm. The most noticeable change in microstructure occurs at 913°C, in which the microstructure begins to show abnormal grain growth (light regions). The percent area of abnormally grown microstructure, in the 1 at% Zr alloy at 913°C, is estimated to be (~20%). At higher temperatures, it is difficult to interpret the optical micrographs. For the 4 at% Zr alloy, optical images at all temperatures were found to be void of any resolvable microstructure. In those samples, the average grain size from x-ray was measured to be 530°C \( \rightarrow \) 10.8nm, 700°C \( \rightarrow \) 17.0nm, 913°C \( \rightarrow \) 44.0 nm, and 1170°C \( \rightarrow \) 45.0nm. In Figures 5.16-5.18, it is apparent that solute concentration within the matrix has an effect on extending the temperature at which abnormal grain growth occurs.
Figure 5.18 (a-d) the microstructural evolution in nanocrystalline Fe with 1 at% Zr versus annealing temperature.

Figure 5.19 gives a low magnification image of the microstructure for pure Fe and 1/3 at% Zr in Fe, which are the same as Figures 5.16 and 5.17. Figure 5.20 gives a low magnification image of the microstructure for 1 and 4 at% Zr in Fe.
Figure 5.19  (a) a low magnification of the microstructural evolution in nanocrystalline Fe.(b) Fe with .33 at% Zr versus annealing temperature.
Figure 5.20  (a) a low magnification of the microstructural evolution in nanocrystalline Fe with 1 at% Zr. (b) Fe with 4 at% Zr versus annealing temperature.
Figure 5.21 is an etched, high-magnification image of 1 at% Zr in Fe, heat treated at 870°C which shows two contrasting regions. These are the same as seen above in the samples containing 1/3 and 1 at% Zr. The darker, granulated regions are nanocrystalline and the lighter, secondary, are recrystallized regions. Vickers hardness tests were accomplished by indenting with 10g load for 15 sec within the two regions. A 10g load was selected in order to avoid boundary effects between nano and large grained regions. The hardness for the recrystallized regions was estimated from the indentation diagonals to be ~3.4GPa and those of the nanocrystalline regions to be 6.7-7GPa. The same was done for the 1/3 at% Zr which resulted for the recrystallized regions a hardness of 3.1GPa and for the nanocrystalline regions to be 5.1GPa. Comparing this data to Figure 5.12, between the data points of 828°C and 913°C, shows that the values follow the given trend line. The increase in hardness of the recrystallized regions, of 3.4 and 3.1GPa, is highly elevated with respect to that grain size of 5-10µm reported for nominally pure Fe (900-600Mpa). Due to the small percent area of abnormal grain growth in both samples (1 and 1/3 at% Zr), this increase in hardness can be associated with the circumferential and underlying nanostructures.
Figure 5.21 the Vickers hardness on etched sample surface for 1 at% Zr at 870°C 1Hr.

Figure 5.22 is a graphical representation of the percent area remaining nanocrystalline after heat treating at elevated temperatures for 0, 1/3, 1 and 4 at% Zr. Above 913°C it was difficult to interpret the microstructures. Therefore higher temperatures are not reported.
Figure 5.22 the percent area remaining nanocrystalline for Fe and Fe with 1/3, 1 and 4 at% Zr versus annealing temperature.

Figure 5.23a is a surface image of an etched particle in cross-section (Fe 1/3 at% Zr annealed at 913°C for 1hr) taken with a focused ion beam. This image reveals the same surface texture as the optical micrographs, granular regions of nanocrystalline microstructure and dark smooth regions of secondary, recrystallized grains. Figure 5.23b is a high-magnification image of the region selected for analysis by focused ion beam (FIB) imaging in image 5.23a. In addition, it shows a cross-sectional surface normal to the etched surface which was cut and prepared using a FIB. Figure 5.23c shows a higher magnification of the cross-sectional area which takes advantage of the ion channeling effect to give crystal
orientation specific contrast of the particle. Immediately apparent is the microstructure consisting of large irregular polycrystalline grains on the order of \(10^{-6}\) m in diameter. Layered between these larger grains are regions of nanocrystalline grains. Micro porosity, associated with incomplete particle bonding, is also present. FIB ion channeling contrast imaging allows for analysis of particles (containing nanocrystalline microstructures) over large areas and site-specific TEM sample preparation. Producing adequate TEM samples, for microstructural analysis, from ultra-hard particles is extremely difficult and is not possible in many cases. Sample quality becomes more important when trying to accurately analyze regions of abnormally grown grains, inhomogenously distributed through the sample.
Figure 5.23  (a) an SEM image of the etched surface of a particle composition Fe 0.33at% Zr annealed 913°C for 1 hour.

(b) a channeling contrast image of a cross section masked in (A) prepared by FIB.

(c) a high magnification channeling contrast image of (B)
Figure 5.24 (a) gives a low magnification ion channeling contrast image of the microstructure of 1 at% Zr, annealed at 913°C for 1 hour. Large regions of nanocrystalline microstructure which appear to be elongated in one direction can be seen. There appears to be a vector field in which the elongation exists as flow patterns with in the field. Regions of instability within the microstructure can also be seen, as made apparent by the localized regions of secondary recrystallization (large grains).

In contrast, Figure 5.24 (b) gives a low magnification ion channeling contrast image of the microstructure of 4 at% Zr, annealed at 913°C for 1 hour. Here, the microstructure appears much finer, very equaixed and uniform in nature, as compared to the 1 at% Zr sample at the same temperature. In addition, microscopic pores can also be seen and are attributed to the mechanical milling process. This is the first evidence that thermal stability of a nanocrystalline microstructure can exist homogeneously and over the entire sample.
Figure 5. 24 (a-b). A low magnification ion channeling contrast image of 1 and 4 at% Zr in Fe at 913°C for 1 hour.
Figure 5.25 gives high magnification FIB ion channeling contrast imaging of all three alloys (1/3, 1 and 4 at% Zr alloys annealed at 913°C for one hour). Figure 5.25a is the 1/3 at% Zr alloy showing a nanocrystalline microstructure, with the long axis of the grains measuring a few hundred nanometers and the short axis measuring ~100nm. Figure 5.25b is the 1 at% Zr alloy showing a nanocrystalline microstructure much finer than the 1/3 at% Zr alloy showing that some of the grains are elongated in one axis. Figure 5.25c is the 4 at% Zr alloy showing a nanocrystalline microstructure much finer than the 1 at% Zr alloy. For the 4 at% Zr, the microstructure appears to be highly equiaxed. It is important to note that the observed microstructures in Figure 5.25a-c are a direct result of the annealing and grain growth that ensued, as deformation was not needed for sample preparation post annealing.

Figure 5.26 shows the microstructure of the as milled 4 at% Zr sample. The inset of the diffraction pattern showing broadened rings indicates the sample is BCC and nanocrystalline. From bright field/dark field images, it was determined that the largest grains present in the film were ~20nm with an average grain size below 10nm.
Figure 5.25  (a) a high magnification ion channeling contrast image of 0.33at% Zr in Fe annealed at 913°C for 1 hour.

(b) a high magnification ion channeling contrast image of 1 at%Zr in Fe annealed at 913°C for 1 hour.

(c) a high magnification ion channeling contrast image of 4at% Zr in Fe annealed at 913°C for 1 hour.
Figure 5.26 microstructure of the as milled 4 at% Zr sample

Figure 5.27 is a low magnification bright field micrograph of the 4 at% Zr at 913°C, showing approximately 10µm² of electron transparency. As is consistent with the optical and FIB images, the entire sample is comprised of a nanocrystalline microstructure. The microstructure is very uniform and homogeneous. The acquired diffraction pattern is
indicative of the crystal structure being BCC. The rings in this diffraction pattern are broken and not as continuous as in the as milled structure which indicates the increase in average grain size due to annealing at 913°C.

Figure 5.27 a low magnification bright field TEM image of 4at%Zr in Fe at 913°C 1hour, inset is the diffraction pattern.

Figure 5.28 is a Z-contrast image taken with a high angle annular dark field detector (HAADF), showing a large portion of the film seen in Figure 5.27. Only the high angle,
(>5°) incoherent, scattered beams were used to form this image. Therefore, the image contrast intensity is proportional to the atomic number. Channeling effects are also possible. The top bright amorphous region is the Pt cap deposited to protect the underlying microstructures. Here it is the atomic number that gives rise to image contrast. Low atomic number phases would appear dark and high atomic phases would appear bright. As can be seen, the microstructure appears very homogenous and void of any low atomic number phases (such as oxides and Fe rich phases) or high atomic phases (such as Zr rich intermetallics). Inset is an x-ray diffraction pattern of 4 at % Zr annealed at 956°C that is 43°C higher than the sample shown in bright field (Fig 5.27) and Z-contrast. The expected phase to precipitate upon annealing, as predicted by the phase diagram and x-ray spectra taken from highly annealed 10 and 7 at% Zr samples, is the Fe₂Zr (laves) phase, which has numerous fundamental peaks, none of which are present in the spectrum. The diffraction spectrum does not show the presence of any other second phases and therefore, at lower temperatures, second phases are not expected to form. The x-ray spectrum, combined with the Z-contrast image, is a strong argument against the formation of secondary phases in the 913°C 4 at% Zr sample.
Figure 5.28 a low magnification Z contrast image of 4at%Zr in Fe at 913°C 1hour, inset is the x-ray diffraction pattern of 4 at%Zr in Fe at 1000°C for 1 hour.

Figure 5.29 shows a high magnification Z-contrast image of 4 at% Zr in Fe at 913°C. The highlighted borders around the grains, as confirmed by area integration intensity profiling, indicates that higher atomic number atoms are present at the grain boundaries. Extended EELS analysis is forthcoming on samples of higher quality to better confirm the solute compositional profile across the grain boundary.
Figure 5.29 a high magnification Z contrast image of 4at%Zr inFe at 913°C and higher magnification indicating grain boundary segregated Zr solute.

Figure 5.30 shows a high magnification bright field image of Fe 4 at% Zr at 913°C. The grains are equiaxed and polyhedron in nature. From the analysis of several similar images, it was again possible to conclude that grain boundary and lattice precipitation of second phases did not occur. The grain size distributions (taken from 400 grains) are relatively narrow, showing that only a small portion of the microstructure is above 75 nm in either the number average or the volume average distributions.
Figure 5.30 is a high magnification bright field TEM micrograph of 4 at% Zr in Fe annealed at 913°C for 1 hour. Insets give the volume and number average grain size distributions as counted from 400 grains.

Figure 5.31 is a low magnification bright field micrograph of the 1/3 at% Zr at 913°C, showing approximately 36μm² of electron transparency. As consistent with the optical and FIB images, the sample is comprised of a composite consisting of large grains embedded in a nanocrystalline microstructure. The acquired diffraction pattern is indicative of the crystal
structure being BCC. The rings in the diffraction pattern are broken and not as continuous as in either the 4 at% Zr as milled structure or at 913°C. This indicates an increase in the average grain size to above 50nm (which is in agreement with x-ray analysis of grain size). In addition, there appears a strong arcing effect in the diffraction pattern indicative of a texturing in the film.

Figure 5.31 a low magnification bright field TEM image of 0.33 at%Zr in Fe at 913°C 1hour, inset is the diffraction pattern.
Figure 5.32 shows that the microstructure of the 1/3 at% Zr is mainly comprised of grains ~ 100nm in diameter. When comparing the average grain size of the 1/3 at% and 4 at% Zr sample, it is apparent that increasing the solute has an effect of decreasing the grain size.

Figure 5.32 a bright field TEM image of 0.33 at%Zr in Fe at 913°C 1hour, inset is the diffraction pattern.
Figure 5.33 shows that the microstructure has regions comprised of elongated grains, as confirmed by ion channeling contrast imaging shown in Figure 5.25a. The length of the short axis of the grains (~80 nm) compares well with the measurements from x-ray diffraction.

Figure 5.33 the bright field TEM image of 1/3 at.% Zr in Fe at 913°C. In addition, two dark fields are shown of the same area.
Figure 5.34 shows an ion channeling contrast image for 4 at% Zr in Fe at 1173°C. Three large grains of different orientation (different contrast) meet at a common point. Dispersed within the grains are precipitates occupying approximately 15 area %, as estimated through digital image analysis.

Figure 5.34 a low magnification ion channeling contrast image of 4at%Zr in Fe at 1173°C for 1 hour.

Figure 5.35, a higher magnification bright field TEM for 4 at% Zr in Fe at 1173°C, shows that a large majority of the precipitates are spheroidal and below 50nm in diameter with an average spacing of ~50 as estimated by the 2D projection. The TEM film thickness is approximately 60nm, therefore the real spatial distance of the precipitates could be as much as $\sqrt{2}$ greater than that of the 2D projection.
Figure 5.35 a bright field TEM image of 4 at%Zr in Fe at 1173°C 1 hour.

Figure 5.36 shows a high magnification bright field TEM image of a single precipitate. In situ energy dispersive spectroscopy (EDS) was performed on the precipitate and the adjacent void region. EDS, as shown in Figure 5.36 (a & b), indicated that the composition of the precipitate was ~57 at% Fe and 42 at% Zr. The void region, or matrix, was indicated to be 96 at% Fe and 3 at% Zr. A small amount of Cr was found in both spectrums and was attributed to contamination by the stainless steel ball bearings during milling. As the Fe-Zr phase diagram predicts, the composition of 42 at% Zr in Fe at 1173°C corresponds to the equilibrium phase Fe$_2$Zr.
Figure 5.36 a high magnification bright field TEM image of 4 at%Zr in Fe at 1173°C 1hour. Circles indicate locations from which EDS spectra were collected.
Figure 5.37 the collected EDS spectra collected from figure (5.36). (a) EDS spectra taken from matrix region, (b) EDS spectra taken from precipitate.
Figure 5.38 gives the data collected over a 16 hour scan by the Rigaku Corporation in a zero background holder on 1 at% Fe annealed at 1373°C. Inset is a table of the approximated grain size, as estimated from the broadening of the Fe fundamental peaks. The grain size estimates are in good agreement with the x-ray broadening spectra performed at NC State University. This is in contrast to what was observed optically for this sample. Optical images of 1 at% Zr in Fe heat treated at 1373°C appeared to not contain any nanocrystalline regions, as can be seen in Figure 5.39.
Figure 5.38 1 at% Zr in Fe annealed at 1373°C in zero background holder, MiniFlex II Scan 16 hours - Collected at the Rigaku Corporation by Lori Fields.
Figure 5.39 high and low magnification optical image of 1 at%Zr in Fe at 1173°C 1hour.
Figure 5.40 (a-d) gives the surface morphology of the Fe 1 and 4 at% Zr samples, heat treated at 1373°C. Figure 5.40 (a) shows, for 1 at% Zr, that heating above the eutectic temperature results in the surface segregation and growth of an isolated secondary phase. Figure 5.40 (b) shows, for 4 at% Zr, that heating above the eutectic temperature results in a large amount of surface segregation leading to complete encapsulation of the as milled particles. Figures 5.40 (c-d) are low magnification images at the same annealing temperatures and compositions, as given in 5.40 a-b. The resulting EDS spectra for the 1 and 4 at% Zr, in Fe particles, identifying the chemical composition of the segregation induced secondary phases are given in Figure 5.41. The spectra indicates that while present, very little oxygen is incorporated in either the secondary phase present in the 1 or the 4 at% Zr samples. The amount of Cr is present in the bulk spectrum and the surface segregate spectrums of the 1 and 4 at% Zr samples are identical. Thus, Cr contamination is a result of milling with tool steel vials. However, as indicated in Figure 5.14, Cr has little effect in influencing the thermal stability of nanocrystalline Fe, even at concentrations of 10 at%.
Figure 5.40  
(a) a high magnification secondary electron SEM image of 1 at% Zr in Fe annealed at 1373°C for 1 hour.

(b) a high magnification secondary electron SEM image of 4 at% Zr in Fe annealed at 1373°C for 1 hour.

(c) a low magnification secondary electron SEM image of 1 at% Zr in Fe annealed at 1373°C for 1 hour.

(d) a low magnification secondary electron SEM image of 4 at% Zr in Fe annealed at 1373°C for 1 hour.
Figure 5.41 the collected EDS spectra collected from figure 38. (a) EDS spectra taken from 1 at% Zr in Fe regions marked on inset. (b) EDS spectra taken from 4 at% Zr in Fe regions marked on inset.
Figure 5.42 shows the loading versus penetration depth for nano-indentation experiments on 10 at% Zr in Fe in the as milled case and heat treated for 5min at 500°C.

Figure 5.42 the loading versus penetration depth for nano-indentation experiments run for 10 at% Zr in Fe in the as milled and the annealed at 500°C for 5 min states.

Figure 5.43 gives the nano-indentation hardness versus milling time for 10at% Zr in Fe. As the trend shows, a slight linear increase (8 to ~9.5GPa) occurs when milling from 10 to 20 hours at room temperature. There appears to be a sudden drop in hardness at 15 hours and this is unexplained. From x-ray analysis, the fundamental peak begins to disappear with increasing milling time. At 20 hours, only the (200) peak remains. DSC curves reveal a slight exothermic signal which was detected and reached a maximum at ~600°C. The
crystallization of Fe rich Zr amorphous alloys with compositions of 7-12 at% Zr have been reported. Reports indicate two exothermic maxima in differential scanning calorimetry one at 600 and one at 630°C. The first peak corresponds to the crystallization of α Fe and the second to the formation of Fe₂Zr or Fe₃Zr. Based on this data it is likely mechanical alloy has produced solid state amorphization of a portion of the Fe 10 at% Zr microstructure. Upon heating the amorphous Fe 10 at% Zr at 500°C, a large increase in the hardness is detected. The heat treated grain size is estimated by x-ray analysis to be 5 nm. This data point (~13GPa, .45) corresponds well with literature values for nanocrystalline Fe of similar grain sizes as given in Figure 5.13.

Figure 5.43 Shows the nano-indentation hardness vs milling time for 10 at% Zr in Fe and the nano-indentation hardness for 10 at%Zr in Fe annealed at 500°C for 5min.
References: Chapter 5


6.1. General Thermal Stability and Microstructure Development

6.1.1. Thermal Stability of 4 at% Zr in Fe

Through TEM, SEM, Optical, and X-ray analysis, at compositions \( \leq 4 \text{ at\% Zr} \), it has been shown that Zr solute resists formation of secondary phases at temperatures \( \leq \alpha \rightarrow \gamma \) in Fe (which is the BCC ferrite to FCC austenite allotropic transformation temperature of 913°C \(^1\) and thermal stability increases with solute concentration. There is strong indication that Zr solute is removed from the Fe lattice, as shown previously by a simultaneous decrease in lattice parameter with an increase in grain size upon annealing. Thermodynamics predicts a strong propensity for Zr to grain boundary segregate in Fe, and as a result, a reduction in the interfacial energy can be realized. The comparison of average grain sizes in pure Fe to 4 at% Zr, in Fe at 913°C, indicates a strong contrasting effect of solute on decreasing grain growth at temperatures at which kinetic modes of stabilization would be ineffective. It is therefore expected that, at temperatures less than \( \leq 913°C \), Zr solute resides in the grain boundaries which therefore results in a reduction in the interfacial energy. At temperatures between 913°C and 1335°C (the eutectic temperature), the phase diagram predicts \( < 1 \text{ at\%} \) or approximately no increase in solid solubility for Zr \(^1\). At 1173°C and \( \sim 30 \text{ at\% Zr} \), the phase field edge of Fe\(_2\)Zr terminates \(^1\). Taking these values and performing the lever rule indicates that the relative proportions, as predicted by the phase diagram of the respective
phases, are 13% Fe$_2$Zr and 87% $\gamma$ Fe. These values correspond well with the area fraction of Fe$_2$Zr: 15 % for the precipitates and 85% for the matrix as estimated from Figure 5.34. Because precipitates were observed to be homogeneously distributed throughout the lattice as opposed to preferentially along the grain boundaries (as shown in Figure 5.34), it is likely that Zr prefers to be in the lattice of Fe at 1173°C. It is this loss of solute due to re-absorption into the lattice and the formation of second phases that results in the unexpected loss of thermal stability in Fe-Zr alloys at these temperatures.

From earlier reports of Fe-Zr alloys, energy dispersive spectroscopy (EDS) and SEM analysis has revealed that annealing at temperatures $\geq$1335°C induces surface segregation, which leads to an oxidized Zr-rich phase$^2$. The 4 at% Zr alloy showed a much stronger surface segregation than lower compositions, which indicates the tendency for Zr to prefer free surface sites as opposed to inter-crystalline sites at these high temperatures or upon partial melting of the microstructure. For the 1 at% Zr, these surface segregates were isolated particles with a diameter less $< 1\mu$m$^2$.

Although TEM and Ion channeling contrast images revealed precipitation and the occurrence of extensive grain growth of Fe$_2$Zr at 1173°C, x-ray diffraction analysis did not reveal these microstructural changes. As found in$^2$, for all Fe-Zr alloys, grain sizes measured using x-ray diffraction at temperatures $\geq$ 1173°C were misinterpreted. This
inaccuracy was most likely a result of misinterpreting the estimated coherency length as the Scherrer method makes no distinction between the strain and grain size contributions to the peak broadening. As can be seen in Figure 5.35 a large number of nano precipitates exist in the matrix of the sample. Therefore if the precipitates are coherent, a large strain would result masking the as annealed grain size. These inaccurate results were further observed in repeated measurements at the parent device corporation (Rigaku). In addition no such indication of the Fe$_2$Zr Laves phases or any other Fe-Zr based phases were observed over Rigaku’s experimental range (0-120°) or any samples examined at NC State. This may be attributed to the size of the precipitates, as 50nm particle will broaden x-ray lines and decrease the intensity of reflecting peaks. The resulting signal may be an indistinguishable above the background and therefore not be detected.

6.1.2. Thermal Stability of 1at%Zr

The addition of 1 at% Zr in Fe resulted in a microstructure more elongated than that observed in the 4at%Zr sample. However a microstructure having an estimated grain size of $< 100\text{nm}$ was retained at 913°C. The microstructure appeared to be largely nanocrystalline with small regions of secondary recrystallization. By comparing the 1 and the 4 at% Zr samples we may conclude that by increasing the solute concentration a more uniform segregation and overall decrease in the anisotropy of interfacial energy occurs.
6.1.3. Thermal Stability of 1/3 at% Zr

The addition of Zr solute into nanocrystalline Fe shows a dramatic, stabilizing effect on the microstructure. The simultaneous change in lattice parameter, with increase in grain size without the formation of secondary phases, is strong evidence of grain boundary segregation. Additionally, Z-contrast images suggest that Zr solute resides on the grain boundaries. Thermodynamics predicts that Zr solute on Fe grain boundaries should provide a very stable system against grain growth. This appears to hold true even at low level impurity concentrations (< 1 at%). The unexpected stability of a microstructure with an average grain size of ~100nm with the addition of only 1/3 at% Zr, supports the idea of grain boundary energy reduction by solute segregation. Such strong thermal stability at low solute concentrations has not been experimentally demonstrated prior to this work and may be attributed to the large change in elastic enthalpy of Zr in Fe of $+92 \text{ kJ/mol}$. Following similar discussions as reported previously, it can be shown that independent of grain size, only 79% monolayer coverage is required to achieve $\gamma = 0$ in Fe Zr systems. The atomic fraction of Zr required to produce a monolayer can also be estimated to be $\sim 0.43 \text{ at\%}$ for an average grain size of 100nm. Therefore, $0.43 \times 0.79 = 0.35 \text{ at\%}$ Zr would be sufficient for $\gamma = 0$. Assuming that Zr solute loss due to surface segregation and/or precipitation did not occur, the 1/3 at% Zr would have enough solute to stabilize a 100nm structure. Additionally, as reported by Schuh et al. in Ni W alloys, grain boundary segregation was most pronounced in
the dilute limits\(^4\). This behavior may likely be relevant for the 1/3 at\% Zr in Fe.

### 6.1.4. Discussion on Abnormal Grain Growth

According to Hillert’s theory of grain growth, it is possible to show that in an ideal grain array, one in which the boundary energy is constant and no impurities are present, abnormal grain growth cannot occur\(^5\). If you consider a large grain of radius \(R\) in a matrix of smaller grains, then the growth rate relative to the matrix grains is given by the following equation 6.1\(^5\):

\[
\frac{d}{dt} \left( \frac{R}{\bar{R}} \right) = \frac{1}{\bar{R}^2} \left( \frac{dR}{dt} - R \frac{d\bar{R}}{dt} \right)
\]  

(6.1)

Where \(R\) is the radius of a large grain and \(\bar{R}\) is the mean grain radius of the assembly. Therefore, a larger grain will grow faster than the matrix grains if the following inequality (6.2) is met.

\[
\left( \frac{\bar{R}}{R} \frac{dR}{dt} - R \frac{d\bar{R}}{dt} \right) > 0
\]  

(6.2)

Where

\[
\frac{dR}{dt} = cM \gamma \left( \frac{1}{\bar{R}} - \frac{1}{R} \right)
\]  

(5)

\[
\frac{d\bar{R}}{dt} = \frac{cM \gamma}{4\bar{R}}
\]  

(6.3)
Although the derivatives are equal when $R = 2 \bar{R}$, the above inequality will never be achieved since this will be a maximum for the function in the equation 6.2 $^5$. Thus, a large grain will always grow more slowly than the average grain size and eventually rejoin the normal size distribution $^5$. Therefore, abnormal grain growth can only occur in systems in which normal grain growth is inhibited and/or when select grains enjoy some growth advantages, other than size, over their neighbors $^5$. The main mechanisms responsible for abnormal growth include free surface effects, second phase particle pinning, and texture effects $^5$. In thin films, the grain sizes can be on the order of the film thickness, which creates a pinning pressure due to the balancing of surface tension at the free surface and boundary tension. This is not observed in our systems (1/3, 1, 4 and 10 at% Zr alloys) since we are dealing with bulk materials in which the grain size is not on the order of the particle size. Therefore, free surface effects, such as thermal grooving, is not a viable method for inducing abnormal grain growth in our systems.

6.1.5. Discounting Particle Pinning as a Mode of Abnormal Grain Growth

Grain boundary precipitates could not be detected from TEM analysis of 4 at%Zr at 913°C. They were not present in the bright field/dark field images. Diffraction pattern did not reveal the presence of extra spots or rings. Z-contrast images did not show the presence of lower or higher atomic number phases. X-ray diffraction studies did not reveal the presence of secondary phases. If precipitation did occur, then the precipitates would have to
be in very low volume fractions. Under the requirements for effective particle pinning, particles must have a size smaller than the grains in which they are pinning and a high volume fraction. Neither requirement was present in the 4 at% Zr sample at 913°C. This suggests that the contribution of any pinning pressure, as a means for thermal stability and or abnormal grain growth, is negligible. It is assumed that other lower concentration samples will show similar results.

6.1.6. Inhomogeneous Solute Distribution as a Mode of Abnormal Grain Growth.

It has been known for a long time that texture can inhibit normal grain growth 5. While it is possible to induce abnormal grain growth in thin films via texture, highly orientated interfaces should not have an active role producing abnormal grain growth in our systems since mechanical alloying is not known to produce textured microstructures in BCC materials.

Though interfacial orientation energy differences may not be present, interfacial energy differences could arise due to inhomogeneous distribution of solute along the grain boundaries. It has been shown by Wynblatt et al. that in the segregated state, solute equilibrium composition and the composition profile across the grain boundary depend on the terminating surfaces of both crystals making up the boundary and on the grain boundary orientation 6. Further computer simulations reveal that solute segregation is stronger at
higher energy boundaries and that grain boundary energy anisotropy could potentially be increased. A recent example of computer modeling on the effect of Pb segregation to Al grain boundaries confirms that an increase in grain boundary anisotropy is possible. In addition, the work of Wynblatt et al. provides evidence that in some systems there exists a clear crystallographic separation between planes for which segregation of grain boundary solute is strong and weak. This could explain the resultant abnormal grain growth observed in all Zr systems but most specifically, the texturing in the diffraction pattern of the 1/3 at% Zr at 913°C. Since segregation may be most pronounced in the dilute limit, the crystallographic polarization of solute segregation could be increased relative to the higher concentrations. Grain boundary systems with less segregated solute would be less stable with respect to grain growth and grow more rapidly than grain boundary systems with higher amounts of segregated solute. At high temperatures, only grain boundary systems with enhanced solute segregation would remain. This would lead to a high population of grains with a small distribution of crystallographic orientation. The excess solute ejected from grain boundaries, which underwent rapid growth, may then reinforce the surrounding nanograins from further growth. Additional computer simulations have recently predicted that based on solute drag alone, i.e. in a sample void of inhomogenities (void of texture, anisotropy in grain boundary mobility/energy, pinning particles and size effects), it is possible to spontaneously induce abnormal grain growth. Although this scenario explains both the staggering of the grain size versus composition as well as the asymmetric abnormal grain growth in the
micrographs, it is unclear how the mechanisms outlined in the reference applies to a nanocrystalline microstructure. It is generally thought that as grain size is reduced (as in the nanoscale), the driving force for growth is too great for solute drag attraction forces to operate, and boundaries in such a system should migrate freely as in normal growth.

### 6.1.7. Discounting and Discussion of Other Possible Stabilizing Mechanisms

**Discounting Particle Pinning**

As reported earlier in Figure 5.15 as-milled samples showed that solubility of Zr was maintained at room temperature, up to 10 atomic percent, without formation of intermediate phases. A decrease in the intensity and an increase in the width of the diffraction peaks occurred with an increase in Zr concentration, indicating a decrease in grain size and increase in strain with increasing Zr concentration. As shown in Figure 5.15, all compositions ≤4 at% Zr maintained complete solubility at all experimental temperatures and times. The loss of solubility, or precipitation of what was determined to be a second phase, Fe₂Zr, occurred at higher temperatures and concentrations of Zr (7 and 10 at% Zr). Precipitation of Fe₂Zr occurred in 7 at% Zr at 1000°C and at 700°C in 10 at% Zr see Figure 5.10. With precipitation, comes the loss of solute from solution and grain boundaries, and the ability to reduce the interfacial energy (the driving force for grain growth). As seen in Figure 5.15 (a and b), the 10 at% Zr alloy, which at 500°C does not precipitate, has better thermal stability.
than the 1 and 4 at% Zr samples. However upon precipitation at 700°C, the 10 at% sample shows more grain growth than the 1 and 4 at% Zr. The grain growth in the 10 at% samples was even more accelerated at higher temperatures, such as 850°C, where the grain size measured was well above the quantifiable range of x-ray line broadening analysis (~100nm). Since the 10 at% Zr showed accelerated grain growth after precipitation, the kinetic approach to thermal stability (particle pinning) is discounted as the mechanism for thermal stability in the other alloys (4, 1 and 1/3 at% Zr) at temperatures below 1173°C. Thermodynamic stability is also supported by the lack of observable, second phases as determined by TEM and FIB characterization techniques as stated above.

6.1.8. Discussion on Solute Drag Effects

With the available data, it is not possible to completely exclude solute drag effects from possible modes of thermal stability. Therefore, a short discussion on the data and possible interpretations of the observed results will be given.

Figure 5.15 shows the effect of solute concentration on grain size stability at 500°C and 700°C. Due to the large difference in atomic radius between Fe and Zr (+28%), it can be assumed that the thermal activation barrier is high for substitutional diffusion. Therefore, at low temperatures (below 700°C), appreciable bulk lattice diffusion is not expected. It is therefore likely that uptake of solute by grain boundaries must result from acquisition during
grain boundary expansion at lower temperatures, which is comparable to what was
determined by Krill et al. Once on the boundary, diffusion of solutes may take place more
rapidly, allowing them to keep up with the boundary as it continues to expand, resulting in an
equilibrium solute concentration in the boundary that is dependent on the temperature and
boundary velocity (which is proportional to the driving pressure).

As shown in Figures 5.15 (a,b), there is an initial rapid increase in grain size within
the first 5-8 minutes, after which the growth stagnates in all alloys. This supports the idea of
solute entrapment, via grain boundary expansion, as the solute concentration present should
have an effect on the final grain size reached. The more fundamental question is: Once the
solute is on the boundaries, is the observed reduction in grain growth a result of solute drag
effects, a reduction in interfacial energy, or both?

It is clear that in Figure 5.15, solute drag effects could potentially explain the effects
of grain size versus composition. For example, in Figure 5.15a, a large separation in grain
size, at lower temperatures (500°C), between the 1 and 4 at% Zr in Fe alloys occurs. At
higher temperatures (Figure 5.15b), where solute drag is expected to be less effective
(700°C), the observation is that the grain size difference is minimal between 1 and 4 at% Zr.
However, at such small grain sizes (~50nm corresponds to a large driving pressure), it
unclear whether the solute drag forces could impede grain growth to the extent of what is observed in the plateau regions of Figure 5.14.

Since solute drag effects dictate that solute resides within the boundaries in which they are pinning, another possibility exists. Once the solute is coating the grain boundaries, diffusion within the boundaries becomes frustrated, resulting in an increase in the activation energy of mobility. That is, thermal stability could strongly be influenced by grain-boundary, solute-induced increases in activation energy, as indicated by Schuh et al. However, since temperature is in the bottom of the exponential, there should exist a strong relationship of increasing grain size with temperature, as indicated by the Arrhenius behavior of mobility. As such, this mechanism is contradicted by the small amount of grain growth that took place from the as milled 4 at% Zr to the 50nm grain size observed at 913°C.

Another assumption is that the staggering of the grain size by composition could be attributed to $\gamma_b \neq 0$ initially. Initially, in the as-milled state (metastable solid solution), the effective grain boundary interfacial energy should be equal to some quantity. However, as the total grain boundary area decreases during boundary expansion under curvature driven grain growth, more solute will be entrapped by the moving boundary. Both an increase in entrapped solute and an overall decrease in grain boundary area will result in an increase in grain boundary solute concentration. Loss of solute from the lattice and incorporation into
the grain boundary is supported by data given in our previously reported paper, citing a decrease in lattice parameter, with increase in grain size during isothermal annealing, without the detection of second phases via x-ray diffraction experiments. This increase in grain boundary solute will result in a continual minimization in the grain boundary energy as the boundary continues to expand, which would result in smaller grain size, as a function of global solute concentration.

6.1.9. Contamination Affects on Stability

An important consideration is that approximately 1 at% Cr has been incorporated in the solution due to milling media such as stainless steel ball bearings. However, as shown in Figure 3, 10 at% Cr in Fe has only a small effect on increasing the thermal stability of nanocrystalline Fe. Therefore, any thermal stability due to the Cr contamination can be neglected as a means of significant thermal stability. In addition, Cr was not detected in any of the observed precipitates and appeared as a background element in the matrix surrounding the precipitates in Figures (5.37 and 5.41).
References: Chapter 6


7.1. Abstract

The investigation of solute segregation in Fe-based Zr alloys was undertaken for the purpose of understanding thermal stability based on the reduction in interfacial energy associated with nanocrystallinity. Fe-based Zr alloys were produced through high energy mechanical alloying that enabled the formation of nano-grained microstructures. These microstructures remained very stable, with grain size < 50nm, at temperatures nearing their respective melting temperatures. Structural and compositional characterization is reported to provide insight on the mechanism of this thermal stability.

Key words:
Nanostructure; Iron alloys; Mechanical milling; Grain growth; Segregation;
7.2. Introduction

Nano-crystalline metals with grain sizes \( \leq 50 \text{nm} \) exhibit extraordinary mechanical properties, as compared to conventional grain size (> 1\( \mu \text{m} \)) counterparts. Properties such as hardness, yield and ultimate tensile strengths in pure metals and alloys depend strongly on grain size. Because of the increased energy associated with the increased grain boundary area, these nanoscale microstructures are thermally unstable due to the propensity to release this excess energy by grain growth. The driving force (P) for grain growth is given by equation 1 [1].

\[
P = \frac{a \gamma_b}{r}
\]  

(1)

where \( a \) is a geometrical correction factor for the grain shape, \( \gamma_b \) the grain boundary energy/area and \( r \) the radius of the grain. Hence, the driving force for grain growth in nanocrystalline alloys becomes enormous as grain size decreases.

It is the thermal instability of nanoscale microstructures which limits the overall processing and applications of nanocrystalline metals and alloys. Therefore, it is imperative to create alloys which are resistant to grain growth at elevated temperatures if these nanograinned materials are to be adopted for commercial applications. Numerous investigations into the thermal stability of such nanostructured metals have been conducted.
The two prominent competing methods for thermal stabilization are a kinetic and a thermodynamic approach. The kinetic approach has its basis for stabilization in the reduction of grain boundary mobility by various pinning forces induced mainly by second phases and defects [2-6]. The limitation with this approach is that all pinning forces can eventually be overcome by thermal activation at higher temperatures leading to temperature limited thermal stability.

In two component systems such as alloys in which solute segregation to grain boundaries is favored, a reduction in the driving force (P) in equation 1 can be achieved by the reduction of $\gamma_b$ [7-10]. The grain boundary energy, $\gamma_b$, varies with solute concentration by the Gibbs adsorption equation 2.

$$\frac{\partial \gamma_b}{\partial \ln c_s} = -RT \Gamma_s \quad (2)$$

Where $\Gamma_s$ is the interfacial excess of the solute atoms.

Therefore, with solute segregation to grain boundaries, $\gamma_b$ will decrease with increasing $c_s$. In this approach $\gamma_b$ has been shown to have only a weak dependence with temperature [11]. It has also been demonstrated with several alloys that the initial slope of the $\gamma_b$ versus $c_s$ plot is more negative when a large difference in atomic size exists between the solute and solvent atoms [12]. This leads to the idea that large elastic enthalpies induce solute segregation to grain boundaries. In such a case where $\gamma_b$ could be reduced to zero, there would be no driving force and hence no grain growth could occur at any temperature.
There exists only a few experimental examples which demonstrate termination of grain growth at extremely elevated temperatures. The two most prominent of these are the work by Krill III et al. [9] and Botcharova et al. [13]. In both cases, alloys subjected to heat treatments in excess of 93% of the respective melting temperatures resulted in a stabilized microstructure with grain sizes less than 100nm. Of the two studies, Krill gave a theoretical approach to the understanding of why this stability occurred. By using the model proposed by Hillert [14] in which the grain boundaries and the volume contained within the grains of a binary alloy are treated as thermodynamically distinct phases, it is possible to construct an expression, equation 3, relating $\gamma_b$ to a measurement of the number of moles of solute segregant per unit grain boundary area (the 2nd equality).

$$
\gamma_b = \gamma_o - \Delta H_{seg} m (n^{GB} (\chi_B^{GB} - \chi_B^a)/(A^{GB})) = \gamma_o - \Delta H_{seg} m (n^{seg}/A^{GB}) \tag{3}
$$

Krill et al. used this expression to show that extraordinary thermal stability demonstrated by their Pd-Zr binary alloys could be attributed to segregation induced reduction in the grain-bounary energy $\gamma_b$. Krill proposed that at an annealing temperature of 1125°C the value of $\gamma_b$ for Pd-Zr alloys was low enough for a metastable state to be established with respect to grain growth. In an attempt to prove this, heat treatments were carried out at 1500°C, corresponding to 95% of the respective alloys melting temperatures. The results showed that
at higher solute concentrations, grain growth between the temperature of 1125°C and 1500°C had ceased!

Following the work of Krill et. al, the work presented here uses Fe, a bcc matrix, in place of Pd, an fcc matrix. Nanocrystalline Fe and Fe based alloys have attracted much attention for their potential uses in industry. While numerous experimental results thus far have reported limited thermal stability in nanocrystalline Fe alloys, [15-22] nothing has been reported to date with the thermal stability equal to that observed in the Pd based Zr alloys of Krill et. al. [9].

Zr was selected for the solute in Fe based alloys for the same basis that Zr was selected in Krill’s work, i.e., Zr in Fe has a large positive elastic enthalpy of +92 kJ/mole and a large negative enthalpy of mixing of -118 kJ/mole [23]. The large elastic enthalpy indicates that these alloys should favor grain boundary segregation of solute atoms. The large negative enthalpy of mixing indicates that once segregates form on a grain boundary, the solute atoms should resist the formation of the several Fe-Zr intermetallic phases indicated by the phase diagram. This combination of elements makes Fe-Zr an ideal candidate to show the effects of solute segregation on thermal stability of bcc nanocrystalline metals.
7.3. Experimental

Iron based zirconium alloys were investigated; the solute concentrations selected for comparison were 1, 4, 7 and 10 atomic percent Zr. Hardened steel vials and 440C stainless steel balls were used for mechanical alloying in a Spex 8000 shaker mill. Milling was accomplished by loading the hardened steel vials with the correct weight ratio of Alpha Aesar Fe and Zr powders (-325 mesh, 99.9 and 98.5% purity respectively) to produce the desired compositions. The ball to powder mass ratio was maintained at 10:1. The vial was sealed in an argon atmosphere (O₂<1 ppm)) prior to milling. Milling took place for 20 hrs at room temperature. The milled powders were subsequently heat treated at 340 500, 700, 850, 1000, 1150 and 1375°C for 60 mins under an Ar/2%H atmosphere.

X-ray diffraction analysis of the ball milled powders was performed with a Rigaku x-ray diffractometer using CuKα (λ=0.1542 nm) radiation, with a diffracted beam graphite monochromator having instrumental broadening ≈ .1°. CuKα₂ peak stripping and background subtraction was accomplished by using Xpowder software http://www.xpowder.com/. The average grain size was calculated from diffraction line broadening using the Scherrer [24] equation and the induced strain was calculated using the Stokes-Wilson analysis [25]. Lattice parameter measurements were made using a Philips X-Pert PRO MRD HR X-Ray Diffraction System using CuKα (λ=0.1542 nm) radiation with high resolution goniometer (min step size is 0.0001).
7.4. Results and Discussion

In general, X-ray spectra of all the as-milled samples showed that solubility of Zr was maintained at room temperature up to 10 atomic percent, without formation of intermediate phases. A decrease in the intensity and an increase in the width of the diffraction peaks occurred with an increase in Zr concentration, indicating a decrease in grain size and increase in strain with Zr concentration. The loss of solubility, or rather precipitation of what was determined to be a second phase, most likely Fe$_2$Zr, occurred at higher temperatures and concentrations of Zr (7 and 10 at% Zr). Precipitation of Fe$_2$Zr occurred in 7 at% Zr at 1000°C and at 700°C in 10 at% Zr. According to the x-ray scans, the other compositions of 1 and 4 at% Zr maintained complete solubility at all temperatures and times including 1375°C for 1hr, as seen in figure 1.

The isothermal change in lattice parameter and average grain size for 4 at% Zr in Fe annealed at 800°C is given in Figure 2. There is an initial rapid increase in grain size followed by a slow increase to reach a grain size of 27 nm after 60 minutes. The lattice parameter shows the inverse trend, that is, an initial rapid drop followed by a slow decrease to .2871 nm after 60 minutes. This is still larger than the lattice parameter of Fe (horizontal line at .2867 nm). Since the x-ray spectra showed no other reflections indicative of a 2nd phase it could be assumed, similar to Krill et. al [9] that the decrease in lattice parameter indicates Zr solute segregation to the grain boundaries. If we assume that the resultant
change in lattice parameter equals the relative change in solute loss from solid solution, then a fraction \( f = \frac{(2.882-2.871)}{(2.882-2.867)} = .73 \) has been removed after the 60 minute anneal. However, preliminary Energy Dispersive Spectroscopy (EDS) in Figure 3 revealed that high temperature annealing also induces segregation of Zr solute to the surface of the as-milled alloyed powder particles (not detectible by X-ray analysis). This precludes the use of Krill’s quantitative analysis for a reduction in \( \gamma_b \) based on 100% solute segregation to grain boundaries in the Fe-Zr based powders. The possibility of surface segregation in Pb-Zr powder particles used in [9] was not reported. Figure 2 shows EDS spectra collected from Fe 1at% Zr heat treated at 1375\(^\circ\)C for 60min. One spectrum is from the bulk material and the other is from a surface segregate. Here it is obvious that the spectrum of the surface segregate shows a larger at% Zr than does the bulk. During heat treating at high temperatures (1200\(^\circ\)C)and higher in hydrogen forming gas the powders took on a different surface color. This was more noticeable at 4 at% Zr than 1% at Zr. EDS on the 4% at Zr in Fe powder yield results showing particles completely coated with white precipitation of composition \( \sim 20 \) weight percent or 13 at% Zr. This is in stark contrast to the data presented for the 1at% Zr in Fe.

The grain size evolution versus \( T/T_M \) is given in Figure 4. The initial grain size of the 1 and 4 at% Zr alloys is 6.7nm and 5.4 nm, respectively. These are consistent the literature values for the grain size (\( \approx 8 \) nm) of Fe based nanocrystalline alloys produce by ball milling.
For pure nanocrystalline Fe, the onset of isothermal grain growth, as determined by DSC, was approximately 0.4\(T_M\), corresponding to a temperature of 450\(^\circ\)C. Figure 4 shows that at approximately 0.5\(T_M\), the grain size for nanocrystalline Fe has already reached a value of about 200 nm. In striking comparison are the results for our ball milled Fe-Zr alloys, which show very little grain growth until about 0.6\(T_M\). Upon reaching about 0.7\(T_M\), grain growth of Fe-Zr alloys ceases altogether at a grain size of about 45 nm. The grain structure remains stable up to temperatures of 92-95\% of the \(T_M\). This behavior is very similar to that in the Pd-Zr alloys produced by Krill et. al., [9] where grain growth continued until approximately 0.75\(T_M\) and then was stable up to 0.95\(T_M\). Krill et. al. [9] reported increasing stability with increasing solute composition up to the maximum at 20 at\% Zr. In contrast, increasing the solute content in our Fe-Zr alloys showed little effect in stabilizing grain growth. No significant increase in stability was observed by increasing the solute concentration from 1 to 4 at\% Zr. This may support the idea that the stabilization is do to thermodynamics and not a kinetic mechanism. Mechanisms which govern kinetic stabilization such as solute drag, particle pinning, ect. should be overcome and not be significant at the temperatures over which thermal stability has been observed is these alloys.

While no precipitation was observed in the X-ray spectra within the detectable limits of X-ray spectroscopy (see Figure 2) one could propose that precipitation may have occurred. Since the amount of precipitation (density of precipitates) is based on the amount of solute in solution prior to precipitation then the data for the 1 and 4 at\% Zr in Fe should have yielded
different thermal stability results. That is the 4% Zr should have had a different onset temperature or yielded a lower grain size than the 1% Zr alloy, which was not the case. This suggest that no precipitation occurred. Both the 1 and 4% Zr alloys showed a net decrease in lattice strain (37%) that mirrored the increase in grain size for the alloys during isothermal annealing.

It has been predicted theoretically that solute segregation to grain boundaries can reduce the effective grain boundary energy to zero [8]. While we cannot yet obtain a reliable quantitative estimate of the critical amount of solute needed to achieve this for Fe-Zr (or most other systems), a useful benchmark can be taken as the atomic fraction of solute needed to form a grain-boundary monolayer. This can be calculated assuming cube-shape grains with a monolayer of solute on otherwise perfect crystal grains, atomic volumes V equal to the elemental values for Fe and Zr, and a grain boundary width of $V_z^{1/3}$ (details omitted here).

Figure 5 shows a plot (solid line) of the atomic fraction of Zr solute needed to from a monolayer of Zr solute on the grain boundary. At the volume average grain size of 45nm (as taken from x-ray line broadening measurements), 1 at% Zr is needed. This leaves one to speculate how much solute is required to achieve thermal stability. As shown in Figure 4, 1at% Zr produced the same extraordinary thermal stability as 4at% Zr. However, EDS on the 1at% Zr powders showed qualitatively that surface segregation occurs and not all of the
solute segregates to the grain boundaries. This supports the conclusion that a complete grain boundary monolayer may not be required for thermal stability.

### 7.5. Conclusions

It has been shown that nano-grained Fe-Zr alloy powders exhibit extraordinary nanoscale grain size thermal stability that extends to temperatures nearing their respective melting points. Decreases in the lattice parameter and surface segregation observed on milled powders particles are indications that the mechanism for thermal stability is that of solute segregation. Based on a simple estimate, and the observation of surface segregation and lattice parameter change in the 1at% Zr alloy it appears that stabilization can be achieved with less than a monolayer of Zr on grain boundaries. Increasing the solute content to 4at% Zr produced no additional stabilization and no intermediate phases. The results obtained here are consistent with models that predict grain-size stabilization through reduction in the effective grain boundary energy by solute segregation.

### 7.6. Acknowledgements

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References


23. F. Ebrahimi, H. Li, Scripta Mater. 55 2006 263.


Figure 7.1: Precipitation upon heating of 7 and 10 at% Zr in Fe for 1Hr

Figure 7.2: Change in lattice parameter and grain size for Fe 4 at. % Zr at 800°C.
Figure 7.3: EDS Fe 1 at% Zr annealed at 1375°C for 60 minutes. Inset shows probe positions.

Figure 7.4: Change in grain size versus normalized temperature (T/T_M) for 0, 1 and 4 at% Zr in Fe
Figure 7.5: Atomic percent solute needed to form a monolayer versus average grain, vertical line (volume Avg) marks the average grain size as determined by (XRD) for Fe 1at.% Zr held for 60min at 1375°C.
The addition of Ni to Fe was selected as a control. Since Ni and Fe have similar atomic radii and low elastic enthalpy of segregation of +1kJ./mol, and at high temperatures Ni enjoys complete solid solubility in Fe, Ni will only have a negligible influence in the thermal stability of nanocrystalline Fe\textsuperscript{1-2}.

Figure 8.1 gives the x-ray diffraction spectra of the as milled Fe with 1, 5 and 10 at\% Ni samples. The addition of Ni to Fe has very little effect of reducing the grain size and increasing the lattice strain. As reported in Chapter 5, Ni initially has an effect of reducing the grain size and increasing the lattice strain of nanocrystalline Fe. However, after the addition of more than 1 at\%, further reduction in grain size and/or increases in lattice strain are no longer observed. The diffraction patterns show that a complete solid solution was maintained throughout the room temperature milling process up to 10 at\% Ni. As predicted by the phase diagram, the formation of secondary phases did not occur up to the highest temperature analyzed of 1173°C for 1 at\% Ni in Fe.
Figure 8.2 (a-b) (a) shows the first fundamental reflection (110) for the solid solution of 1 at% Ni in Fe for two different temperatures. The peak labeled 3GPa at 700°C 1HR refers to a 1at% Ni in Fe sample that was originally annealed at 700°C for 1 hour and then x-rayed; 3GPa refers to the sample’s Vickers micro hardness. The same sample was then re-heat treated at 900°C re-x-rayed and the hardness re-checked. This peak is labeled 2GPa at 700-900 1HR. The most notable events here are the decrease in peak intensity, increase in the full width at half maximum and the disappearance of the Kα2 peak while heat treating at a higher temperature. This would suggest a refinement of grain size with increasing the annealing temperature, i.e. a recrystallization event. However, congruent with the decrease in grain size, is a decrease in hardness. This decrease in hardness with a decrease in grain size is counterintuitive.
Figure 8.2b shows the change in grain size and lattice strain for 1 at% Ni in Fe versus annealing temperature. Initially the lattice strain decreases with an increase in grain size at 500°C. Above 500°C and up to 700°C the lattice strain increases with an increase in grain size and decreases with a decrease in grain size. This is opposite to the general relationship of increasing grain size and decreasing lattice strain typically observed. At 700°C, a maximum in grain size is reached in an almost asymptotic fashion. After 700°C, the grain size and lattice strain oscillate until reaching an equilibrium value at about 1173°C.

Figure 8.2  (a) first fundamental reflection (110) for the solid solution of 1 at% Ni in Fe for two different temperatures.

(b) grain size and lattice strain for the solid solution of 1 at% Ni in Fe as a function of annealing temperature: Solid squares for grain size, Open squares for strain.
The filled in circles correspond an average of 3 separate experiments, all of which gave the same results as discussed in 8.2a. That is, the samples were first heat treated at 700°C resulting in an average grain size of ~157nm and hardness of (3GPa), then subsequently heat treated at 900°C, resulting in an average grain size of 65 nm and a hardness of 2GPa.

An experiment was conducted to see if the grain size refinement process was reversible. That is, a fresh as-milled sample was first heat treated at 900°C x-rayed and then re-heat treated at 700°C and re-x-rayed. These points can be seen in 8.2b as open circles. The results confirm that very little increase in grain size occurred upon re-heat treating at a lower temperature. To investigate what was occurring microstructurally, samples were prepared for optical microscopy.

Figure 8.3(a-c) gives the microstructural changes occurring on either side of the transition and the peak observed in Figure 2b. Figure 8.3a shows a high magnification optical micrograph for 1 at% Ni in Fe at 616°C for 1 hour. The micrograph shows large regions of nanocrystalline microstructure and the occurrence of isolated regions of secondary recrystallization. Figure 8.3b shows the microstructure at 700°C for 1 hour. The micrograph indicates that large regions of secondary recrystallization have now occurred with an estimated 30% area nanocrystalline microstructure remaining. This is a significant
improvement in thermal stability of pure Fe which showed optically 0% area nanocrystalline microstructure remaining at 700°C for 1 hour. This result is interesting as Ni is suggested by its thermodynamic parameters to not influence the thermal stability of Fe.

Figure 8.3c gives the microstructure at 870°C. Optically, it appears at this temperature that 0% area nanocrystalline microstructure remains. To summarize the optical images, the % area nanocrystalline remaining diminishes with increasing temperature. However, images 8.3b and 8.3c are in contrast to the x-ray grain size measurements. At 700°C, the x-ray measurements were unable to detect the remaining 30% area nanocrystalline and at 870°C the x-ray was predicting an average grain size of 65nm, though optically, 0% area nanocrystalline microstructure remained.

Figure 8.4(a-c) gives low magnification optical images of the same three samples in Figure 8.2(a-c). Figure 8.3c shows that some of the mechanically alloyed particles were void of contrast after etching.
Figure 8.3  
(a) high magnification optical micrograph for 1 at% Ni in Fe annealed at 616°C for 1 hour.

(b) high magnification optical micrograph for 1 at% Ni in Fe annealed at 700°C for 1 hour.

(c) high magnification optical micrograph for 1 at% Ni in Fe annealed at 870°C for 1 hour.
Figure 8.4  (a) low magnification optical micrograph for 1 at% Ni in Fe annealed at 616°C for 1 hour.

(b) low magnification optical micrograph for 1 at% Ni in Fe annealed at 700°C for 1 hour.

(c) a low magnification optical micrograph for 1 at% Ni in Fe annealed at 870°C for 1 hour.

Figure 8.5(a-c) shows low magnification ion channeling contrast images of the same samples shown in Figures 8.3 and 8.4. Again, it is apparent that with increasing the annealing temperature an increase in the amount of secondary recrystallization takes place.
Figure 8.5.  (a) low magnification channeling contrast micrograph for 1 at% Ni in Fe annealed at 616°C for 1 hour.

(b) low magnification channeling contrast micrograph for 1 at% Ni in Fe annealed at 700°C for 1 hour.

(c) low magnification channeling contrast micrograph for 1 at% Ni in Fe annealed at 870°C for 1 hour.
In Figure 8.6 (a-c), 5a is a re-plot of Figure 8.2b. Figure 8.6b gives a high magnification ion channeling contrast image of the 1 at% Ni in Fe at 616°C. From Figure (x-ray results) the grain size is estimated to be 100nm and is in good agreement with the average grain size in Figure 8.6b. Figure 8.5c shows a bright field TEM image of the microstructure of 1at% Ni at 870°C. From x-ray, the grain size is estimated to be 65nm. Again, the average grain size in Figure 8.6c is in good agreement with the grain size plotted on Figure 8.6a. Regions such as reported in Figure 8.5c, were dispersed in pockets ~500nm in diameter and represent <2 area% of the sample. This may explain why optically, these regions were absent.
High Mag Fe 1%Ni FIB Contrast and TEM

Figure 8.6  
(a) Image of Fig 8.2b
(b) high magnification channeling contrast micrograph for 1 at% Ni in Fe annealed at 650°C for 1 hour.
(c) TEM bright field micrograph for 1 at% Ni in Fe annealed at 870°C for 1 hour.
The research presented here on Ni in Fe is interesting and requires extensive research to complete. Influences such as electronic contributions to the reduction in interfacial energy, may need to be considered since the current thermodynamic parameters alone cannot explain the observed increase in thermal stability. Currently, a more in depth and complete investigation is under way to give light on the observed results.
References: Chapter 8


Results on Pd 20at% Zr: CHAPTER (9)

The following results are from a small concurrent study to reproduce the results of research published in “Thermodynamic stabilization of nanocrystallinity” by Krill et al.\(^1\) The main objective was to reconcile conflicting findings between the research reported in this thesis and the Krill study. Successful reproduction would suggest that the FeZr system deviates from the theory discussed by Krill et al; the converse would suggest that this theory needs revision.

Figure 9.1 (a-b) gives secondary electron SEM images of 20 at% Zr in Pd for the as-milled and heat treated at 1373°C for 1 hour samples. A large portion of the image contrast is attributed to the atomic number since atomic number dictates the number of back scatter electrons that are produced. Other than the contrast attributed to particle boundaries and/or pores Figure 9.1a is void of any atomic number contrast. This is consistent with the formation of a solid solution and the lack of secondary phase formation. This meta-stable solid solution was confirmed by x-ray analysis. The as-milled grain size estimated by x-ray peak broadening measurement was found to be 6nm. After heat treating the same sample at 1273°C for 1 hour in a reducing atmosphere of Ar\(_{98}\%\)-H\(_2\%\) a large amount of precipitation can be seen to have occurred. The calculated phase percent was found by digital image...
analysis to be approximately 9 area%. The average precipitate diameter was found to be 2.7µm.

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<tr>
<td>1273°C</td>
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Grill ~ 4nm
Grill 1500°C 57nm

Figure 9.1 (a) SEM (secondary electron) micrograph for ~20 at% Zr in Pd annealed at 24°C.
(b) SEM (secondary electron) micrograph for ~20 at% Zr in Pd annealed at 1273°C for 1 hour.

Figure 9.2(a-c) give the chemical analysis (EDS spectra) of the samples reported in Figure 9.1(a-b). Figure 9.2a gives the chemical composition of the as milled 20 at% Zr in Pd. Extensive contamination with Fe resulted from milling in tool steel vials. This is attributed to the cold welding of Pd to the steel vial at room temperature milling. However, the elastic enthalpy for segregation of Fe in Pd is small (+16kJ/mol) ~ 17% of Zr in Fe<sup>2</sup>.
Therefore the Fe contamination may not play a significant role in the thermal stability.

Figure 9.2b gives the chemical composition of the observed precipitates in the 20 at% Zr in Pd sample heat treated at 1373°C. The precipitates are absent of Fe; they are Zr and oxygen rich. Figure 9.2c gives the composition of the matrix, that being 70 % Pd 20 at% Zr with extensive Fe contamination.
Figure 9.2  (a) EDS spectrum for as-milled Pd 20 at% Zr.

(b) EDS spectrum on Zr oxide particle formed in the as-milled Pd 20 at% Zr annealed at 1373°C for 1 hour.

(c) EDS spectrum for matrix of as-milled Pd 20 at% Zr annealed at 1373°C for 1 hour.

Krill ~ 2 at% Fe
Negligible amounts of N and H
1-5% Oxygen
RT Milling
Figure 9.3(a-d) gives the surface morphology of the 20 at% Zr in Pd in the as milled and heat treated at 1373°C samples. (a) a low magnification secondary electron SEM images shows that the average as milled particle size is ~40µm. (b) shows the effect of loose powder being pressure-less sintered at 1373°C. Extensive particle necking and mass movement due to diffusion has occurred. (c) shows a high magnification image of the as milled powder. (d) gives a high magnification image of the heat treated sample. Extensive surface diffusion has occurred due to the high temperature anneal.
Figure 9.3(a-d). Surface morphology of the 20 at% Zr in Pd in the as milled and heat treated at 1373°C samples

Figure 9.4 shows an ion channeling contrast image of a uniaxially pressed disk which was further sintered at 1373°C. The density of the sample was estimated to be 99.5% dense. Apparent in the cross-section is the large grains of various orientations.
Figure 9.4 ion channeling contrast image of a uniaxially pressed disk which was further sintered at 1373°C

Figure 9.5 shows the fracture surface of the disk in Figure 9.4 induced by impact shearing the disk. The dark semi spherical particles observed within the fracture surface are the Zr oxide particles. As the average particle size is approximately 40µm the larger features in the fracture surface are the cross sections of the grains which underwent transgranular failure. It is estimated that the average grain diameter of the matrix is 5µm.
Figure 9.5 fracture surface of the disk in Figure 9.4 induced by impact shearing the disk.

Figure 9.6(a-b) shows high resolution ion channeling contrast images for 20 at% Zr in Pd annealed at 1373°C for 1 hour. The small speckles in the image are attributed to nanoscale precipitates. There were no regions that were identifiable as being nanostructured matrix grains.
Figure 9.6 (a-b) high resolution ion channeling contrast images for 20 at% Zr in Pd annealed at 1373°C for 1 hour

Figure 9.7 (a-b) (a) gives the data reported by Krill. In this graph the stability of the alloys increases with increased at% Zr with 20 at% Zr being the most stable. The 20 at% Zr samples shows the same plateau in grain growth as does the Fe-Zr systems. That is, after a specific annealing temperature grain growth appears to stop all together. When our hardness data against the work of Krill Figure 7a an interesting trend develops. Literature states that the hardness for nanocrystalline Pd is ~6GPa. This point is in good agreement with our hardness data at room temperature. Initially with heat treating the hardness goes up and reaches a value of ~10GPa and then begins to decrease. By the time the temperature reaches 1373°C the hardness has fallen to ~3.5GPa. This is consistent with what was found microstructurally that is an average grain size of 5µm and the dispersion of large and nano-scale oxides. Similar results were reported in our Fe-Zr. That is, x-ray gave no indication of further grain growth after annealing to a certain temperature but the hardness value continued
to decrease. The final result being large matrix grains having precipitated large and nanoscale secondary phases.

Figure 9.7 (a-b) (a) gives the data reported by Krill
(b) hardness data for Pd 20% Zr

Precipitates Only Seen Optically at 1373°C

X-ray grain size estimates in this study were similar to the sizes reported in the Krill study. 6nm and 52nm were measured for the as-milled and heat treated Pd 20 at% Zr respectively; which is comparable to the 4nm and 57nm reported by Krill for said treatments. Figure 9.4 shows a FIB cross-section of a sample treated at 1373°C for an hour; the exact
conditions which yielded a 52nm by x-ray estimation. The grains in the image are clearly not nanocrystalline meaning that the x-ray broadening is due to some other source.

Currently a more extensive study of this system and the high temperature microstructural evolution is currently under way. Extra measures are being taken to ensure a low level Fe contamination more in comparison with what was reported in the work of Krill et al \(^1\). As such a far comparison cannot be made until such levels of contamination are reduced.
References: Chapter 9


Abstract

The intermetallic ε₁ compound Cu₃Ge was produced through a mechanical alloying procedure that enables the formation of a nano-grained microstructure. There is a dependence of grain size (20nm to 11nm) on milling conditions. The microstructure remained very stable even at temperatures to 500°C for 5 hours which is a minimum of 76% of the melting temperature. The materials produced by these methods were in the form of powders with particle size ranging from the 200nm to 10μm. The morphology of the particles varied with the largest being rough and irregular and the smallest being spherical. Preliminary resistivity measurements showed low resistivity, 8.8μΩ-cm, which is comparable to that previously reported for thin films with grain sizes thousands of times larger. Nanoindentation was also performed, yielding an elastic modulus ~ 110GPa.

A. Nanostructured intermetallics, B Thermal stability, B mechanical properties at ambient temperatures, B Electrical resistance, C Mechanical alloying.
Introduction

Mechanical alloying is an efficient process by which to produce nanostructured materials with grain sizes less than 100 nm by mechanical attrition of coarser-grained materials. This process includes repeated welding and fracturing of powders typically in a high energy ball mill. This re-welding and fracturing continues until the elemental powders making up the initial charge are blended on the atomic level, such that either a solid solution and/or phase change result [1]. The chemistry of the resulting alloy is comparable to the percentages of the initial elemental powders. With continued milling time, grain size reduction occurs, which eventually saturates at a minimum value that has been shown to scale inversely with melting temperature of the compound [2].

Because of their nanoscale dimensions and large surface/volume ratios, nanocrystalline materials exhibit unique mechanical, [2-3], electronic,[4-6], magnetic[7-8] and chemical[9-12] properties that differ from their larger-grained counterparts. It is these unusual properties that have spawned the recent explosion of scientific research in the field now termed nanoscience or nanotechnology. However, because of the increased energy associated with the increased grain boundary area these nanoscale microstructures, and hence extraordinary properties, are thermally unstable due to the propensity of grain growth. The driving force (P) for grain growth is given by [13].

\[ P = a\gamma_b/r \]  

where \( a \) is a geometrical correction factor for the grain shape, \( \gamma_b \) the grain boundary energy and \( r \) the radius of the grain. Hence, the driving force for grain growth in nanocrystalline alloys becomes enormous.
This thermal instability limits the overall processing and applications of such alloys. Therefore, it becomes imperative to create alloys which are resistant to grain growth at elevated temperatures if these nanograined materials are adopted. There are two ways in which grain growth of nanocrystalline alloys can be minimized; the first involves grain boundary pinning by various methods, which include pinning by impurity atom atmosphere drag, pores and second phases, and the second is a thermodynamic approach involving the reduction in grain growth by reducing the grain boundary energy $\gamma_b$. The second approach deals with solute segregation to grain boundaries. Theoretical models have predicted that this diffusion of select dilute solutes to grain boundaries in nano-crystalline alloys can reduce the driving force for grain growth to zero by reducing $\gamma_b$ to zero [14-16]. It has also been reported in some intermetallic compounds that grain growth in nanostructured compounds decreases as ordering and the rate of ordering increase due to diffusion of impurities atoms [17]. The engineering significance of this reduced grain growth is quite apparent, since microstructure and grain size have a large influence on the physical properties of metals and alloys. This influence becomes even more apparent when the grain size can be maintained at 50nm or below.

The enhanced mechanical properties of nanocrystalline alloys have been well documented over the past 15 years with yield strength and hardness up to ten times that of coarse grained counterparts [1, 18]. It is thus possible to allow pure elemental copper to have mechanical properties equivalent to austenitic stainless steel or make pure elemental iron have a hardness of 10GPa, which is near that of low hardness ceramic materials [3-19]. The electrical properties of nanocrystalline materials have not been investigated as thoroughly. Thus we report the results of an investigation on the mechanical, electrical and thermal stability properties of a nanocrystalline $\varepsilon_1$ compound Cu$_3$Ge produced by high energy mechanical milling.

Cu$_3$Ge is a potential alternative for Cu, which has numerous deleterious effects when used as interconnects in microelectronic devices [20-22]. In contrast to Cu, the $\varepsilon_1$ compound Cu$_3$Ge has been reported
to be resistant to oxidation to temperatures in excess of 400°C and has better adhesion characteristics while suppressing the diffusion of Cu into silicon [23-24]. It has also been reported that Cu₃Ge has a room temperature resistivity of 6-10µΩ-cm which is nearly a constant value over a wide composition range from 25 to 35 atomic percent Ge [25-26]. This compound was shown to have a reduced resistivity comparable to high purity copper when small amounts of Ga or Au are added. It has further been shown that Cu₃Ge can make low resistance p and n type ohmic contacts to GaAs substrates which are more thermally stable than the current contact metallurgies [27-28]. These properties make the ε₁ compound Cu₃Ge an ideal material for the next generation of electronic materials used for high power applications. In previous studies this compound has been prepared via solid-state reactions in which electron beam evaporation and deposition of Cu and Ge was used to form thin films onto various substrates, most specifically Si, and subsequently annealed to produce the compound[29]. In the current work, the ε₁ Cu₃Ge compound was synthesized via mechanical alloying to produce micron size particles with nano-sized grains.

**Experimental**

Ge powder was first produced by placing high purity cleaved Ge wafers in a polished hardened tool steel vial loaded with a 10:1 mass ratio of 440 stainless steel ball bearings to Ge. The vial was then sealed in an Ar atmosphere(O₂<1 ppm) prior to mechanical milling. Milling occurred at room temperature for ~15 min in a SPEX 8000 high-energy shaker mill. The resultant Ge powder was sifted through a 2500 mesh screen, which yielded average particle sizes <5 µm. X-ray diffraction(XRD) analysis confirmed that neither oxidation nor amorphization of the powder occurred during the milling process. The mechanically milled Ge powder was always stored in a sealed glass vial in an Ar environment. The ε₁ compound Cu₃Ge was prepared by loading the milled Ge powder with the correct weight ratio of Alpha Aesar Cu powder(170+425 mesh, 99.9%) into a hardened and cleaned steel vial to produce the desired Cu-25 atomic % Ge. The ball to powder mass ratio was
maintained at 10:1, and the vial was sealed under vacuum ($10^{-4}$ Torr) prior to milling. Mechanical alloying in the SPEX 8000 shaker mill was then performed at room and liquid nitrogen temperatures for various times. Liquid nitrogen milling was accomplished by placing the vial in a thick nylon sleeve modified to allow placement into the high energy mill as well as to allow an inflow and outflow of liquid nitrogen. After the ball milling procedure was completed, the Cu$_3$Ge powder was removed from the steel vial in an Ar glove box and placed in a glass vial. The milled, nanocrystalline grain size Cu$_3$Ge powder consisted of agglomerated particles that ranged in size from 1-100$\mu$m.

X-ray diffraction analysis of the Cu$_3$Ge powders was performed with a Rigaku x-ray diffractometer using CuK$_\alpha$ ($\lambda=0.1542$ nm) radiation. Formation of Cu$_3$Ge was confirmed by the x-ray analysis, and the grain size and strain induced by the ball milling process were determined. The average grain size from diffraction line broadening using the Scherrer [30] equation was calculated along with the induced strain using the Stokes-Wilson analysis [31]. Microscopic examination of the resultant ball-milled Cu$_3$Ge powders was performed in both scanning (JEOL 6400F and Hitachi S3200) and transmission electron microscopes. The Hitachi SEM was also equipped with an energy dispersive x-ray spectrometer (EDS) for chemical analysis. Powder specimens for SEM investigation were solution cast onto a Si wafer. A semiquantitative EDS analysis also indicated the approximate compositions to be 75 at % Cu/25 at % Ge with trace amounts of Fe. A thin disk specimen was then prepared by uniaxial cold pressing at 3.5GPa in a tungsten carbide 12 mm diameter die. This sample was subsequently heat treated by pressure-less sintering at 500 °C for 5 hours under an Ar/2%H$_2$ atmosphere. Resistivity and x-ray analysis measurements were carried out on the sample after sintering. The resistivity measurements were conducted over the temperature range 14-300K using the 4 probe linear method method. Nano-indentation was also performed on select samples using a Hysitron TribolIndenter.
Results and Discussion

Phase Formation and Microstructure

Analysis of the XRD patterns in Fig 1. show that the samples tested are consistent with the orthorhombic crystal structure (with slight monoclinic distortion) of the Cu₃Ge phase with a=0.263 nm, b=0.420 nm, and c=0.457 nm. We have previously shown [32] that the Cu₃Ge phase has an ordered structure of the Cu₃Ti type. As demonstrated by the results in Fig.1, during high-energy mechanical alloying of a mixture of Cu and Ge elemental powders, Cu and Ge react to form Cu₃Ge phase even at liquid nitrogen temperatures. This is most likely due to an enhanced diffusivity of the reacting elements in the composite powder formed during milling. It has been reported [33] that the diffusivity can be enhanced by the introduction of structural defects such as grain boundaries and interfaces. It would then follow that the establishment of reaction couples with nanometer sizes by mechanical alloying has led to the decrease of reaction temperature.

Figure 1 also shows the effect of milling temperature and time on compound formation and grain size for the ε₁ compound Cu₃Ge. By ten hours of room temperature milling, the ε₁ compound has formed and the grain size has saturated at 21 nanometers with an internal lattice strain of .49%. With further milling at room temperature for 20 hrs there was no significant change; the grain size and strain remain close to the values of the 10 hr sample. A change in the peak intensity and broadening begins to be apparent when comparing the “10 hr + 3 hr cryo” and the “7.5 hr cryo” samples to the room temperature milled samples. The “7.5 hr cryo milled” sample shows the largest change in grain size down to 11nm with the highest strain of .89%. The diffraction peaks for the “7.5 cryo” sample, while still present, were an order of magnitude less intense than the room temperature milled and heat treated sample. While the peak a 53.5 degrees is not present in the room temperature milled samples and could not be indexed to another Cu-Ge phase, it is suggested that this sample represent an unknown distortion of the ε₁ phase. It is known that it is possible to alter the physical properties, such as ductility, of intermetallics through mechanical milling. This is primarily due to disordering of the
lattice and the introduction of crystal defects created by the mechanical process itself. The effect of these changes leads to an increase in the free energy of the system. This free energy dictates any microstructural changes (solid solution, disordered intermetallic or amorphous phase) that may result in a specific metallic system after mechanical milling.

It has been reported that the long range order parameter (S) in many intermetallic systems is reduced and can become zero as the result of mechanical milling[34]. One of the indications that disordering has taken place in an intermetallic system is the loss of superlattice lines from the x-ray diffraction pattern. For the Cu₃Ge superlattice, lines occur for planes (100), (011), (110), (102), (120) and (013), and their respective 2θ values are 33.15, 28.31, 35.89, 50.67, 53.89 and 64.18°. Since the atomic number of Cu (29) and Ge (32) are similar, the diffracted intensities of superlattice lines were not resolvable above the noise in the x-ray diffraction measurements, and hence plotting the integrated intensity of those reflections in the usual manner of assessing the order parameter (S) was not possible. It is apparent by the collective spectrums that for the three peaks at 39.5, 45.3 and 72° a shift to higher angles occur as one moves down the graph, while a shift to a lower angles for the peak at 43°. This suggests that a nonuniform expansion of the unit cell is occurring which implies that disordering or a change in impurities occurs.

The 20 hr room temperature milled sample that was heat treated at 500°C for 5 hr shows remarkable grain size stability. This temperature represents 76% of the melting temperature at this composition with only a two times increase in the grain size. While XRD does not provide insight into the grain size distribution, one can only speculate that a large portion of the cumulative grains center about a mean diameter of 45nm. It has been shown with chemically disordered alloys that grain growth kinetics increase; however, once ordering takes place or develops, grain growth can be reduced [17]. It is suggested here that this may partly be the reason for the unusual grain stability of this nano-grained Cu₃Ge. That is, the room temperature milled compounds are
only partially disordered giving rise to good thermal stability. Other potential mechanisms for the remarkable thermal stability observed are that Cu₃Ge is an intermetallic electron compound with an electron to atom ratio of 7:4 and that the presence of small concentration of Fe impurities in the Cu₃Ge may stabilize the grain boundaries by lowering the grain boundary energy.

**Mechanical Properties**

Nano-indentation was performed on the 20hr room temperature milled, 20 hr room temperature milled and heat treated at 76% of Tₘ for 5hrs, and the 7.5hr cryo-milled samples. Individual particles were selected for indentation to minimize particle size and boundary effects. Several indentations were performed on each sample, and the average hardness and Young’s modulus were calculated. Typical data are shown in Fig 2. Figure 2a shows the hardness versus displacement curves for the three different samples tested. The cryo-milled sample with the smallest grain size (11nm) had more displacement than the heat-treated sample with (45nm) grain size. Figure 2b is a Hall-Petch plot of the three samples showing again that the cryo-milled sample (11nm) has the lowest hardness. Figure 2c shows the respective elastic moduli for the three samples. Again, the modulus for the cryo-milled sample is much different than that for the other two samples. This could be attributed a change in the crystal structure. The average hardness for the non-heat treated specimen was 6.4 GPa while an average hardness of 5.7 GPa and 4.7GPa was recorded for the heat-treated and cryo-milled samples, respectively. The standard deviations for the above three samples were 0.4, 0.3 and .35 GPa, respectively. Since Cu₃Ge is an intermetallic compound, it is expected that its hardness should be much higher than that of other copper-based metals [35-36]. In general, most nano crystalline copper samples have a hardness of ~ 2.3 GPa with a 20nm grain size; however, the highest hardness was reported for magnetron sputtered samples having a 10nm grain size equating to a 3 GPa hardness[35]. This is still two times lower than the hardness reported here. The yield strength for this nano-crystalline Cu₃Ge can be taken as1/3 the hardness, which equates to 2 GPa, while for typical nano copper it equates to 0.77GPa.
The Elastic modulus was calculated using the equation[37]

$$\frac{1}{E_r} = 1 - \nu^2_{\text{ind}}/E_{\text{ind}} + 1 - \nu^2_{\text{Cu3Ge}}/E_{\text{Cu3Ge}} \quad \text{[II]}$$

where $E_r$ is the reduced modulus, $\nu$ Poisson’s ratio for the indenter and sample, and $E$ is the respective elastic moduli. A Poisson’s ratio of 0.3 was assumed for calculation purposes. The resulting elastic moduli were 112 GPa for the room temperature milled sample, 108GPa for the heat treated sample and 82GPa for the cryomilled samples with standard deviations of 3.6, 9.8 and 5.2 GPa, respectively. These moduli are comparable to or lower than that of copper 110 GPa and less than the 130 GPa for germanium. However, a Hall-Petch coefficient based on the two higher hardness data points was calculated to be 10.1 GPa nm$^{0.5}$ which is comparable to several types of nanograin copper produced having slopes of 10.9 GPa nm$^{0.5}$ [35].

**Electrical Properties**

In Fig.3, we show the resistivity as a function of temperature (14-300K) for nanograin Cu$_3$Ge. The linear resistivity behavior indicates that our specimens exhibit metallic conductivity [33], which is dominated by electron-phonon scattering. At the lowest temperatures, the residual resistivity should become essentially independent of temperature. One of the previous authors has shown [38] that carriers in Cu$_3$Ge are predominantly holes with a hole mean free path of 43 nm (40 nm for pure Cu). This value for the mean free path is comparable to or even larger than the average grain size, indicating that the grain boundaries do not significantly contribute to the residual resistivity. This is consistent with the results of our previous studies showing that the residual resistivity is dominated by surface scattering rather than grain boundary scattering. In this context, it should be mentioned that our samples contain approximately 5% porosity. It is then very likely that internal surfaces are responsible for part of the rather high residual resistivity, which is a factor of ~4 higher than that reported earlier [26, 38] for 0.2 µm-thick-films of Cu$_3$Ge. On the other hand, the room
temperature resistivity in Fig. 3 for a specimen with a 45 nm grain size is 8.8 \( \Omega \text{-cm} \), which is comparable to the range of 6-10 \( \Omega \text{-cm} \) reported for 0.2 \( \mu \text{m} \) thin films of \( \text{Cu}_3\text{Ge} \) having grain sizes in the range of 0.1-1 \( \mu \text{m} \) [25-26, 38]. Again, this indicates that grain boundaries are not a significant contributor to the overall resistivity.

On the basis of the data in Fig. 3, the temperature coefficient of resistivity \((\rho_0^{-1} \frac{d\rho}{dT})\) is calculated to be 1.47 \( \times 10^{-3} \) /K for the reference temperature of 273 K. The parameter \( \frac{d\rho}{dT} = 0.017 \mu \Omega \text{-cm/K} \) calculated from this TCR is comparable to that (0.02 \( \mu \Omega \text{-cm/K} \)) reported by Aboelfotoh, et al [38]. The resistivity data also enable us to estimate the thermal conductivity of our specimen at room temperature assuming validity of the Wiedemann-Franz law. Our estimated value of 83 W/mK is comparable to that of other metallic alloys, e.g., \( \kappa \approx 100 \) W/mK for brass and \( \approx 70 \) W/mK for Al-14%Mg.

Also, employing electron dispersive spectroscopy (EDS), it was found that the \( \text{Cu}_3\text{Ge} \) milled powder contained trace amounts of Fe contamination, which is most likely associated with milling in the steel vials. Chemical analysis of the powder by ICP-emission spectrometry quantified the concentration of Fe in the \( \text{Cu}_3\text{Ge} \) powder to be 0.266 at%. Thus, it may be possible to reduce the resistivity value of the mechanically milled compound by reducing this unintentional impurity. It may also be possible to lower the resistivity further by the small atomic additions of either Au or Ga to the milled compound [25].

**Conclusions**

It has been demonstrated that nano-grained \( \varepsilon_1 \) \( \text{Cu}_3\text{Ge} \) can be produced through mechanical alloying at room or liquid nitrogen temperatures. Although the material itself exists in powder form with particles ranging in size from 150nm to 10 \( \mu \text{m} \), the individual grains of these particles are nano-crystalline (20nm) and remain nano-crystalline (45nm) after heat treating at 76% of the melting temperature, which shows extraordinary
thermal stability of grain size. There have been relatively few reports in the literature of such thermal stability in other nano-crystalline materials. It was also shown that the mechanical properties of nano Cu$_3$Ge have the same Hall Petch coefficient as many currently reported nanocrystalline copper samples. The hardness is on the order of two times larger than the currently reported for nanocrystalline copper samples.

It has also been demonstrated that the milled and heat treated Cu$_3$Ge samples exhibit low resistivity, which is comparable to that of deposited thin films with significantly larger grain sizes. This shows that the resistivity of the ε$_1$ compound Cu$_3$Ge has virtually no dependence on grain size or percentage of grain boundary area, which may have implication for next generation interconnects.

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References: Chapter 10


Figure 1: Comparative X-ray spectra for milled and annealed compounds indicating grain size and induced strain.
Figure 2: 2a: Comparative load versus depth nano indentation curves for Cu3Ge. 2b: Changes in Elastic Modulus for Cu3Ge. 2c: Hall Petch plot for Cu3Ge
Figure Three: Resistivity as a function of temperature for the 20 hour room temperature milled and sintered for 5hrs at 500°C.

\[ y = 0.0157x + 4.2 \]
Self-assembled 3D Cu-Ge nanoweb composite

Here we describe an inexpensive and beautifully easy method to produce the prototype of a new class of materials.

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3D Cu-Ge nanoweb, mechanical milling and sonochemical

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11.1. Abstract

The inexpensive combination of cryogenically milled Cu$_3$Ge powders sonochemically processed in a standard ultrasonic cleaner has led to the prototype of an heretofore undescribed class of materials. This prototype is a nanostructured composite composed of 4.5 nm diameter Cu nanocrystals embedded in a 3D amorphous CuGeO$_3$ polyhedron web matrix. The diameter of the wires comprising the matrix are typically 5-15nm. Complete structural and compositional characterization is reported to provide additional insight and firm designation on the observation of this previously undescribed class of materials. The large surface to volume ratio of these nanoweb composites may offer unique advantages based on altered optical or electronic and magnetic properties. For example, quantum confinement of the Cu dots in the amorphous 3D amorphous nanowebs is possible. Nanostructures in general have altered properties and the same is expected in nanostructured composites.
11.2. Introduction

Nanocrystalline materials in general include any materials that have nanoscale dimensions such as nanowires, nanocrystals, nanophased composites, and nanograined materials. Because of the nanoscale dimensions and large surface/volume ratios, nanocrystalline materials exhibit unique mechanical [1-2], electronic [3-5], magnetic [6-7] and chemical [8-11] properties that differ from their larger scaled counterparts. It is these unusual properties that have spawned the recent explosion of scientific research in the field now termed nanoscience or nanotechnology. For example, nanowires have been proposed to have a role as active components/interconnects in nanoscale devices and have been fabricated by nanolithographic techniques, vapor-liquid-solid growth, electron beam irradiation, and sonochemistry. Field effect transistors, light emitting diodes, and logic gates have all been fabricated with nanowires [12-13].

Most recently, single phase nanoweb like structures fabricated by hydrogen/oxygen plasma treatment [14] and dealloying [15] have been reported; however, their processing is very different, and the nanostructures are fundamentally more simple than the 3D structures presented here, as will be evident by the data provided. Structures such as the ones presented here, termed nanoweb composites, offer the potential for applications in catalysis, as sensors, electron confinement structures, and as filters in inorganic and biological systems.

Sonochemical synthesis, or sonication, is a particularly attractive technique for the fabrication of nanoscale materials since it occurs at ambient temperature and pressure, and
thus, is relatively simple and inexpensive [16-19]. This sonication process involves the formation, growth, and implosive collapse of bubbles in a liquid, which can produce high velocity inter-particle collisions, microjet impact and shock wave damage of particles in suspension [18]. The collapse of microscopic bubbles in the high pressure regime can result in localized hot spots with temperatures to 5000 K, pressures to 1000 atmospheres, and cooling rates as high as $10^{10}$ K/s [19]. The energy released from this process, known as cavitation, results in enhanced chemical reactivities and accelerated reaction rates. Trigonal Se nanowires produced by aging in the dark after sonication have been reported to have 40 nm diameters and also to exhibit interconnected networks with high photoconductivity [19]. It was suggested that this process may allow self-guided growth of interconnects for nanodevices. Ge nanocrystals, ≈5 nm diameter, have also been fabricated by an ultrasonic solution reduction technique [16].

Mechanical alloying produces metallic nanostructured materials with a grain size less than 100 nm by mechanical attrition of coarser-grained materials [20]. The targeted use of mechanical alloying here was to produce homogenous powders of the equilibrium intermetallic phase Cu$_3$Ge. However, not only can mechanical alloying be used to synthesize equilibrium phases but also non-equilibrium phases which include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys [20]. It is these qualities that may later prove important in engineering starting powders for tailored end product results.
It is by the combination of low temperature mechanical milling and sonochemical synthesis of the Cu$_3$Ge powders that we now report the observation of a previously undescribed self-assembled nanoweb composite comprised of Cu nanocrystals in a 3D nanoweb of amorphous Cu-Ge oxide.

11.3. Experimental

The Cu-Ge nanowebs discussed here were produced by a combination of low temperature mechanical milling and subsequent sonochemical synthesis of Cu$_3$Ge powders, which enabled 3D self-assembly of interconnected nanocrystals.

The $\varepsilon_1$ compound Cu$_3$Ge was prepared by loading the milled Ge powder with the correct weight ratio of Alpha Aesar Cu powder (170+425 mesh, 99.9%) into a hardened and cleaned steel vial to produce the desired Cu-25 atomic % Ge. The ball to powder mass ratio was maintained at 10:1, and the vial was sealed under vacuum ($10^{-4}$ Torr) prior to milling. Mechanical milling in the SPEX 8000 shaker mill was then performed at liquid nitrogen temperature for 7.5 hours. This was accomplished by placing the vial in a thick nylon sleeve modified to allow placement into the high energy mill as well as to allow an inflow and outflow of liquid nitrogen. After the ball milling procedure was completed, the Cu$_3$Ge powder was removed from the steel vial in an Ar glove box and placed in a glass vial. The milled, nanocrystalline grain Cu$_3$Ge powder consisted of agglomerated particles that ranged in size from 1-100 m.
X-ray diffraction analysis of the Cu₃Ge powder was performed with a Rigaku x-ray diffractometer using CuKα (λ=0.1542 nm) radiation. Formation of Cu₃Ge was confirmed by the x-ray analysis, and the grain size and strain induced by the ball milling process were determined. The average grain size from diffraction line broadening using the Williamson-Hall [21] and Scherrer [22] equations was calculated to be 41.7 and 19.7 nm, respectively, while the induced strain was estimated to be 0.004.

Microscopic examination of the resultant ball-milled Cu₃Ge powder was performed in both scanning (JEOL 6400F and Hitachi S3200) and transmission (200kV TOPCON 002B) electron microscopes. The Hitachi SEM was also equipped with an energy dispersive x-ray spectrometer (EDS) for chemical analysis. Powder specimens for TEM and SEM investigation were solution cast onto a standard lacy carbon grid and Si wafer, respectively. An electron diffraction pattern of the ball-milled powder also confirmed Cu₃Ge formation. Transmission electron micrographs of the Cu₃Ge microstructure provided an average grain size of 26.9 nm, which is within the range of grain sizes determined by XRD analysis. A semiquantitative EDS analysis also indicated the approximate composition to be 75 at% Cu/25 at% Ge.

Subsequent to the x-ray and microscopic characterization, the liquid nitrogen, ball-milled Cu-Ge powders were dispersed in methanol in a glass vial. This suspension (in its vial) was then sonicated in a Branson 2200R-4 standard laboratory ultrasonic bath operated at 40 kHz and heated to 60°C for 2.5 hours. After sonication, the suspension was allowed to settle for 5 min. Then a small amount of liquid was pipetted from the surface and deposited
onto a Si wafer for field emission scanning electron microscope observation. The solution contained particles ranging in size from 200 nm-3 µm with the surface of the milled and sonicated powders exhibiting pits with an average diameter of 70 nm. It should be noted that these pits on the surface of the particles were only observed after the sonication process. The remaining, sonicated suspension of milled Cu$_3$Ge powders and methanol was kept in its original vial and allowed to age in ambient light. It was from these aged solutions that the 3D nanowebs reported here have been observed.

For TEM and STEM sample preparation, the glass vile containing the sonicated powders in methanol were momentarily agitated and either a lacy carbon grid or a protochip SiN membrane was dipped into the solution such that particles were dispersed onto the respective grids for subsequent TEM and STEM observation. A JEOL 2010F HRTEM was utilized to acquire high resolution images of the nanoweb structures and to determine the crystalline and/or amorphous nature of the web structure. A Hitachi HD2300 STEM was also employed to collect secondary electron, diffraction contrast and Z-contrast images. For chemical composition determination both electron energy loss spectra (EELS) and energy dispersive spectroscopy (EDS) were employed to acquire nanoscale compositional information.

11.4. Results Section

Figure I shows dedicated scanning transmission electron micrographs (STEM) of two nanoweb structures that have been observed in Z-contrast (ZC) mode from our sonicated Cu-
Ge solutions. These ZC images reveal a nanoweb structure comprised of open areas, interconnected nanowires or ribbons, and brighter contrast nodules embedded on and in the nanowires.

**Figure I.** Dedicated STEM images of two interconnected structures, with magnification of select areas.
We designate this previously undescribed class of materials as a nanostructured composite. This nanostructured composite may be similar to the recently reported nanosized hollow iron oxide fabricated by sonochemical synthesis [23]. Z-contrast images provided preliminary data regarding chemical composition of the materials creating the nanoweb structure. The brighter contrast from the nodules or nanocrystals incorporated in the lower contrast nanoweb structure suggest that the nodules have a higher atomic number than the matrix in which they exist. An oxide of Cu-Ge, for example, would have a lower contrast due to its lower average atomic number.

When high resolution transmission electron microscopy (HRTEM) is used complimentary to scanning TEM (STEM) data, structure property relationships of nanostructures can be interpreted for better understanding of nanoweb properties. From digital image analysis of the insets in Fig 1, the bright nodules were determined to have an average diameter of ≈4.5 nm while the interconnected nanowires are typically 5-15 nm in diameter.
Figure II a, is a HRTEM micrograph in Scherzer focus showing two nodules of the nanoweb; the presence of lattice fringes indicates a crystalline material.

![HRTEM micrographs showing nodules.](image)

**Figure II.** High resolution TEM images of embedded nodules. (a) two ≈4nm nodules showing lattice spacing, (b) larger nodule ≈15nm showing polycrystalline structure, (c) small nodule showing dendritic like growth.

While the lattice fringes indicate that the bright nodules are crystalline, the lack of lattice fringes in the lower contrast interconnecting nanowires indicates them to be amorphous. Due to the random orientation of the nodules or nanocrystals, the lattice fringe spacing of 0.223 nm cannot be used to confirm if the particles are pure Cu or a CuGe alloy. Only when nanocrystals are orientated in zone axis can Bloch wave-based assumptions be used to identify specific d-spacings of pure elements or alloys. Other HRTEM micrographs from the nanowebs also show ≈5 nm regions of lattice fringes embedded within the
amorphous wires. Figure II b is a HRTEM micrograph showing a larger 15 nm polycrystalline nodule embedded on the surface of the supporting web. Finally, Fig. IIc shows one of many exhibited protrusions from the periphery of a web structure. In many cases, amorphous finger-like projections were at the leading edges of these nanoweb structures. At the tips of the projections were nanoscale nodules. As can be seen, the far end of the nodule is covered by an amorphous layer, which is copper oxide as noted later in the discussion of the EELS results. Many of these nodules on the amorphous projections were crystalline based on the observation of lattice fringes.

An electron diffraction pattern (supplementary figure SI) was obtained with selected area diffraction, which showed concentric rings typical of a polycrystalline sample. The bright spots and rings indicate that the nanoweb-structure consists of randomly orientated crystals. The ring spacing is directly proportional to the d-spacings and can be indexed to Cu. It is not possible to observe the diffuse diffraction rings of the amorphous ribbons, which create the interconnecting matrix of the nanowebs, due to the intense bright center of the pattern.

The web structures were also observed in a JEOL operating in STEM mode. The major contrast differences are created by elastic scattering or diffraction of incident electrons. Complimentary bright and dark field images (supplementary figures SII a,b) were taken of a selected area of a web structure. The bright field captured using a low angle annular dark field detector (LAADF) showed the nodular features on the amorphous regions to be darker, which indicates electrons being diffracted and is more typical of a crystalline lattice. This is
consistent with the lattice fringe analysis noted previously. The web structures were then imaged under dark field imaging conditions with a high angle annular dark field detector (HAADF) that produces atomic number contrast in the resulting image. This shows both chemical and mass-thickness contrast. The nodules under this type of imaging appeared in bright contrast which is the inverse to their appearance under diffraction contrast imaging. The brighter contrast is indicative of the small nodules having higher atomic number than the nanowire matrix and the crystalline versus amorphous nature of the nodule versus the nanoweb, respectively. Electron energy loss spectra (EELS) comparison of the chemical composition of the interconnected wires and the embedded nanocrystals in the web is shown in Fig. III (a,b).
Figure III. Two EELS spectra, (A) spectra taken from the interconnecting amorphous nano-web, (B) spectra taken from a metallic nanocrystalline nodule. Spectrum (B) shows only the Cu-L$_{2,3}$ region after background subtraction. See supporting information for spectra on the same scale.
In the region of the interconnecting matrix in Fig. III (a), core-loss edges from Cu, Ge and O are observed while only Cu is detected in the nanocrystalline nodules of Fig. III (b). A small amount of oxygen was also present in the spectrum of the nanocrystals and can be attributed to surface oxidation of the metallic particles, as can be observed in the EELS spectra of supplemental Fig SIII. This oxidation is supported by noting the outer film associated with these particles as seen in Fig. II. Nanoscale chemical and structural analysis indicated that the interconnected nanowires in the web are amorphous CuGeO$_3$ while the embedded nodules are nanocrystalline Cu. The electron-loss near edge structure (ELNES) of the Cu-L$_{2,3}$ edge in the EELS edges confirm this composition by comparing the ELNES to standards of pure Cu and Cu$^{2+}$ (CuO). A micrograph, which shows the location where selected EELS spectra were acquired is given in supplemental Fig. SIV.

**11.5. Discussion Section**

There have been many reports on the assembly of interconnected nanowire networks with the use of templates. However, there have been fewer reports of truly self-assembled networks of nanowires without the assistance of sol-gels or surface topographies. Most have attributed the formation of self-assembled networks on the reduction in free energy as the main driving force [14,19].
Using a sonochemical synthesis process similar to that employed here, Gates, et al [19] reported the growth of trigonal Se nanowires by a solid-solution-solid transformation mechanism. Trigonal Se forms on the surface of amorphous Se colloids due to localized heating and solubility differences as a result of sonochemical cavitation. The trigonal Se nanowires grow from these seeds at the expense of the amorphous Se. It was suggested [19] that this spontaneous process occurs because the crystalline Se nanowires have a lower free energy than the amorphous colloids; that is, the driving force for spontaneous growth was attributed to lowering of free energy. Aging in the dark resulted in nearly complete amorphous $\rightarrow$ trigonal transformation. This aging time, which could take up to 10 days, was dependent on the number of seeds present in the solution containing the amorphous colloids and the type of solution.

The formation of two dimensional self-assembled, crystalline gallium oxide nanowebs, which are quite similar to the 3D CuGeO$_3$ nanowebs reported in Fig. 1, was attributed to multiple nucleation and coalescence by an oxidation-reduction reaction at the molecular level [14].

Nano-sized droplets of liquid Ga were produced via a reduction reaction of Ga$_2$O$_3$ with hydrogen radicals in a hydrogen plasma. It has also been shown that the heat from cavitation implosions decomposes water into reactive hydrogen and hydroxyl radicals, capable of decomposing metal oxides into metallic ions in solution [24]. These nano-sized droplets were reported to self-assemble into extensive 2D nanoscale networks of Ga$_2$O$_3$. The wires formed parallel to the supporting substrate in a unique, interconnected polyhedron
architecture. It was suggested that the bonding of wires at intersections reduced the overall surface energy associated with unsatisfied bonds and that typically such a mechanism can only occur in systems where small particles are free to move as in liquid suspensions [14].

While the 3D interconnected Cu-Ge nanowebs observed in Fig. I have similarities to those reported by Gates, et al [19] and Graham, et al [14], the exact nature and driving force for their formation is unclear. However, one is tempted to speculate. It is clear that sonochemical synthesis is a high energy process that can result in high temperatures and large cooling rates during micro-bubble collapse. There can be increased surface area due to fragmentation of particles by acoustically-induced microjets and shock waves, and melting due to the heat of collision between acoustically-accelerated particles. Initially, the low temperature mechanically milled Cu₃Ge powder consisted of agglomerated particles ranging in size from 1-100 μm but having a nanocrystalline grain structure. During initial sonication, the powder’s average particle size was most likely reduced by fragmentation of the larger particles due to microjet impact and fatigue failure leaving behind smaller particles with large amounts of surface damage (pits) as observed in the images before and after sonication. Particles are also accelerated and able to attain high velocities because of shock waves generated by the cavitation process. In the extreme environment of cavitation, the smaller particles, including those created from surface damage areas, could be transformed
into an amorphous structure by the high temperatures and cooling rates experienced during micro-bubble collapse. These amorphous regions in the solvent then tend to self-assemble into interconnected nanowebs. Formation of Cu nanodots from amorphous regions may then be associated with the aging process, similar to that reported for Se nanowires [19]. Lowering the surface energy associated with removal of unsatisfied bonds is also a potential driving force for self-assembly. The nanocrystalline nodules may also be attributed to a lowering of free energy and/or localized solubility differences during cavitation. This process would lead to the formation of nano-crystallites in the alcohol solution containing the amorphous web structures or to localized nanocrystals embedded on the web itself. On the basis of our nanoscale characterization, the structure and composition of this nanoweb composite appears uniform. This suggests that oxygen incorporation most likely arises from the explosive nature of the sonication process in methanol and/or the reduction of oxides. Enhanced reactivities and radical formation are likely in this process. This scenario then suggests that subtle differences in structure and composition may be observed dependent upon the solvent used during sonication, which has been reported previously [18, 25, 26]. Li, et al have reported that different solvents influence reaction rates and hence, particle morphologies of Au ions; high rates favor nanorods or plates while lower rates yield spherical particles. This is consistent with Suslick’s suggestion [18] that the solvent vapor pressure should be low for enhanced bubble collapse efficiency. Hayashi, et al [26] have also reported that alcohol solvents accelerate ultrasonic reduction and protect the metal from reoxidation.
We have reported the observation by transmission electron microscopy of 3D interconnected Cu-Ge nanowebs fabricated by a combination of low temperature mechanical alloying and sonochemical synthesis. Understanding the driving force for formation of this nanostructured composite may lead to new understanding of self-assembled systems in general and may provide an ability to control such occurrences. It may also be possible that the 4.5 nm Cu nanocrystals in the amorphous nanowebs exhibit quantum confinement, which may show high order optical nonlinear susceptibility as reported recently for nanocomposite thin films of dielectric matrices doped with metal nanocrystals [27]. The large surface to volume ratio of the nanowebs produced by this simple process may thus offer unique advantages based on altered optical or electronic and magnetic properties. For example, CuO and CuGaO₂ are wide bandgap materials, which have been proposed for optical and field emission applications [28]. Crystalline CuGeO₃ has also been reported to be one of the very few inorganic compounds to exhibit a spin-Peierls transition [29-30]. Only by further investigations on matters such as these will the impact of the discovered structures be realized.

11.6. Conclusion

The first report of a previously undescribed class of materials, self-assembled nanostructured composites, has been presented. The substantiation of this prototype as a new class of materials is linked to its in intricate morphologies. Because of its morphological nature many challenges still exist in the ability to gather information for the understanding of
its technological importance. It was demonstrated that the 4.5 nm nanocrystals were metallic Cu. The distribution or percent coverage of these nanocrystals varies from web to web as does their mean separation distance. It was also shown that the web matrix is composed of an amorphous CuGeO₃ oxide arranged in a 3D polyhedron morphology. The diameter of these web interconnects are ≈ 5 -15 nm. The combination of metallic quantum confining structures isolated by an insulating matrix allows for an exciting combination of properties for future foreseeable studies.
References: Chapter 11


Figure Captions

**Figure I.** Dedicated STEM images of two interconnected structures, with magnification of select areas.

**Figure II.** High resolution TEM images of embedded nodules. (a) two ≈4nm nodules showing lattice spacing, (b) larger nodule ≈15nm showing polycrystalline structure, (c) small nodule showing dendritic like growth.

**Figure III.** Two EELS spectra, (A) spectra taken from the interconnecting amorphous nano-web, (B) spectra take from a metallic nanocrystalline nodule. Spectrum (B) shows only the Cu-L$_{2,3}$ region after background subtraction. See supporting information for spectra on the same scale.
Figure I.
Figure 2.
Figure 3.
11.8. Supplemental Information

Included for supporting information are several images as listed as follows: A diffraction pattern, two STEM images (DF and BF) showing 3D structures, two EELS spectra and one DF image showing origins of EELS spectra.

Figure SI. Selected area diffraction pattern produced by imaging a large number of nodules. The pattern was indexed to that of Pure Cu. The measured d spacing corresponded to the theoretical d spacing for Cu as given by the Joint Committee on Powder Diffraction Standards (JCPDS).
Figure SII. A: Dark and B: Bright field images of nanocrystals and supporting structure.
Figure SIII: A: The EELS spectra of the Cu nodules (red) and the CuGeO3 web. We see a small amount of oxygen in the spectrum of the nodules which we attribute to surface oxide. B: The EELS spectra of the Cu nodules (red) and the CuGeO3 web after background subtraction in the range of the Cu-L edge. The oxide-ELNES shows a clear peak at the onset of the Cu-L3 edge, which we attribute to Cu$^{2+}$. The edge does only shift a little which means the core levels in this material must shift a lot.
Figure SIV: Micrograph indicating locations were selected EELS spectra were acquired, from the CuGeO₃ interconnected web and embedded nanocrystalline Cu nodules.
Conclusions: CHAPTER (12)

It has been shown that the addition of Zr to Fe has led to the formation of nanocrystalline alloys extremely resistant to grain growth at elevated temperatures. This is true even in the dilute case of only 1/3 at% Zr. It was shown that increased solute content led to an increase in thermal stability of the microstructure. That is the microstructure of 4 at% Zr < 1 at% Zr < 1/3 at% Zr < 0 at% Zr. The average grain size in the 4 at% Z at 913°C was ~ 50nm. The average grain size in the 1 at% Z at 913°C was ~ 50-100nm. The average grain size in the 1/3 at% Z at 913°C was ~ 100-150nm. The onset temperature for rapid grain growth in pure nanocrystalline Fe was shown to be ~ 450°C. It was possible with the addition of Zr to increase this onset temperature by a factor of 2X while dramatically decreasing the growth rate. It was observed that with grain growth a simultaneous decrease in lattice parameter occurs without the formation of secondary phases. This indicates the movement of solute out of the lattice into the grain boundaries and this is concurrent with the preliminary Z-contrast images and TEM results. As such the thermal stability of these alloys at high temperatures was attributed to reduction in grain boundary energy via the diffusion of Zr solute. At low temperature below 700°C solute drag may have an effect on extending the onset for grain growth as well as suppressing it. At higher temperatures solute drag may still occur, but the exact magnitude of the retarding force should be insignificant. Particle pinning was discounted as means of thermal stability as 2nd phase particle were not observed in any of the
samples below 913°C. It was shown that by increasing the Zr solute content a decrease in the amount of abnormal grain growth could be realized. This suggests that at lower solute concentrations inhomogenities exist in the solute distribution within the grain boundaries, leading to differences in interfacial energies which results in explosive growth of select grains. Above, 913°C it is found the 4 at% Zr sample dramatically loses the thermal stability as is evident by the micron scaled microstructure and the low Vickers hardness at 1173°C. The low hardness is concurrent with the precipitation of the Fe₂Zr phase. The phase amount of Fe₂Zr is in good agreement with what the phase diagram predicts as the equilibrium phase amount. Because the alloys with Zr solute less that 4at% have similar hardness at 1173°C the microstructures could also be similar. It is unclear whether the BCC to FCC transition influences the location of solute and hence the thermal stability of the alloys. Annealing above the eutectic temperature, results in surface segregation of Zr solute whose concentration has been shown to increase with alloy composition.

Finally while having a high elastic enthalpy in a solvent solute combination is ideal for maximizing a decrease in interfacial energy, having a equal high negative enthalpy of mixing may be more important. While the driving force to reduce the interfacial energy is high, the potential of lowering the systems energy by the formation of secondary phase can be greater. Therefore, the thermal stability of an alloyed system can only be as good as the systems’ ability to resist the formation of secondary phases.
Some of the remaining questions are: How much solute resides in the grain boundary? Is, as theoreticians describe, a complete monolayer necessary for interfacial energy to be zero? How is the solute distributed (homogeneously/in homogeneously) among the grain boundaries? If Zr solute is distributed uniformly, is the interfacial energy reduction homogenous? Finally, what electronic effect does the solute have on the grain boundary and its role in interfacial energy reduction? EELS or ELNES, in combination with Z-contrast imaging and computer modeling, have recently become powerful tools for determining structure-property relationships at grain boundaries and interfaces for the following: probing local stoichiometry, analyzing impurity segregation and determining electronic structure such as changes in density of states/atomic coordination, changes in valance, charge transfer and bonding type of the solvent and solute at the grain boundaries. Noting changes like these will give information about the mechanisms governing the decrease in interfacial energy in these systems, as well as other systems not yet foreseen. Analysis with these techniques will likely yield valuable data in the future.
Additional future work on engineering the $\alpha \rightarrow \gamma$ transformation in Fe-Zr is of interest for the purpose of attaining even higher thermal stability applications. The kinetics of grain growth of a system showing interfacial energy reduction during an allotropic transformation is not yet understood. Thus, it is not known, at this point, how the BCC versus FCC matrix phases will respond differently to Zr stabilization at temperatures between 913°C and 1173°C. In pure Fe, the $\alpha \rightarrow \gamma$ transformation occurs at 913°C. The phase diagrams Fe-Cr and Fe-Ni show that Cr additions produce a closed $\gamma$ domain, whereas Ni additions produce an open $\gamma$ domain on the respective phase diagrams. Additions of Cr in excess of 13 at% will eliminate the $\alpha \rightarrow \gamma$ transformation at all temperatures. Thus, Fe-Cr alloys will reveal the effect of the BCC $\alpha$ Fe matrix at the highest possible annealing temperatures. In contrast, the addition of Ni will lower the $\alpha \rightarrow \gamma$ transformation temperature and will reveal possible effects of the FCC $\gamma$ matrix over a broad range of annealing temperatures. Both Cr and Ni have a very small elastic size misfit in Fe ($< 1\%$). This means that neither of these alloy additions will produce the large elastic size-misfit enthalpy of segregation associated with Zr additions to Fe. Based on the size-misfit effect, neither Cr or Ni should be candidates for grain-boundary segregation and contaminate thermodynamic grain-size stabilization.
Bulk consolidation must be attempted. To accomplish this high temperatures are needed. It is unclear how the solute at the grain boundaries will affect the bulk lattice diffusional processes required for densification during sintering. Thus intense experimentation will be required to maximize the sintering effects.

Abnormal grain growth is normally observed as being detrimental to the properties of the sample in which it occurs. However, in this case, the ability to engineer the percent area of abnormally grown grains, by adjusting the heat treating schedule and the solute concentration (0-4 at% Zr), can be a benefit. It is well known that bimodal grain size distributions in nanocrystalline metals and alloys leads to increases in uniform elongation, the prerequisite for extensive ductility, as well as suppressing fatigue crack growth rates. Thus, bulk mechanical testing should be performed to have an understanding of the mechanical properties.