Development of Fe-Si material for magnetic applications

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2007

Zuo, B. (2007). Development of Fe-Si material for magnetic applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/35964>

<https://doi.org/10.32657/10356/35964>

9529620

DEVELOPMENT OF Fe-Si MATERIAL FOR MAGNETIC APPLICATIONS

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A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

2007

ABSTRACT

This project investigated the mechanochemical synthesis of nanograined Fe-Si based alloys, the thermal stability of the nanograins, sintering and the magnetic properties of sintered products. Initially, synthesis and thermal stability of a set of nanostructured alloys based on the $\text{Fe}_{75}\text{Si}_{25}$ composition with ternary additions of Al, Cu and Nb were investigated. The milling conditions required to achieve nanograined and fully alloyed powder were first determined. Thermal stability investigations showed that Al and Nb additions inhibited grain growth more effectively than Cu. However, the Nb containing alloy formed the second phase Fe_2Nb which is undesirable for soft magnetic applications. Hence Al was chosen as the promising ternary additive for further detailed studies on sintering and magnetic properties. The sintering behaviours of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ were assessed by conventional pressureless sintering and Spark Plasma Sintering of the nanocrystalline powder compacts. It was shown that $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ always sintered better and resulted in smaller grain sizes compared to the binary $\text{Fe}_{75}\text{Si}_{25}$, irrespective of the sintering method and the temperature used. Magnetic property measurements showed that the $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ sintered products exhibited higher saturation induction compared to $\text{Fe}_{75}\text{Si}_{25}$ sintered under the same conditions. This is attributable to their higher sintered density. Thus, addition of Al to $\text{Fe}_{75}\text{Si}_{25}$ is beneficial to attain a nanograined structure, to sinter easily and to derive improved saturation magnetic moment. The grain growth behavior of the two alloys was critically analyzed with the aid of available grain growth theories and it was inferred that grain boundary segregation of alloying elements is the cause of the restraint in the growth of the initial nanograins of α -Fe solid solution. In

$\text{Fe}_{75}\text{Si}_{25}$ alloy when the disordered α -Fe phase transforms to the ordered Fe_3Si at high temperatures, a sudden depletion of grain boundary segregants is predicted which results in the rapid growth above the ordering temperature. In $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ however, the ordering is incomplete with persistence of some degree of grain boundary segregation causing reduced grain growth even after ordering is detected.

ACKNOWLEDGEMENT

The work described in this report could not have been completed without the input and assistance of a number of individuals. I would like to thank the following people and organizations for their assistance during my studies.

First, my supervisor Associate Professor Thirumany Sritharan, for leading me with his knowledge and assisting me in conducting this work, without whom I might never have made it this far. His support, patience and guidance through these years have provided me with the opportunity of developing my own passion for science.

I also need to acknowledge the many people that I have met in the School of Materials Science and Engineering. Life in the School has been easier with the help of the secretaries and the administrative staff. I can't forget to thank Thomas and Eric for their assistance in the operation of ball mill and the equipment maintenance. I thank Irene and Lee Chin at the Advanced Material Characterization Lab for sharing her knowledge about SEM and XRD. I am grateful also to Guo Jun for allowing me to benefit from her technical expertise and the outstanding microscopy facilities.

I would also like to express my gratitude to my friends Du Siwei, Xu Cong and family for support and understanding throughout this process. The School of Materials Science and Engineering for providing funding and equipment for my research.

TABLE OF CONTENTS

ABSTRACT.....i

ACKNOWLEDGEMENTiii

TABLE OF CONTENTS.....iii

LIST OF FIGURESiii

LIST OF TABLES.....iii

1 INTRODUCTION3

2 LITERATURE REVIEW3

2.1 Nanocrystalline Materials3

2.1.1 Structure of Nanocrystalline Materials3

2.1.2 Synthesis of Nanocrystalline Materials3

2.2 Synthesis of Nanocrystalline Materials by Mechanical Alloying.....3

2.2.1 Historical Perspective3

2.2.2 The Process of Mechanical Alloying.....3

2.2.3 Mechanism of Alloying3

2.2.4 Formation of Nanostructure by Mechanical Alloying3

2.2.5 Formation of Solid Solution by Mechanical Alloying.....3

2.3 Thermal Stability of Nanocrystalline Materials.....3

2.3.1 Grain Growth in Nanocrystalline Materials.....3

2.3.2 Stability against Grain Growth3

2.4 Consolidation of Nanocrystalline Materials3

2.4.1 Consolidation Characteristics of Nanocrystalline Powders.....3

2.4.2 Spark Plasma Sintering (SPS).....3

2.4.3 Consolidation Mechanisms in SPS3

2.5	Magnetic Properties and Materials	3
2.5.1	Magnetic Domains	3
2.5.2	Magnetic Properties Derived from a Hysteresis Loop.....	3
2.5.3	Soft Magnetic Nanocrystalline Materials	3
2.6	Motivation for Studying Nanocrystalline Fe-Si.....	3
3	EXPERIMENTAL PROCEDURES	3
3.1	High-Energy Ball Milling	3
3.2	Annealing of As-Milled Powders	3
3.3	Consolidation of As-Milled Powders.....	3
3.3.1	Conventional Cold Compaction and Vacuum Sintering.....	3
3.3.2	Spark Plasma Sintering (SPS).....	3
3.4	Characterization of As-Milled Powders.....	3
3.4.1	Powder Morphology Characterization.....	3
3.4.2	Characterization of Crystal Size and Structure	3
3.5	Magnetic Property Measurements	3
4	RESULTS....	3
4.1	Evolution of Powders during Ball Milling.....	3
4.1.1	Particle Morphology Evolution.....	3
4.1.2	Crystal Structure Evolution.....	3
4.2	Thermal Stabilities at Elevated Temperatures	3
4.2.1	Effects of Addition of Al on the Thermal Stability of Fe ₇₅ Si ₂₅	3
4.2.2	Effects of Addition of Nb on the Thermal Stability of Fe ₇₅ Si ₂₅	3
4.2.3	Effects of Addition of Cu on the Thermal Stability of Fe ₇₅ Si ₂₅	3
4.3	Grain Growth Kinetics of Fe ₇₅ Si ₂₅ and Fe ₇₅ Si ₁₅ Al ₁₀	3
4.3.1	Grain Growth and Structural Evolution during Annealing.....	3

4.3.2	Determination of the Activation Energy of Grain Growth	3
4.4	Sintering Behavior and Magnetic Properties	3
4.4.1	Sintering Behavior	3
4.4.2	Magnetic Properties.	3
5	DISCUSSION	3
5.1	Formation of Nanocrystalline Solid Solutions during MA	3
5.1.1	Particle Morphology Evolution.....	3
5.1.2	Grain Refinement and Strain Accumulation.....	3
5.1.3	Formation of Solid Solutions	3
5.2	The Effects of Al, Nb and Cu on the Thermal Stability of Fe ₇₅ Si ₂₅ during Annealing.....	3
5.3	Grain Growth Kinetics and Ordering Transformation of Fe ₇₅ Si ₂₅ and Fe ₇₅ Si ₁₅ Al ₁₀	3
5.3.1	Fe ₇₅ Si ₂₅	3
5.3.2	Fe ₇₅ Si ₁₅ Al ₁₀	3
5.4	Sintering Behaviors of Fe ₇₅ Si ₂₅ and Fe ₇₅ Si ₁₅ Al ₁₀	3
5.5	Magnetic Properties of Fe ₇₅ Si ₂₅ and Fe ₇₅ Si ₁₅ Al ₁₀	3
5.6	Proposed Material and Process Design for Further Material Optimization and Process Improvement.	3
5.7	Scientific Advancements and Technical Accomplishments	3
6	CONCLUSIONS.....	3
6.1	Mechanochemical Activation	3
6.2	Ordering and De-segregation in Fe ₇₅ Si ₂₅	3
6.3	Sintering Fe ₇₅ Si ₂₅ and Fe ₇₅ Si ₁₅ Al ₁₀	3
6.4	Magnetic Properties of Sintered Products.....	3

6.5 Contribution to Fe-Si based Magnetic Materials.	3
PUBLICATIONS.....	3
Journal Papers	3
Conference Papers	3
REFERENCES....	3
APPENDICES....	3
Appendix A	3
Appendix B	3
Appendix C	3

LIST OF FIGURES

Figure 2-1 Schematic arrangement of atoms in an equiaxed nanocrystalline metal.....	3
Figure 2-2 (a) Fritsch Pulverisette P-5 four station ball mill. (b) Schematic depicting the ball motion inside the ball mill. Courtesy of Gilson Company, Inc., Worthington, OH.	3
Figure 2-3 Ball-powder-ball collision of powder mixture during mechanical alloying[Wiechert, W., 2000].	3
Figure 2-4 Narrow particle size distribution caused by tendency of small particles to weld together and large particles to fracture under steady-state conditions [Lee, PY., et al., 1998].	3
Figure 2-5 Refinement of particle and grain sizes with milling time. Rate of refinement increases with higher milling energy, ball-to-powder weight ratio, lower temperature, etc.....	3
Figure 2-6 Nanocrystalline structures emerge by high-energy impacts of particles[Fecht, H. J., 1995].	3
Figure 2-7 Comparison of sintering onset in nanocrystalline and conventional ZrO ₂ . [Skandan, G., 1995]	3
Figure 2-8 Schematic diagram of spark plasma sintering process [Jung,Y.G., et al., 2002]	3
Figure 2-9 A schematic of the profile of process variables pressure, temperature and density in SPS [Jung,Y.G., et al., 2002].	3
Figure 2-10 The electronic structure of the 3d orbital for transition metals. Unpaired electrons contribute to the magnetic nature of these metals [Jiles, D., 1991].....	3
Figure 2-11 Origin of Domains [Kittel, Charles., 1949].....	3
Figure 2-12 Reversal of magnetization between adjacent domains does not occur abruptly, but extends through the thickness of the boundary or will result in separating the two domains[Kittel, Charles., 1949].....	3
Figure 2-13 The effect of magnetization on domains.	3
Figure 2-14 Schematic of a hysteresis curve for a magnetic material defining some technical magnetic parameters.	3

Figure 2-15 Effective permeability, μ_e , vs. saturation magnetic flux density, B_s , for soft ferromagnetic materials (after A. Makino, et al., 1995).	3
Figure 2-16 Herzer [1997] diagram of coercivity, H_c , dependence on grain size.	3
Figure 2-17 Cartoon illustrating N nanocrystalline grains of dimension D in a volume L^3_{ex} . [Herzer, G., 1990]	3
Figure 2-18 Phase diagram of the Fe-Si system according to Kubaschewski [Kubaschewski, 1982].	3
Figure 3-1 A sketch of the die for cold pressing of ring-shaped preform. The left-hand side represents the situation at the starting and the right at the final stage of the deformation process.	3
Figure 3-2. A schematic diagram of SPS system.....	3
Figure 3-3 A schematic of the profile of process variables pressure, temperature and density in SPS.	3
Figure 3-4 AMH-20 hysteresisgraph system.	3
Figure 3-5 Typical configuration for measuring the hysteresis loop of magnetically soft materials.	3
Figure 4-1 SEM morphology of powders before milling: (a) Fe; (b) Si; (c) Al.	3
Figure 4-2 SEM morphology of $Fe_{75}Si_{25}$ powders after milling times of (a) 15h; (b) 25h; (c) 40h; (d) 60h; (e) 80h; (f) 100h.....	3
Figure 4-3 SEM morphology of $Fe_{75}Si_{15}Al_{10}$ powders after milling times of (a) 15h; (b) 25h; (c) 40h; (d) 60h; (e) 80h; (f) 100h.	3
Figure 4-4 X-ray diffraction (XRD) patterns of (a) $Fe_{75}Si_{25}$ and (b) $Fe_{75}Si_{15}Al_{10}$ powders after different milling times (0–100h).	3
Figure 4-5 A schematic diagram of FWHM.	3
Figure 4-6 Crystallite size/strain separation calculation according to the Williamson-Hall approximation given by Eq. (3-2) using the instrumental broadening-corrected "pure" profile breadth, $\delta(2\theta)$, which also calculated from Eq. (3-1). ($Fe_{75}Si_{25}$ powder milled for 60 h).	3
Figure 4-7 Lattice parameter calculation according to the Cullity approximation. ($Fe_{75}Si_{25}$ powder milled for 60 h).	3
Figure 4-8 Crystalline size of $Fe_{75}Si_{25}$ and $Fe_{75}Si_{15}Al_{10}$ powders as a function of milling time.	3

Figure 4-9 Strain of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ powders as a function of milling time.	3
Figure 4-10 Lattice parameter of powders as a function of milling time.	3
Figure 4-11. Plots of grain size against annealing temperatures for the two compositions.	3
Figure 4-12 X-Ray diffractograms of ball milled and annealed powders of (a) $\text{Fe}_{75}\text{Si}_{25}$.and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$.The annealing temperatures are indicated in the figure. Note the appearance of DO_3 superlattice reflections at 773 K and higher temperatures.	3
Figure 4-13 X-ray diffraction (XRD) patterns powders after annealing at different temperatures.	3
Figure 4-14 The bright field TEM micrograph of a $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ specimen milled for 60h with its SAD pattern in inset. The materials has some isolated crystals in an amorphous matrix.	3
Figure 4-15. Plot of grain size against annealing temperature for annealing time of 30min for three alloys. The rapid grain growth beyond some temperature is evident.	3
Figure 4-16 X-ray diffraction (XRD) patterns of $\text{Fe}_{75}\text{Si}_{15}\text{Cu}_{10}$ powders after annealing at 773K for different times.	3
Figure 4-17 Plot of grain size against annealing time at 773K for three alloys.	3
Figure 4-18. Plots of grain size of (a) $\text{Fe}_{75}\text{Si}_{25}$.and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing temperature.	3
Figure 4-19. Plots of internal strain of (a) $\text{Fe}_{75}\text{Si}_{25}$.and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing time.	3
Figure 4-20. Plots of lattice parameter of (a) $\text{Fe}_{75}\text{Si}_{25}$.and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing temperature.	3
Figure 4-21. Plots of LRO of (a) $\text{Fe}_{75}\text{Si}_{25}$.and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing temperature.	3
Figure 4-22. A plot of grain size of (a) $\text{Fe}_{75}\text{Si}_{25}$.and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing time for the different temperatures. Curves are fitted according to Eqn. (2-9) and the fitting k values are tabulated in Table 4-2.	3
Figure 4-23. Arrhenius plot of $\ln k$ against $1/T$ for the k values in Table 4-2. The activation energies obtained for the two straight lines are also given. Q1 and Q2	

are the activation energies for $\text{Fe}_{75}\text{Si}_{25}$, and Q3 and Q4 are those for $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$	3
Figure 4-24. Optical Micrograph of $\text{Fe}_{75}\text{Si}_{25}$ alloy after sintering at 1333K(a), 1393K(b), 1453K(c) and 1513K(d) for 1h.....	3
Figure 4-25. Optical Micrograph of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy after sintering at 1333K(a), 1393K(b), 1453K(c) and 1513K(d) for 1h.....	3
Figure 4-26. Optical Microscope (a) and Bright field transmission electron micrograph (b) of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy sintered with SPS at 1243K for 5 min with corresponding selection area diffraction pattern as insert.....	3
Figure 4-27. X-Ray diffractograms of $\text{Fe}_{75}\text{Si}_{25}$ (a) and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ (b) after SPS at the various temperatures indicated.	3
Figure 4-28. Plots of relative density and grain size against sintering temperature for $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ after SPS and conventional sintering.	3
Figure 4-29. Hysteresis loops of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloys after conventional sintering at various temperatures.	3
Figure 4-30. Plots of density, grain size, maximum induction, maximum permeability and coercivity of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ against sintering temperatures.....	3
Figure 5-1. The variations of solute concentrations at GBs and in the crystal against temperature for various cases and the corresponding differences between GB and crystal concentration. (a) GB concentration of Si with disordered boundary C_{disGB}^{GB} in $\text{Fe}_{75}\text{Si}_{25}$ alloys (b) Crystal Si concentration with disordered boundary C_{disGB}^{Cry} in $\text{Fe}_{75}\text{Si}_{25}$ alloys, (c) ΔC of Si for disordered boundary in $\text{Fe}_{75}\text{Si}_{25}$ alloys, (d) Si GB concentration with ordered boundary C_{ordGB}^{GB} in $\text{Fe}_{75}\text{Si}_{25}$ alloys, (e) Si Crystal concentration with ordered boundary C_{ordGB}^{Cry} in $\text{Fe}_{75}\text{Si}_{25}$ alloys, (f) Si ΔC for ordered boundary. (g) GB concentration of Al with disordered boundary C_{disGB}^{GB} in $\text{Fe}_{75}\text{Al}_{25}$ alloys. (h) Al GB concentration with ordered boundary C_{ordGB}^{GB} in $\text{Fe}_{75}\text{Al}_{25}$ alloys, (i) ΔC of Al for disordered boundary in $\text{Fe}_{75}\text{Al}_{25}$ alloys, (j) Al ΔC for ordered boundary in $\text{Fe}_{75}\text{Al}_{25}$ alloys. The ΔC regions for the two temperature ranges are shown enclosed in thin rectangles.	3
Figure 5-2. Plot of Bs versus Porosity of (a) $\text{Fe}_{75}\text{Si}_{25}$ and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy. Curves are fitted according to Eqn. (5-14). Triangle dots represent $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, the diamond dots for $\text{Fe}_{75}\text{Si}_{25}$	3

LIST OF TABLES

Table 2-1 Attributes of nanocrystalline ferromagnetic materials produced by an amorphous precursor route [McHenry, Michael E., 1999].3

Table 4-1 $\delta(2\theta)\cos\theta_0$ and $\sin\theta_0$ calculation according to the Williamson-Hall for $\text{Fe}_{75}\text{Si}_{25}$ powder milled for 60 h3

Table 4-2 Maximum grain size and the growth rate constant for different temperatures computed using Eqn. (2-9).3

1 INTRODUCTION

Recent developments of nanocrystalline magnetic materials have initiated numerous activities for the development of advanced magnetic devices for energy transfer, for high-powered and miniature electric motors, for medical applications and for the sensor and magnetic recording industry. Approaches to improving intrinsic and extrinsic soft ferromagnetic properties involve (a) tailoring chemistry and (b) optimizing the microstructure. Significant recent development in the understanding of magnetic coercivity mechanisms has led to the realization that for very small grain sizes $D_g < \sim 100$ nm, H_c decreases rapidly with decreasing grain size. This can be understood by the fact that smaller grain size leads to more random magnetic orientations within each domain and therefore results in a smaller magnetic anisotropy.

The commercial Finemet alloys were first produced in amorphous form and were then control annealed to produce a nanocrystalline grain structure [Yoshizawa, Y., et al. 1988]. The requirement to produce the amorphous state means several alloying elements essential for amorphization must be added even though they may not have a role subsequently in the application. Since nanocrystalline materials have been produced by high-energy ball milling methods in several metallic systems, it was decided to use this simpler technique to directly produce nanocrystalline powder from conventional elemental powders.

Soft magnetic properties require that nanocrystalline grains be exchange coupled and therefore processing routes yielding freestanding nanoparticles must include a compaction method in which the magnetic nanoparticles end up exchange coupled. Once a nanocrystalline powder is produced it must be densified in some manner to form it into a useful solid component. Methods of powder densification are available but their main disadvantage is the use of high temperatures where grain growth occurs. If the grains grow too big the advantage of nanocrystallinity could get lost. Hence, it is important to control grain growth during densification.

The objective of the project is to investigate the synthesis and structure-property relationship of nanocrystalline Fe-Si alloys for magnetic applications. This project will focus on the following tasks in the first stage:

- Feasibility of producing Fe-Si based nanocrystalline alloys via high-energy ball milling of elemental powder precursors,
- The thermal stability of the nanocrystalline structure in such as-milled alloys
- The effects of ternary alloying additives Al, Nb and Cu.

This will give an insight to the mechanism that controls the thermal stability of Fe-Si based alloys. Subsequent work will focus on consolidation of the binary Fe-Si alloy with and without ternary additives, their sintering, the microstructures and magnetic properties of the resulting products. The inter-relationship between processing-structure-magnetic properties will be determined to design the alloy chemistry and the process parameters for the mechanochemical synthesis of nanocrystalline material for use as soft magnets.

2 LITERATURE REVIEW

2.1 Nanocrystalline Materials

The field of nanocrystalline materials as a major identifiable activity in modern materials science results to a large degree from the work in the 1980s of R. Birringer, H. Gleiter and coworkers [R. Birringer, et al. 1984], who synthesized ultrafine-grained materials by the in situ consolidation of nanoscale atomic clusters. The ultrasmall size (< 100 nm) of the grains in these nanocrystalline materials can result in dramatically improved-or different-properties from conventional grain-size (> 1 μm) polycrystalline or single crystal materials of the same chemical composition. This is the stimulus for the tremendous appeal of these materials.

There are a number of bulk properties that may be dramatically changed when the microstructure is nanoscale. These are (1) the mechanical properties of nanostructured materials for a variety of potential structural applications, and (2) ferromagnetic materials with nanoscale microstructures for potential applications as soft magnetic materials and permanent magnet materials, and for other special applications such as information storage, magnetoresistance spin valves, and magnetic nanocomposite refrigerants.

2.1.1 Structure of Nanocrystalline Materials

Nanocrystalline materials are single-phase or multi-phase materials, the crystal size of which is of the order of a few (typically <100 nm) nanometers in at least one dimension. Because of the extremely small size of the grains, a large fraction of the atoms in these materials is located in the grain boundaries (Figure 2-1) and thus the material exhibits enhanced combinations of physical, mechanical, and magnetic properties (compared to material with a more conventional grain size, i.e., >1 μm). Nanocrystalline materials show increased strength, high hardness, extremely high diffusion rates, and consequently reduced sintering times for powder compaction.

Figure 2-1 Schematic arrangement of atoms in an equiaxed nanocrystalline metal.

2.1.2 Synthesis of Nanocrystalline Materials

There are many ways to synthesize nanostructured materials, including

- rapid solidification [Guo, W. H., et al., 2000],
- inert gas condensation [Hockel, P.G., et al., 1996],
- electrodeposition [Trudeau, Michel L., et al., 1999],
- sputtering [Chandra, Ramesh., et al., 1999],
- mechanical alloying [Fecht, H. J., et al., 1990],
- crystallization of amorphous phases [Kojima, Akinori., et al., 1997],
- chemical processing [Kear, B. H., et al., 1995], etc.

Amongst the different options for preparations, mechanical alloying approach has received significant attention because of its simplicity, need for relatively inexpensive equipment, and the possibility of producing large quantities, which can be scaled up to several tons.

2.2 Synthesis of Nanocrystalline Materials by Mechanical Alloying

Mechanical alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill. Originally developed to produce oxide-dispersion strengthened (ODS) nickel- and iron-based superalloys for applications in the aerospace industry, MA has now been shown to be capable of synthesizing a variety of equilibrium and

non-equilibrium alloy phases starting from blended elemental or prealloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys.

2.2.1 Historical Perspective

Mechanical alloying (MA) is a powder processing technique that allows production of homogeneous materials starting from blended elemental powder mixtures. John Benjamin and his colleagues at the Paul D. Merica Research Laboratory of the International Nickel Company (INCO) developed the process around 1966 [Benjamin, J. S., 1990]. The technique was the result of a long search to produce a nickel-based superalloy, for gas turbine applications, that was expected to combine the high-temperature strength of oxide dispersion and the intermediate-temperature strength of gamma-prime precipitate. The required corrosion and oxidation resistance was also included in the alloy by suitable alloying additions. This process was initially referred to as “milling/mixing” and latter was referred as “mechanical alloying”, which has now come to stay in the literature. Mechanical alloying is normally a dry, high-energy ball milling technique and has been employed to produce a variety of commercially useful and scientifically interesting materials.

2.2.2 The Process of Mechanical Alloying

The actual process of MA starts with mixing of the powders in the right proportion and loading the powder mix into the mill along with the grinding medium (generally steel balls). This mix is then milled for the desired length of time until a steady state is reached when the composition of every powder particle is the same as the proportion of the elements in the starting powder mix. The milled powder is then consolidated into a bulk shape and heat treated to obtain the desired microstructure and properties.

2.2.2.1 Milling Equipment-Planetary Ball Mills

A popular mill for conducting MA experiments is the planetary ball mill (referred to as Pulverisette) in which a few hundred grams of the powder can be milled at a time (Figure 2-2a). These are manufactured by Fritsch GmbH in Germany and marketed by Gilson Co., in the US and Canada. The planetary ball mill owes its name to the planet-like movement of its vials. These are arranged on a rotating support disk and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the vials rotating around their own axes and that produced by the rotating support disk both act on the vial contents, consisting of material to be ground and the grinding balls. Since the vials and the supporting disk rotate in opposite directions, the centrifugal forces alternately act in like and opposite directions. This causes the grinding balls to run down the inside wall of the vial -- the

friction effect, followed by the material being ground and grinding balls lifting off and traveling freely through the inner chamber of the vial and colliding against the opposing inside wall -- the impact effect (Figure 2-2b).

Even though the disk and the vial rotation speeds could not be independently controlled in the earlier versions, it is possible to do so in the modern versions. In a single mill one can have either two or four milling stations. Recently, a single-station mill was also developed. Grinding vials and balls are available in eight different materials -- agate, silicon nitride, sintered corundum, zirconia, chrome steel, Cr-Ni steel, tungsten carbide, and plastic polyamide.

Figure 2-2 (a) Fritsch Pulverisette P-5 four station ball mill. (b) Schematic depicting the ball motion inside the ball mill. Courtesy of Gilson Company, Inc., Worthington, OH.

2.2.2.2 Process Variables

Mechanical Alloying is a process involving a number of both independent and interdependent variables. For a particular alloy system the variables include the type of mill, intensity of milling (velocity of the grinding medium, frequency of impacts, energy transfer efficiency, etc.), type of milling media, ball-to-powder weight ratio, the atmosphere under which the powder is milled, purity of the powders, milling time, milling temperature, and nature and amount of the PCA used [Suryanarayana, C., 2001]. All these have a significant effect on the constitution of the powder. It has been reported that the final constitution of the powder is dependent upon the size of the grinding medium used. For example, when balls of 15 mm diameter were used to mill the blended elemental Ti–Al powder mixture, a solid solution of aluminum in titanium was formed. On the other hand, use of 20 and 25 mm diameter balls resulted in a mixture of only the titanium and aluminum phases, even after a long milling duration [Lai, M.O., 1998]. The ball-to-power weight ratio has a significant effect on the time required to achieve a particular phase in the powder being milled. The higher the BPR, the shorter is the time required. For example, formation of an amorphous phase was achieved in a Ti–33at%Al powder mixture milled in a SPEX mill in 7 h at a BPR of 10:1, in 2 h at a BPR of 50:1 and in 1 h at a BPR of 100:1 [Suryanarayana, C., 1992]. At a high BPR, because of an increase in the weight proportion of the balls, the number of collisions per unit time increases and consequently more energy is transferred to the powder particles and so alloying takes place faster. Maurice and Courtney [Maurice, D, et al., 1996] compared the alloying behavior in the SPEX mill and the attritor and identified some of the commonalities and differences between the two devices. While the lamellar thickness of the component metals and the hardness

are almost the same in both the milling devices, the time required for completion of the process was estimated as 15 minutes in the SPEX mill and 11,000 minutes in the attritor. The composite particle diameter was also calculated to be 52 μm in the SPEX mill while it was 910 μm in the attritor. They showed that these differences arise because of the differences in the average impact velocity (0.5 m/s in the attritor and 4 m/s in the SPEX mill) and the average impact frequency (0.88/s in the attritor and 7/s in the SPEX mill). Although it has been long known that the SPEX mill is much more energetic than the attritor, this provides a more quantitative comparison.

2.2.3 Mechanism of Alloying

During high-energy milling the powder particles are repeatedly flattened, cold welded, fractured and rewelded. Whenever two steel balls collide, some amount of powder is trapped in between them. Typically, around 1000 particles with an aggregate weight of about 0.2 mg are trapped during each collision (Figure 2-3).

Figure 2-3 Ball-powder-ball collision of powder mixture during mechanical alloying[Wiechert, W., 2000].

The force of the impact plastically deforms the powder particles leading to work hardening and fracture. The new surfaces created enable the particles to weld together and this may lead to an increase in particle size. Since, in the early stages of milling, the particles are soft (if we use either ductile-ductile or ductile-brittle material combination), their tendency to weld together and form large particles is high. A broad range of particle sizes develops, with some as large as three times bigger than the starting particles. The composite particles at this stage have a characteristic layered structure consisting of various combinations of the starting constituents. With continued deformation, the particles get work hardened and fractured by a fatigue failure mechanism and/or by the fragmentation of fragile flakes [Fecht, H.-J., 1995]. Fragments generated by this mechanism may continue to reduce in size in the absence of strong agglomerating forces. At this stage, the tendency to fracture predominates over cold welding. Due to the continued impact of grinding balls, the structure of the particles is steadily refined, but the particle size continues to be the same. Consequently, the inter-layer spacing decreases and the number of layers in a particle increase.

However, it should be remembered that the efficiency of particle size reduction is very low, about 0.1% in a conventional ball mill. The efficiency may be somewhat higher in high-energy ball milling processes, but is still less than 1%. The remaining energy is lost mostly in the form of heat, but a small amount is also utilized in the elastic and plastic deformation of the powder particles.

After milling for a certain length of time, steady-state equilibrium is attained when a balance is achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average

composite particle size. Smaller particles are able to withstand deformation without fracturing and tend to be welded into larger pieces, with an overall tendency to drive both very fine and very large particles towards an intermediate size. At this stage each particle contains substantially all of the starting ingredients, in the proportion they were mixed together and the particles reach saturation hardness due to the accumulation of strain energy. The particle size distribution at this stage is narrow, because particles larger than average are reduced in size at the same rate that fragments smaller than average grow through agglomeration of smaller particles (Figure 2-4).

Figure 2-4 Narrow particle size distribution caused by tendency of small particles to weld together and large particles to fracture under steady-state conditions [Lee, PY., et al., 1998].

From the foregoing it is clear that during MA, heavy deformation is introduced into the particles. This is manifested by the presence of a variety of crystal defects such as dislocations, vacancies, stacking faults, and increased number of grain boundaries. The presence of this defect structure enhances the diffusivity of solute elements into the matrix. Further, the refined microstructural features decrease the

diffusion distances. Additionally, the slight rise in temperature during milling further aids the diffusion behavior, and consequently, true alloying takes place amongst the constituent elements.

The specific times required to develop a given structure in any system would be a function of the initial particle size and characteristics of the ingredients as well as the specific equipment used for conducting the MA operation and the operating parameters of the equipment. But, in most of the cases, the rate of refinement of the internal structure (particle size, crystallite size, lamellar spacing, etc.) is roughly logarithmic with processing time and therefore the size of the starting particles is relatively unimportant. In a few minutes to an hour, the lamellar spacing usually becomes small and the crystallite (or grain) size is refined to nanometer dimensions (Figure 2-5). The ease with which nanostructured materials can be synthesized is one reason why MA has been extensively employed to produce nanocrystalline materials.

Figure 2-5 Refinement of particle and grain sizes with milling time. Rate of refinement increases with higher milling energy, ball-to-powder weight ratio, lower temperature, etc.

2.2.4 Formation of Nanostructure by Mechanical Alloying

Nanocrystalline materials have been synthesized by a number of techniques starting from the vapor phase (e.g., inert gas condensation), liquid phase (e.g., electrodeposition, rapid solidification), and solid state (e.g., mechanical attrition). The advantage of using MA for the synthesis of nanocrystalline materials lies in its ability to produce bulk quantities of material in the solid state using simple equipment and at room temperature. The first report of synthesis of a nanostructured material by MA is by Thompson and Politis in 1987 [Thompson, J. R., et al., 1987]. Koch [Koch, C. C., 1993] has summarized the results on the synthesis and structure of nanocrystalline materials produced by mechanical attrition [Koch, C. C., 1997].

Basically, it has been found that the elemental processes leading to grain size refinement include three stages (Figure 2-6):

Figure 2-6 Nanocrystalline structures emerge by high-energy impacts of particles[Fecht, H. J., 1995].

(i) Initially, the deformation is localized in shear bands consisting of an array of dislocations with high density.

(ii) At a certain strain level, these dislocations annihilate and recombine to form small angle grain boundaries. The subgrains formed via this route are already in the nanometer size range with diameters often between 20 and 30 nm. During further attrition the sample volume exhibiting small grains extends throughout the entire specimen.

(iii) The orientations of the each grain with respect to their neighboring grains become completely random. Probably superplastic deformation processes such as grain boundary sliding cause this self-organization into a random nanocrystalline state.

2.2.5 Formation of Solid Solution by Mechanical Alloying

Mechanically alloyed powders exhibit extension of equilibrium solid solubility limits. In addition to synthesizing stable (equilibrium) solid solutions, it has also been possible to synthesize metastable (non-equilibrium) supersaturated solid solutions by MA starting from blended elemental powders in several binary and higher order systems [Suryanarayana, C., 2001]. It was also suggested that the enhanced solid solubility might be due to the high dislocation density produced during milling [Eckert, J., et al., 1993]. Diffusion is aided by the increased defect density and a local rise in temperature. The combination of these effects would permit sufficient diffusion to occur in the interfacial regions of the nanocrystalline grains to form solid solutions. It was suggested that the formation of supersaturated solid solutions is closely related to the formation of nanocrystalline phases [Suryanarayana, C., 1990]. The large volume fraction of atoms in the grain boundaries in these materials is expected to

enhance diffusion and consequently the solid solubility levels in these types of systems. In a nanocrystalline structure, there is an increase in the grain boundary volume. Further, the diffusivity of the component atoms is increased due to the large amount of structural defects and the local stresses in such a material. Under these conditions, the solute atoms substitute the solvent atoms in the grain boundaries and vice versa. The rapid diffusion of atoms from one grain into the other leads to quick homogenization and results in the formation of solid solutions.

2.3 Thermal Stability of Nanocrystalline Materials

2.3.1 Grain Growth in Nanocrystalline Materials

Grain growth in nanocrystalline materials is primarily driven by the excess energy stored in the grain or interphase boundaries. Grain growth studies have been carried out for various nanostructured materials (NsM) using TEM [Hoefer, H.J., et al., 1990; Ganapathi, S.K., et al., 1991; Boylan, K., et al., 1991; Malow, T. R., et al., 1997], DSC [Chen, L. C., et al., 1988] and X-ray diffraction [Malow, T. R., et al., 1997]. The materials studied were prepared by crystallizing glasses [Jiang, J. Z., 1997], sliding wear [Ganapathi, S.K., et al., 1991], inert gas condensation [Hoefer, H.J., et al., 1990; Kumpmann, A., et al., 1993;], electrodeposition [Erb, U., 1995; Iordache, M. C., et al., 1999], and mechanical milling [Cao, Peng., et al., 2001; Gao, Z., et al., 1993]. Studies of the grain growth process in NsM produced by the crystallization of glasses have the attractive feature that pore-free nanocrystalline materials are obtained. Obviously, the synthesis of NsM by crystallization of glasses

is limited to the specific chemical compositions that permit the preparation of the glassy state, e.g. by rapidly cooling, by a sol–gel process, etc. Moreover, only those glasses are suitable for grain growth studies in NsM that convert the glassy phase directly into a crystalline phase of the same chemical composition. For example, a stable tetragonal (Fe, Co)Zr₂ phase forms directly from the ternary Fe–Co–Zr amorphous phase, while in the binary amorphous Fe–Zr alloys, a metastable f.c.c. FeZr₂ phase first forms that later transforms to the equilibrium tetragonal FeZr₂ phase. Grain growth studies performed for both the stable and metastable phases have showed that the grain size increases with annealing time for both cases [Spasov, T., et al., 1993]. It has also been noted that grain growth starts at a low temperature in the nanocrystalline sample with smaller grains [Liu, K., W., et al., 2001] and that grain growth is rapid above a certain temperature and becomes negligible for longer annealing times.

Analogous to the growth of cells in soap froths, the boundaries move toward their centers of curvature and the rate of movement varies with the amount of curvature. The driving force for grain boundary migration in high-purity, single-phase materials, arises from its curvature. A classical theory for grain growth proposed by J. E. Burke [Burke, J. E., 1949] deduces that the growth rate is related to $D(t)$ the average grain size at any instant t by,

$$\frac{dD(t)}{dt} = \frac{\alpha}{D(t)} \quad (2-1)$$

where, α is a temperature dependent rate constant. Integrating Eqn. 2-1 gives the ideal parabolic law for grain growth,

$$D^2(t) - D^2(0) = kt \quad (2-2)$$

where, $D(0)$ is the initial average grain size at $t = 0$ and $k = 2\alpha$. Such ideal behavior is rarely observed experimentally and thus a generalized power law of the form,

$$D^n(t) - D^n(0) = kt \quad (2-3)$$

is often used to quantify grain growth kinetics where n is an empirical exponent. In most of the studies involving nanocrystalline materials, the value of n is different from the value of 2, deduced from the parabolic relationship for grain growth [Burke, J. E., 1949]. Experimental values of n vary between 2 and 4 [Atkinson, H. V., 1988], because other mechanisms, such as pinning of grain boundaries by pores, solute atoms or inclusions, may also be operative. The fact that pores [Hoefler, H.J., et al., 1990; Hahn, H., et al 1990] and impurity doping [Averback, R. S., et al., 1993] have considerable effect on the grain growth characteristics was demonstrated in TiO_2 . For an initial grain size of 14 nm, when the porosity was about 25%, the grain size (after annealing for 20 h at 973K) was 30 nm [Hahn, H., et al 1990]. When the porosity was reduced to about 10%, the grain size for a similar annealing treatment was dramatically increased to 500 nm.

In general, n seems to change during grain growth and tends toward the ideal value of 2 as is found in high-purity materials or at high annealing temperatures. The values obtained for n from grain growth measurements seem to depend—at least in some systems—on the evaluation of the experimental data. For example, Krill and coworkers [Michels, A., et al., 1998] re-evaluated Marlow and Koch's results [Marlow, T. R., et al., 1996]. Marlow and Koch reported $n=3$, but Krill and co-workers showed that the same measurements can be equally fitted to an impurity drag model with a growth exponent of $n=2$.

Another problem associated with grain growth in nanocrystalline samples containing grain boundary impurities has recently been highlighted [Michels, A., et al., 1999]. During grain growth, the boundary area available to the segregant is reduced. Thus, if all impurity atoms remain in (or close to) the boundaries, their concentration must increase with grain growth which should manifest itself in an enhanced drag force (rather than being independent of grain size as is commonly assumed). Recent measurements using Pd–Zr solid solutions seem to confirm the expected impurity drag enhancement [Michels, A., et al., 1999]. Naturally, in NsM this effect will be enhanced relative to a coarse grained polycrystal due to the large reduction of the boundary area during grain growth.

Abnormal grain growth in NsM has been observed at room temperature or slightly above in some instances, e.g. in Cu, Ag, Pd [Kumpmann, A., et al., 1993; Gertsman, V.Y., et al., 1994] and crystallized metallic glasses of the FINEMET type [Jiang, J. Z., 1997]. Similar to the observation of Hahn et al., Gertsman and Birringer [Gertsman, V.Y., et al., 1994] also noted that grain growth occurs preferentially in the denser materials. Anomalous grain growth has been suggested to be due to: (a) a certain non-uniformity of the grain size distribution in the as-prepared samples (so that the larger grains act as nuclei); and (b) impurity segregation. If the impurity distribution is spatially non-uniform, enhanced grain growth may occur in regions of lowest impurity content. The reason why such abnormal grain growth does not occur in many coarse-grained polycrystalline materials has been attributed to the enhanced grain boundary enthalpy (leading to high driving forces) and/or non-equilibrium grain boundary structures (leading to increased mobility of grain boundaries) in the nanocrystalline materials.

In the case of materials with lower purity and/or alloying with certain solutes, the long-time grain growth shows a stagnation of the growth process which is supposed to be associated with the pinning effect of grain boundaries by second-phase particles, impurities, pores and surfaces. Burke [Burke, J. E., 1949] took this drag effect into account by introducing a growth-retarding term μ into Eqn. 2-1. The amended equation given in Eqn. 2-4 is, in effect, amounts to having a constant pinning force for grain growth.

$$\frac{dD(t)}{dt} = \frac{\alpha}{D(t)} - \mu \quad (2-4)$$

As $t \rightarrow \infty$, the grain growth rate reaches zero for some value of the average grain size $D(\infty) = D_{\max}$. Thus,

$$D_{\max} = \alpha/\mu \quad (2-5)$$

Substituting for μ from Eqn. 2-5 into Eqn. 2-4, and solving with the initial condition $D(t) = D(0)$ gives,

$$\frac{k}{D_{\max}^2} t = \frac{D(0) - D(t)}{D_{\max}} + \ln \left(\frac{D_{\max} - D(0)}{D_{\max} - D(t)} \right) \quad (2-6)$$

where $k = \alpha$. This is called the “grain growth model with impediment”.

Recently, Michels et al [Michels, A., et al, 1999] have proposed a modification to Eqn. 2-6 that is specifically suitable for NC materials with segregating solutes, especially in specimens which are in a highly non-equilibrium state. In such systems, the grain boundary segregation of solute atoms increases rapidly when the grains grow leading to an increase in the drag force. This effect may be incorporated into Eqn. 2-6 by assuming grain growth retarding force to increase linearly with grain size, such that

$$\frac{dD(t)}{dt} = \frac{a}{D(t)} - \mu D(t) \quad (2-7)$$

Solving Eqn. 2-7 gives

$$D(t) = \sqrt{\frac{a}{\mu} + \left(D^2(0) - \frac{a}{\mu} \exp(-2\mu t) \right)} \quad (2-8)$$

As $t \rightarrow \infty$, the grain growth rate reaches zero for some value of the average grain size

$D(\infty) = D_{\max}$. Thus, solving Eqn 2-7 gives $D_{\max} = \sqrt{\frac{a}{\mu}}$, and Eqn. 2-8 can be expressed

as

$$\frac{D^2(t) - D_{\max}^2}{D^2(0) - D_{\max}^2} = \exp\left[-\frac{2kt}{D_{\max}^2}\right] \quad (2-9)$$

The rate constant k is given in the units nm^2s^{-1} , and it can be expressed in the Arrhenius form,

$$k = k_0 \exp\{-Q/RT\} \quad (2-10)$$

where R is the gas constant, T is absolute temperature, k_0 is a constant and Q the activation energy for grain growth.

The nano-materials produced by MA are often characterized by a large quantity of impurities which are introduced from either the milling materials (Fe, Cr, or ceramic materials) or the milling atmosphere (mainly O_2 and N_2 contaminations). It has been reported that the Fe contamination is about 18 at. % during the synthesis of NiAl from Ni and Al powder blends when stainless steel media are used [Murty, B. S., et al., 1996]. Impurities are known to retard grain growth by means of two mechanisms: first, segregated impurities induce a “solute drag” on the movement of the grain boundaries [Cahn, J. W., 1962]; second, grain boundary segregation reduces

the specific grain boundary energy and thereby the driving force for grain growth [Hondros, E. and Seah, M., 1983]. In view of the important influence of solute/impurities on grain growth kinetics, Michels' equation has been employed in this study to analyze the grain growth kinetics.

2.3.2 Stability against Grain Growth

Several reports on nano-grained materials by repeatedly MA have showed promising thermal stability that may be related to the grain boundary segregation of solute atoms and/or dispersoid particles [Koch, C. C., 1993]. As for the thermal stability of intermetallics, Isonishi and Okazaki [Isonishi, K. et al, 1993] reported that in nanocrystalline NbAl₃ prepared by MA grain growth occurs only in a temperature range from 1048 to 1173 K and ceases at 1273 K regardless of annealing time.

Several approaches have been proposed for preventing grain growth. One aim is to slow down the growth kinetics by reducing the driving force (the grain boundary free energy) or the grain boundary mobility. In these cases the material remains in an unstable state where small local rearrangements of the grain boundary planes can reduce the material's free energy, but the time interval and temperature required for significant grain growth to take place are increased. The second type of stabilization aims at achieving a truly metastable state where each small variation of the total grain boundary area increases the free energy of the material. In this case a large energy barrier has to be overcome, e.g. by thermal activation, in order to start the evolution towards the equilibrium state, the single crystal.

Second phases act as pinning sites for grain boundaries in essentially the same way as do pores during sintering: the total free energy of a segment of boundary intersecting a second phase is reduced by the product of the cross-section of the phase and the specific boundary free energy. Zener (quoted by Smith [Smith, C. S., 1948]) derived a relation between the stable grain radius R and the second phase radius r and its volume fraction f : $R/r \approx 3/4f$. This relationship implies that if a fine dispersion of small phases can be generated, then small volume fractions of phase can stabilize a microstructure to a very fine grain size. In the stable microstructure the location of each boundary corresponds to a local energy minimum, and the material is therefore in a metastable state. When the temperature is increased, grain growth will remain suppressed until the second phases dissolve in the matrix or until they become mobile. A number of experimental investigations of this effect are reviewed in Refs [Weissmuller, J., 1996; Handwerker, C. A., et al, 1989]. Retarded grain growth will also result from solute drag effects. In many solid solutions, solute atoms are known to segregate to the boundaries forming a solute cloud in the vicinity of the boundary.

If the boundary migrates, three mechanisms may operate depending on the relative rates of boundary and solute-cloud mobilities.

- If the boundary migrates slowly, it drags its solute cloud along with it, thus reducing the boundary mobility and, hence, grain growth.
- If the boundary migrates very fast, it breaks away from the solute atoms and moves freely.
- At intermediate migration rates, the boundary breaks loose locally from its cloud and this impurity-free segment bulges out. The resulting

increase of the boundary area reduces the rate of motion of the impurity-free boundary segment and permits the impurity cloud to be formed again (“jerky motion”).

All three modes of boundary motion have been observed experimentally in coarse-grained polycrystals [Gleiter, H., 1972]. The first two cases are likely to occur in NsM as well. In fact, pinning of the grain boundaries in nanocrystalline Ni solid by the Ni_3P precipitates in a crystallized Ni–P amorphous alloy [Boylan, K., et al., 1991] and segregation of Si to grain boundaries in a Ni–Si solid solution [Knauth, P., et al 1993] have been found to be responsible for preventing grain growth in nanocrystalline phases. In addition to the kinetic factors discussed so far, energetic considerations may also affect the growth rate of the crystallites in NsM. For example, Lu [Lu, K., 1993] studied the thermal stability of 7–48 nm grains in a Ni–P alloy and concluded that samples with smaller grain sizes have enhanced thermal stabilities, suggesting that the grain growth temperatures and the activation energy for growth in a nanocrystalline solid are higher in comparison with coarser grains. This is attributed to the configuration and the energetic state of the interfaces in the nanocrystalline materials.

Grain boundary segregation means concentration in the core of the grain boundary differs considerably from the concentration in the interior of the crystals. Therefore, the grain boundaries are enriched or depleted in solute depending on the segregation pattern. This can have two beneficial effects on the stability of the microstructure. The first effect is solute drag and was discussed in the previous paragraph. The second effect is a reduction of the driving force for grain growth.

Reduction in grain boundary energy means that grains are very stable. They will not want to grow. This will decrease the driving force for grain growth. If the driving force for grain growth is small, kinetics will be low. According to the Gibbs adsorption equation [Gibbs, J. W., 1928], the grain boundary free energy decreases when solute segregates to the boundary. Experimental evidence shows that the decrease can be substantial [Hondros, E. D., 1983], and the theory indicates that in alloy systems with a large atomic size mismatch, the grain boundary free energy may even be reduced to zero [Weissmueller, J., 1993; Weissmuller, Jorg., 1994; Krill, C. E., et al., 1995]. As a consequence of the solute enrichment at the grain boundaries and of the large specific grain boundary area, theory and experiment [Weissmueller, J., et al., 1992; Terwilliger, C. D., et al., 1995] show that nanocrystalline materials also have an enhanced overall solubility for solute with a large heat of segregation.

The potential existence of alloy systems with a vanishing grain boundary free energy has led to speculations on the existence of a metastable nanocrystalline state in which grain growth requires that the nucleation barrier for the formation of a second phase be overcome by thermal activation [Weissmueller, J., 1993; Weissmuller, Jorg., 1994; Krill, C. E., et al., 1995]. While there is as yet no definite experimental proof of the existence of a metastable nanocrystalline state, there are a number of experimental observations that favor its existence. Y–Fe is an alloy system with a large atomic size difference, suggesting a large enthalpy of grain boundary segregation. In Y–Fe alloys (prepared by inert gas condensation) Fe segregates to the grain boundaries [Weissmueller, J., et al., 1992;]. In agreement with the theoretical predictions, the grain size of the alloy samples decreases as the alloy concentration is enhanced, and reaches values as small as 2 nm. Although alloys with a low Fe molar fraction, χ_{Fe} ,

undergo grain growth upon annealing, alloys with higher χ_{Fe} show little grain growth before the equilibrium phase YFe_2 nucleates, indicating that energetic factors are responsible for the suppression of growth. The grain size of mechanically alloyed Pd–Zr solid solutions has also been found to decrease with increasing solute concentration, and the heat release upon annealing indicates that solute (Zr) segregates to the grain boundaries, thereby reducing the specific grain boundary energy and impeding grain growth [Krill, C. E., et al., 1995]. It has also been demonstrated that alloying ceramic nanometer-sized particles results in a drastic change in the grain size and density, with a substantially lower grain size in the densely sintered body [Terwilliger, C. D., et al., 1994]. Finally, the existence of stable liquid microstructures with a nanometer-scale structure and a large number of internal interfaces, the microemulsions, lends support to the expectation that solid microstructures can also be stabilized against growth at very fine grain sizes and elevated temperatures.

In NsM consisting of nanometer-sized crystallites of TiN embedded in an amorphous Si_3N_4 matrix, the rate of crystal growth was observed to decrease with increasing crystal size [Veprek, S., et al., 1999]. In fact, if the crystal size was about 1 nm no measurable crystal growth occurred at temperatures below 1473 K (which is about 80% of the decomposition temperature). If the crystal size was about 10 nm, the grain growth started at 1073 K. The physical reasons for this “inverse” grain growth kinetics are not yet fully understood [Veprek, S., et al., 1999], but some attempt has been made in terms of the high cohesive energy of the amorphous/crystalline interface.

2.4 Consolidation of Nanocrystalline Materials

Consolidation of the milled powders into bulk, full density compacts while retaining the nanoscale grain size is a major challenge for practical applications of nanophase materials. Magnetic permeability of loose powders and compacts that are not fully dense are dependent on geometry and porosity. Low values of initial permeabilities in non-optimally compacted materials are believed to be due to residual porosity. Since the permeability of a magnetic core is reduced as a result of air pockets, then the loss factor is reduced proportionally.

Consolidation of milled powders is therefore an important step for reliable and reproducible determination of the magnetic/mechanical properties of the fabricated materials and is required for most industrial application. Consolidation of the ball milled powders into bulk, full density compacts while retaining nanoscale grain size is a major challenge. Many sintering techniques, e.g., hot pressing, hot extrusion, sintering-forging, and hot isostatic pressing have been employed to consolidate the mechanically alloyed powders. An attractive technique that has been used for consolidation of several metallic and ceramics powders is spark plasma sintering (SPS). In recent times researchers have used SPS for preparing bulk, fully dense nanocrystalline materials, using the mechanical alloying method as a source of the nanocrystalline powders [Ryu, Jong Ryol., et al., 2000]. In this consolidation technique, the sintering procedure takes place in a very short time (consolidation is achieved within 5 min). Hence, grain growth during sintering can be minimized and the sintered powders may maintain their unique nanocrystalline properties.

2.4.1 Consolidation Characteristics of Nanocrystalline Powders

Addressed below are specific densification issues related to the nanocrystalline nature of the particulates that affect the thermodynamics and kinetics of the atomic processes involved in densification. The very fine grain size leads to observed anomalies in transport processes (e.g., reduced electro- and thermal conductivity) since the grain size becomes comparable to the characteristic length of the transfer processes. Also, various mass transport mechanisms responsible for sintering (e. g., grain boundary diffusion) exhibit a particle size dependence that may vary from one transport mechanism to another. Similarly, short diffusion distances will inherently enhance processing kinetics, as well as increase the rate of grain growth. Finally, significant changes in the densification processing mechanisms are expected based on the inability to generate dislocations in nanometer scale crystals. It is accepted that dislocations may be generated by Frank-Read sources only in nanocrystals that exceed a certain grain size (in the order of tens of nm) [Grvaznov, V. G., et al., 1991]. Below this size, no dislocation plasticity is possible. This leads to difficulties in applying deformation-assisted techniques for densification of nanocrystalline materials. However, at this minimal grain size, other deformation mechanisms such as grain boundary sliding and diffusion may become active.

- **Thermodynamic and kinetic effects**

The free energy of nanocrystalline materials is strongly increased due to the enhanced contribution to the interfacial energy. This additional free energy provides

not only a higher driving force for processes such as sintering and grain growth, but also modifies the equilibrium phases.

Significantly enhanced kinetics is expected for processes that display direct grain size dependence. For sintering, this dependence may be calculated using the equation for the densification rate (dL/Ldt) developed by Johnson and co-workers for all stages of sintering [Johnson, D. Lynn., et al., 1992]:

$$-\frac{dL}{Ldt} = \frac{\gamma\Omega}{kT} \left(\frac{\delta D_b \Gamma_b}{d^4} + \frac{D_v \Gamma_v}{d^3} \right) \quad (2-11)$$

where L is the density, γ is the surface energy, Ω is the atomic volume, kT has the usual meaning, δ is the grain boundary width, D_b and D_v are the grain boundary and bulk diffusivities, Γ_b and Γ_v are functions of density and d is the grain size. From this equation, it is seen that decreasing grain size by three orders of magnitude (e.g., from μm to nm) could enhance sintering rates by up to 12 orders of magnitude. Consequently, the onset of sintering is consistently reported to be significantly lower in nanoparticulate materials as compared to conventional micron grained materials as shown in the example for ZrO_2 in Figure 2-7 [Skandan, G., 1995].

Figure 2-7 Comparison of sintering onset in nanocrystalline and conventional ZrO_2 [Skandan, G., 1995]

- **Pressure effects**

As already mentioned, the classical time-temperature-pressure trade-off for sintering brings distinct advantages to the densification of nanocrystalline materials by further lowering final temperatures with the benefit of suppressing grain growth. Pressure application during sintering is known to achieve full densification of some nanocrystalline powders with minimal grain growth. One such example is given by Hahn who sintered nanocrystalline TiO_2 to its theoretical density at 723-823 K ($0.35 T_m$) applying 1 GPa with no grain growth [Hahn, H., 1993]. In addition, pressure is a convenient solution to the exaggerated grain coarsening problem at densities above 90%. For the same final density (91%), sinter-forging nanocrystalline TiO_2 retained a grain size of 87 nm, while pressureless sintering resulted in a grain size of 400 nm [Mayo, M.J., et al., 1993].

The degree of densification that can be achieved is directly related to the point (elapsed time) in the process at which pressure is applied. As already known, large pores are unlikely to collapse even at very high pressures when the temperature is “low”. However, under pressure when some elevated temperature is reached, densification is much easier. If the pressure is applied after heating, there is less resistance to deformation. For instance, Schwarz et al. achieved full density and retained fine grain size (44nm) in mechanically alloyed Al_3CuZr using a hot forging technique with pressure applied only when the system achieved sintering temperature [Schwarz, R.B., et al., 1992].

2.4.2 Spark Plasma Sintering (SPS)

Usual processes for powder densification involve sintering, hot pressing, or hot isostatic pressing. A major problem with these techniques is that the time required for consolidation at high temperature is long, and coarse microstructures are inevitably formed. An additional problem arises when reactive materials that require protective atmospheres are consolidated. Further, long times for processing by conventional consolidation methods are not desirable from the point of view of manufacturing and cost-effective productivity.

The SPS process, in addition to sintering, could be an “in-situ” cleaning method that can create pure materials that are rapidly densified to high densities. SPS is the sintering technique that generates plasma between individual particles of the material to be sintered. With the application of an adequate pressure to the material and utilizing the activated particle surfaces caused by the plasma rapid sintering is achieved. The plasma is generated by instantaneous electric pulsed-powder application control with high current and adequate voltage settings.

There are several advantages that accrue from using SPS as a consolidation method. Firstly, the resistance heating of particles significantly shortens the high temperature exposure that is essential to achieve sintering. The reason why SPS can sinter parts with the short sintering time is that the plasma environment created by electrical discharge causes the removal of surface oxides on the particles. Consequently, concentration of heat occurs, and possibly, an activation of the particle surface and a rapid neck formation. In the next stage, intense heat is produced at the

inter-particle contact zone as direct current flows through the particle. Therefore, the rapid heating rate in SPS is achieved by the combination of plasma generation and resistance heating, which is favorable for hindering surface diffusion process resulting in minimized grain growth. In addition, the electrical energy that is supplied in combination with mechanical pressure contributes to very short actual consolidation times thereby preventing the formation of coarse microstructure. Secondly, the discharge plasma that is generated among powder particles confers a significant surface cleaning ability that leads to enhanced particle sinterability. In contrast to powder metallurgy techniques that can offer only protection against oxidation, SPS leads to consolidation of powders concomitant with the removal of previously formed surface oxides or absorbed gases.

A schematic diagram of the SPS process is shown in Figure 2-8, in which a vertical single-axis pressurization mechanism, a special power supply, a water-cooled vacuum chamber, and a cooling water control are shown.

Figure 2-8 Schematic diagram of spark plasma sintering process [Jung,Y.G., et al., 2002]

A typical profile of temperature and pressure used in SPS is shown in Figure 2-9. During stage 1, the pressure is applied and increased to a predetermined value steadily and maintained throughout stage 2 and 3. At stage 2, the pulse discharge is initiated resulting some minor heating and plasma formation as the particle surface is activated. At stage 3, the pulse plasma is removed, and resistance heating is started. The pressure and resistance heating are gradually removed in stage 4.

Figure 2-9 A schematic of the profile of process variables pressure, temperature and density in SPS [Jung, Y.G., et al., 2002].

2.4.3 Consolidation Mechanisms in SPS

Since the SPS technology is new, only limited experimental data on the SPS consolidation is available. At this stage of scientific development, it is only clear that the accelerated SPS densification is due to some combination of electrical discharge, resistance heating, and pressure application effects. In electrical discharge, energy emission is concentrated at particle contacts that attain high temperature. These concentrated heat effects at particle surfaces may cause surface melting and oxide breakdown, similar to surface effects in electrodischarge machining. This first step of the SPS process may be partially regarded as an activation of particle surface or an “in-situ” cleaning action of powder particles by the removal of surface oxides and adsorbed gases. The elimination of surface oxides is important for two reasons. Firstly, the newly cleaned and activated surfaces contribute to enhanced diffusion. Secondly, for many materials the oxide film on particle boundaries in consolidated material may have deleterious effects on their physical and mechanical properties. This in-situ cleaning action becomes more important for oxygen sensitive powders for which protection from oxygen contamination in early stages of powder preparation is practically impossible [Yamazaki, K., 1996]. In some other applications of pulse electrical current, such as for thermosynthesis of chemical compounds, an enhanced reaction has also been observed [Omori, M., 2000]. This enhanced reaction rate has been confirmed in SPS consolidation of several metallic and ceramic powders. The intensification of the reaction rate in SPS may be also attributed to the breakage of the oxide films on the surface of reacting powders. The next step in the SPS consolidation is the resistance heating. Generally, resistance heating is known to cause full densification by a liquid sintering mechanism. It is assumed that local surface melting

occurs due to higher electrical resistance of surface oxides. However, even for a normal sintering process (using conventional furnace heating), the microstructural characteristics shown to support the liquid formation are not always convincing. Moreover, in the SPS process the prior plasma activation step removes surface oxides and melting due to higher electrical resistance of surface films is less likely to occur.

- **Temperature uniformity and sample size limitation**

Both the maximum temperature achieved and the time that the sample is exposed to it are important for the sintering. It was reported that the hottest parts in graphite tooling are the upper and lower punches [Salamon, D., et al., 2007]. Besides, a temperature gradient is also present between punches and cylinder, but it is very small (giving difference in temperature of about 10 °C). Therefore, the sample height is an important variable in sintering. The shorter the sample, the lesser is the sample surface that is in contact with the relatively colder cylindrical part, and therefore, the larger the surface in contact with the hotter punch part. In order to achieve a temperature variation within 10 °C, the sample height in this project will be controlled to be less than 5mm. This is in agreement with the recommendation in the tool manual.

2.5 Magnetic Properties and Materials

2.5.1 Magnetic Domains

An atom can be regarded as a positively charged nucleus surrounded by electrons that not only move around the nucleus in definite orbits, but also spin on their own axes. It has been found that magnetism is associated almost entirely with this spinning motion of the electrons in the third shell of the atomic structure. Here, then, is the similarity between permanent magnets and electromagnets. The spinning motion of the electrons is the same as the electrons moving through a coil of wire. The effect is the same as what Faraday found: magnetic field is produced by charges in motion or by an electric current. In most materials there is an identical number of electrons spinning in one direction as in the other since the polarity of the magnetic field is determined by the direction of the electron spin, the equal numbers of opposite magnetic fields cancel each other out, and there is no magnetic field produced. The peculiarity of a ferromagnetic material is that there are more electrons spinning in one direction than in the other as seen in the list of transition metals (Figure 2-10).

Atomic number	Element	Electronic structure of 3d	Moment (μ_B)
21	Sc		1
22	Ti		2
23	V		3
24	Cr		5
25	Mn		5
26	Fe		4
27	Co		3
28	Ni		2
29	Cu		0

= electronic spin orientation

Figure 2-10 The electronic structure of the 3d orbital for transition metals. Unpaired electrons contribute to the magnetic nature of these metals [Jiles, D., 1991].

Each atom then is a small electromagnet. We now see the basic building block of all magnetism, namely the atomic magnet, which, because of the direction of electron spin, has a magnetic moment. We need only enlarge the picture of the atomic magnet to see how a ferromagnetic material produces magnetic flux. The idealized picture is one where all the atoms are so arranged that the electrons spin in the same direction. In this case, all of the atomic magnetic moments will also be in the same direction and their magnetic forces will be combined. A magnetized piece then derives its magnetism from the coordinated circular spin of the electric charges in the third shell of the atom. We need only find how it is possible to align the elemental magnets and we will have the complete story.

Our discussion so far has neglected one important factor – the kinetic theory of matter. According to this well-established theory, atoms are constantly vibrating and rotating. The higher the temperature of the material, the higher will be the kinetic energy of the atoms; that is, they will be vibrating more vigorously. If each atom of our magnet were to act independent of its neighbor, the atoms would be vibrating and rotating with so much energy that it would require an external large magnetizing force to align these particles. Such a force would have to be far greater than anything we can produce. Therefore, it is necessary that some internal force be present to restrict the independent action of the atoms. Such a force does exist in some elements, and accounts for the difference between magnetic and non-magnetic materials. This electrostatic force, called exchange interaction, maintains neighboring groups of atoms parallel against the forces of thermal agitation. It can then be seen why a material becomes non-magnetic when it is heated above its Curie temperature. The additional heat provides enough atomic thermal agitation to overcome the

constraining forces of exchange interaction, and it is no longer possible to maintain the atomic alignment. It would be ideal if this exchange interaction would align all the atoms in the magnet, in which case tremendously strong permanent magnets would result. However, such is not the case.

Figure 2-11 Origin of Domains [Kittel, Charles., 1949].

The existence of domains is a consequence of energy minimization (Figure 2-11). A single domain specimen is associated with a large magnetostatic energy, but the breakup of the magnetization into localized regions (domains), providing for flux closure at the ends of the specimen, reducing the magnetostatic energy. Provided that the decrease in magnetostatic energy is greater than the energy needed to form magnetic domain walls, multi-domain specimens will arise. The subdivision process may be expected to continue until the energy required to establish an additional boundary layer or interface, separating two domains magnetized oppositely, is greater than the reduction in magnetic field energy consequent on the finer subdivision. It

may be appreciated that a boundary layer does indeed have a certain amount of energy associated with it: on opposite sides of the boundary the magnetization is directed in anti-parallel directions; now since the exchange forces favor parallel and oppose anti-parallel orientations of the magnetization, they will naturally require the expenditure of energy to establish a boundary layer. In these limited volumes, called domains, all the atomic moments are aligned, and the domain is magnetically saturated at all times. The concept of a domain is the most significant factor in understanding magnetism, as it represents the practical building block of magnets. A magnetic material is saturated magnetically at all times. In the unmagnetized condition, the domains are not randomly oriented, and internal flux paths exist; no field exists outside the magnet.

When a magnetizing field is applied, it is only necessary to control the orientation of the domains to control the potential energy of the magnet. More precisely, the external magnetizing field changes the balance of the much larger internal energies of the magnetic system. (This is similar, in a sense, to the case where a relatively small current controls large values of power in an electrical circuit.) External work is required to orient the domains and magnetize the piece. It is important to recognize that a like amount of external work is required to demagnetize the piece. Once magnetized, a piece will stay that way until external energy is applied. We have seen that the distinguishing feature of ferromagnetic materials is the presence of an internal force that holds groups of atoms parallel, forming domains. Where two domains come together, the change in direction of magnetization does not occur abruptly, but extends over hundreds of atomic planes forming "domain boundaries." This is shown schematically in Figure 2-12 [Kittel, Charles., 1949]. The reason for the gradual nature of the change is the fact that for a given total change of

spin direction the exchange energy is lower when the change is distributed over many spins than when the change occurs abruptly.

Figure 2-12 Reversal of magnetization between adjacent domains does not occur abruptly, but extends through the thickness of the boundary or will result in separating the two domains[Kittel, Charles., 1949].

Between the domains, atomic magnets are progressively rotated, becoming less stable. It can be readily seen that these intermediate areas will be easily affected by an external field, since less energy is required to change their magnetization. Magnetization consists of: (1) stretching the domain boundaries, (2) growth of those domains oriented in the same direction as the applied field, (3) rotation of the domains against its normal direction of magnetization. This is shown in simplified form in Figure 2-13, with the corresponding effect of magnetization of the material plotted against magnetizing force. At first, the effect is to stretch the domain boundaries, which causes only a slight magnetization of the piece. This initial magnetization is reversible; the domain boundaries will return to their original position if the field is removed. As the intensity is increased, the boundaries move and those domains more closely aligned with the field grow at the expense of the unfavorably aligned ones. This is accompanied by a sharp increase in irreversible magnetization. Finally, the

domains are rotated, or forced, to align with the applied field. This creates only a slight increase in magnetization; when the field is removed, the domains will rotate back to their preferred direction. The boundaries of soft magnetic materials must be made easy to move in response to low fields, whereas the boundaries of permanent magnets must be made difficult to move so they will resist demagnetizing fields.

Figure 2-13 The effect of magnetization on domains.

2.5.2 Magnetic Properties Derived from a Hysteresis Loop

When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the imposed magnetizing field is removed. It must be driven back to zero by a field in the opposite direction. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called a hysteresis loop, as shown in Figure 2-14. The lack of retraceability of the magnetization curve is the property called hysteresis and it is related to the existence

of magnetic domains in the material. Once the magnetic domains are reoriented, it takes some energy to turn them back again.

Figure 2-14 Schematic of a hysteresis curve for a magnetic material defining some technical magnetic parameters.

The B-H plot (Figure 2-14) for a ferromagnetic material indicates substantial utility for engineering applications. A large rise in B occurs during initial magnetization (shown by the dashed line). The magnetic permeability, μ , of a particular material is defined as the ratio of flux density to field strength within it. The initial permeability (μ_i) is the slope of tangent to the dashed line from the zero point. The induction reaches a large saturation value (B_s =Saturation Induction) upon

application of sufficient field strength. Much of that induction is retained upon removal of the field (B_r = Remanent Induction). A coercive field (H_c = Coercivity) is required to reduce the induction to zero. By cycling the field strength through the range indicated, the B-H plot continuously follows the path shown by the solid line. This is known as a hysteresis loop.

2.5.3 Soft Magnetic Nanocrystalline Materials

The discovery of nanocrystalline Fe-based soft magnetic materials was about twenty years ago. The first class of such materials was the melt-spun Fe-Si-B alloys containing small amounts of Nb and Cu [Yoshizawa, Y., et al. 1988]. The Fe-Si-B-Nb-Cu amorphous phase transforms to a body-centered cubic (bcc) Fe-Si solid solution with grain sizes of about 10 nm during annealing at temperatures above the crystallization temperature. The presence of small amounts of Cu helps increase the nucleation rate of the bcc phase while Nb retards the grain growth. These "Finemet" alloys provide low core losses (even lower than amorphous soft magnetic alloys such as Co-Fe-Si-B), exhibit saturation induction of about 1.2 T, and exhibit very good properties at high frequencies, comparable to the best Co-based amorphous alloys. These were first developed in Japan and have stimulated a large amount of research and development worldwide to optimize the magnetic properties [McHenry, M.E., et al., 1999].

While many of the soft magnetic properties of Finemet-type nanocrystalline alloys are superior, they exhibit lower saturation inductions than Fe-metalloid amorphous alloys, mainly because of the lower Fe content to attain amorphization and

because of the addition of Nb and Cu (or other elements to control the nucleation and growth kinetics). In order to remedy this problem, another class of Fe-based nanocrystalline alloys was developed. These "Nanoperm" alloys are based on the Fe-M-B (M=Zr) system; they contain larger concentrations of Fe (83-89 at.%) compared to the Finemet alloys (~ 74 at.% Fe) and have higher values of saturation induction (~ 1.6-1.7 T). The Nanoperm nanocrystalline alloys have very low energy losses at power frequencies of (60 Hz), making them potentially interesting for electrical power distribution transformers. Figure 2-15 [Makino, A., et al., 1995] compares the soft magnetic properties of Finemet, Nanoperm, and other materials.

Figure 2-15 Effective permeability, μ_e , vs. saturation magnetic flux density, B_s , for soft ferromagnetic materials (after A. Makino, et al., 1995).

2.5.3.1 Magnetism of Nanocrystalline Soft Magnets

Approaches to improving intrinsic and extrinsic soft ferromagnetic properties involve (a) tailoring chemistry and (b) optimizing the microstructure. Significant in microstructural control has been recognized that a measure of the magnetic hardness (the coercivity, H_c) is roughly inversely proportional to the grain size (D_g) for grain sizes exceeding $\sim 0.1\text{--}1\text{ }\mu\text{m}$ (where the D_g exceeds the domain (Bloch) wall thickness, δ_w). Here grain boundaries act as impediments to domain wall motion, and thus fine-grained materials are usually magnetically harder than large grain materials. Significant recent development in the understanding of magnetic coercivity mechanisms has led to the realization that for very small grain sizes $D_g < \sim 100\text{ nm}$, [Herzer, G., 1997], H_c decreases rapidly with decreasing grain size, as shown in Figure 2-16. This can be explained by the fact that the domain wall, whose thickness, δ_w , exceeds the grain size, now samples several grains and fluctuations in magnetic anisotropy at the grain size length scale are irrelevant to domain wall pinning. This concept of random anisotropy suggests that nanocrystalline and amorphous alloys have significant potential as soft magnetic materials.

Figure 2-16 Herzer [1997] diagram of coercivity, H_c , dependence on grain size.

Random anisotropy [Alben, R., Budnick, J., et al 1978; Alben, R., Beck, J. J., et al, 1978] has been realized in a variety of amorphous and nanocrystalline ferromagnets as illustrated in Figure 2-15. It shows two important figures of merit for soft magnetic materials, magnetic permeability, and their inductions. Combined high permeabilities and magnetic inductions are seen for amorphous Fe- and Co-based magnets with more recent improvements in the envelope occurring with the development of nanocrystalline alloys FINEMET, NANOPERM and HITPERM. The last of these combines high permeabilities, large inductions with the potential for high temperature application due to the high Curie temperature of the α' -FeCo nanocrystalline phase. Typical attributes of nanocrystalline ferromagnetic materials produced by an amorphous precursor route are summarized in Table 2-1.

Table 2-1 Attributes of nanocrystalline ferromagnetic materials produced by an amorphous precursor route [McHenry, Michael E., 1999].

Typical composition	Nanocrystalline phase	B _s (T)	T _c (K)
Fe _{73.5} Si _{13.5} B ₉ Nb ₃ Cu ₁	<i>b.c.c.-FeSi, DO3-FeSi</i>	1.0-1.2	<1043
Fe ₈₈ Zr ₇ B ₄ Cu	<i>b.c.c.-FeSi</i>	1.5-1.8	1043
Fe ₄₄ Co ₄₄ Zr ₇ Cu	<i>b.c.c.-FeCo, B2-FeCo</i>	1.6-2.1	>1238

The basis for the random anisotropy model is illustrated in Figure 2-17. The concept of a magnetic exchange length and its relationship to the domain wall width and monodomain size is important in the consideration of magnetic anisotropy in nanocrystalline soft magnetic materials. The Herzer argument considers N grains, with random crystallographic easy axes, within a volume of L^3_{ex} , to be exchange coupled. Herzer's prediction illustrates that the coercivity should grow as the sixth power of the grain size [Herzer, G., 1990]:

$$H_c \sim H_K \sim D^6 \quad (2-12)$$

Figure 2-17 Cartoon illustrating N nanocrystalline grains of dimension D in a volume L_{ex}^3 .
[Herzer, G., 1990]

2.5.3.2 Potential Applications for Nanocrystalline Soft Magnets

Recent developments of nanocrystalline magnetic materials have initiated numerous activities for the development of advanced magnetic devices for energy transfer, for high-power and miniature electro motors, for medical applications and for the sensor and magnetic recording industry. Most of the progress achieved so far has been due to the discovery of new materials with extremely small (0.1 J/m^3) or extremely large magnetocrystalline anisotropy (10^7 J/m^3), as well as the tailoring of high coercivities, H_c , which are determined by the microstructure and vary from 0.1 A/m to several MA/m . Further progress in these fields is possible if we succeed to develop materials with optimal property spectra where magnetic, electrical, mechanical, corrosive and thermal properties are optimized simultaneously.

2.6 Motivation for Studying Nanocrystalline Fe-Si

- **Discovery of iron alloyed with silicon for transformer cores**

During the latter half of the nineteenth century considerable research on magnetic materials had been carried out, and measurement techniques became well established. Many properties of wrought iron, steels, nickel, cobalt, and even some nickel-iron alloys were determined, and it is to be regretted that the full import of the results was not realized.

In the early 1900s the first major improvement in materials for transformers took place when Sir Robert Hadfield introduced iron alloyed with silicon that gave higher permeabilities and appreciably less loss than earlier steels. Various percentages of silicon were utilized and the alloys were sold under a variety of trade names. These were produced from hot-rolled sheets and had isotropic properties. Strain-relieving annealing was sometimes employed, and various coatings were used to reduce eddy current losses.

These sheets were used in the form of butt lapped strips for the magnetic cores or power transformers and had only about half of the previous iron losses. The most popular alloy was 3-4% Si in Fe. Larger contents of silicon were investigated and Si contents up to 7% were found to have superior magnetic properties, but the material was brittle and could not be easily machined or stamped.

- **Grain-oriented silicon iron**

Silicon irons with a number of improvements were utilized for transformers until the late 1930s when a breakthrough occurred due to the introduction of grain oriented silicon iron. This was the important invention of N. P. Goss, who termed the product Goss iron [Richardson, B., 1986].

This was achieved by altering the silicon content in the steel, cold rolling the strip to the desired thickness, followed by high-temperature annealing at 1200°C to evolve secondary recrystallization. Large grains were produced, oriented in the rolling direction resulting in greatly improved magnetic properties along the strip. More loss, however, arose across the strip, and this led to considerable research on methods of utilizing as far as possible constructions where the flux went along the grains. Obviously toroids here had a big advantage, and subsequently C cores and E cores were introduced, particularly for small transformers.

While improvements were taking place prior to the 1960s such as making thinner Goss material to reduce eddy currents, research was continuing to produce better steels. Japan came to the forefront and patented their Hi-B Steel that is extensively used today. Here larger grains are evolved and a small tensile stress is imparted to the steel by using a glass surface coating applied at high temperature and resulting in reduced electrical loss.

- **Fe-Si binary system**

In the Fe-rich region the Fe(Si) solid solution has several structures. The fcc solid solution γ -phase is stable from 1183 to 1665 K and has a maximum solubility of 3.8 at% Si, see Fig. 2-18 [Kubaschewski, 1982]. Beyond the γ -phase there are disordered *bcc* α -iron (A2) and the ordered structures α_2 (B2) and α_1 (DO₃). The ferromagnetic-paramagnetic transition line (dash-dot) slopes downwards from pure Fe at 1043 K to the solvus line with maximum solubility of 25 at% Si at $T \approx 793$ K. There are four compounds: β -Fe₂Si, η -Fe₅Si₃, ϵ -FeSi, β -FeSi₂ or ξ_β and α -FeSi₂ or ξ_α . The β -FeSi₂ phase is almost a line compound and there is no wide range of nonstoichiometry. The ϵ -phases FeSi (cubic B20 structure) extends from about 49.0 to 50.8 at.% Si (at 1423 K). Three phases (Fe₂Si, FeSi and ξ_α) melt congruently. The composition of the high-temperature tetragonal ξ_α -phase is close to stoichiometry of Fe₂Si₅ alloy and it is metallic. Low-temperature (below 1258 K) modification of the FeSi₂, orthorhombic β -phase, is a semiconductor.

- **Amorphous magnetic alloys**

Metals and alloys are usually found in the crystallized state with long range order, on the other hand amorphous metallic alloys can also be produced with no long range atomic order, which are also called glassy alloys or non-crystalline alloys. Such a structure can be obtained by rapid solidification from the gas or liquid phases by various processes including melt spinning and splat quenching [McHenry, M. E., et al., 1999]. The amorphous structure can result in unique magnetic, mechanical,

electrical and corrosion resistant behavior. The main classes of magnetic amorphous alloys include: transition metal-metalloid (TM-M) alloys, rare earth-transition metal (RE-TM) alloys and transition metal-zirconium or hafnium alloys.

Figure 2-18 Phase diagram of the Fe-Si system according to Kubaschewski [Kubaschewski, 1982].

The typical composition of magnetic TM-M alloys is 80 atom percent of iron, cobalt or nickel with the remainder being boron, carbon, silicon, phosphorus or aluminum. The additive elements lower the melting point and make it possible to form the amorphous phase. The lack of long range order determines many of the properties of the metallic glass. From a thermodynamic point of view, they are in a metastable state [Buschow, K. H. J., 1985]; they are topologically and chemically isotropic and homogeneous; and the average distance between nearest neighbors is slightly larger than in crystals. This kind of structure is responsible for their unique electrical, thermal, mechanical and magnetic properties. For the magnetic properties, the net magnetic moment decreases due to the addition of nonmetals, the dilution of the transition metals and modifications to the local environment of the magnetic moment carriers [Graham, C. D., 1980]. The saturation magnetization of amorphous alloys is found to be lower than those of the usual crystalline compounds. This is due to the high nonmetal content rather than the amorphous nature. The effective magnetic moment of a metallic glass can be either slightly higher or lower than that of the crystalline alloy with the same composition. [[Graham, C. D., 1980]].

- **Nanocrystalline Fe(Si) soft magnetic materials**

The Fe-Si-B-Nb-Cu amorphous phase transforms to a body-centered cubic (bcc) Fe-Si solid solution with grain sizes of about 10 nm during annealing at temperatures above the crystallization temperature [Yoshizawa, Y., et al. 1988]. The presence of small amounts of Cu helps increase the nucleation rate of the bcc phase while Nb retards the grain growth. Nanocrystallites were considered as an array of

randomly distributed crystals with near neighbor exchange and random directions of the magnetocrystalline anisotropy for each grain [[McHenry, Michael E., 1999]. The nanocrystalline crystals are exchange coupled across an amorphous matrix. These nanocrystallites have no orientation relationship with the matrix and, therefore, the magnetocrystalline anisotropy of each crystal has a set of easy axes that are independent of the neighboring crystals.

However, it is not easy to produce bulk magnetic materials in NC form by conventional metal processing techniques. One option the industry uses is to form an amorphous ribbon by rapid solidification, and then control annealing to nucleate the nanocrystals of a specific phase [McHenry, Michael E., 1999]. Another is to mechano-synthesize in a high-energy ball mill to produce NC alloy powders from the elemental powders [Koch, C. C., 1993]. The ball milling process leaves the powder in a state of internal strain and thus stress relaxation by annealing is also a necessary processing step. In either option, therefore, subsequent high temperature processing of the NC material is inevitable and, thus, the material must be resistant to grain coarsening that could result in the loss of the advantageous properties. When designing alloys, one must take into account both the processing and the service requirements. This is clear in the design of magnetic alloys for rapid solidification, where specific alloying elements are added to aid the amorphisation during solidification, and some others are added for nucleation of the nanocrystals during subsequent annealing [McHenry, Michael E., 1999]. The additions required for good magnetic performance could be quite different to those required for the processing. Similar alloy design principles may have to be used when designing magnetic alloys

to be produced by the mechanosynthesis route. The alloy design requirements may be framed in the form of the following questions:

- i. What elements aid the breakdown of the crystals rapidly to NC levels?
- ii. What elements control the growth of the nanocrystals during subsequent high temperature processing?
- iii. What elements enhance the magnetic performance of the material?
- iv. How do elements added for each purpose interfere with other requirements?

Since, modern magnetic materials are very complex alloys, it was decided to make some preliminary investigations on the effects of three elements on design requirements (i) and (ii) above, individually, in a simple Fe-Si binary system. The conventional Fe-Si soft magnetic alloy, besides being a simple system, is commercially used in laminated sheet form in large tonnages. Hence, Fe and Si in the base binary alloy satisfy the requirement (iii). The requirement (iv) needs more work to be done and will not be discussed in this report. The ternary additions to Fe-Si chosen in this study, Al, Cu and Nb, are frequently used in the commercial Fe-based amorphous magnetic alloys. One specific base material composition, namely $\text{Fe}_{75}\text{Si}_{25}$, was chosen for the study. New alloys were made by replacing 10at% of Si in the base alloy by Al, Cu or Nb.

3 EXPERIMENTAL PROCEDURES

3.1 High-Energy Ball Milling

The milling was performed in a planetary mill (Pulverisette 5) manufactured by Fritsch GmbH in Germany. To prevent oxidation and contamination during mechanical alloying, the process was performed in an argon atmosphere. For grinding under protective gas, lids with two valves were used. After filling the grinding bowl with grinding balls and the raw material, the lid was put on with a seal. The grinding bowls were inserted and clamped in the grinding bowl holder. The gas hose was connected to argon gas supply with the aid of an attached hose clip. The de-airing fitting was screwed onto one of the two valves. The coupling of the gas hose was fitted onto the free valve. The inert gas feed was slowly opened and the de-airing fitting was pressed so that the air could escape from the grinding bowl. The flushing period was 1 minute as recommended in the manual. After flushing, the inert gas feed was closed and the de-airing fitting was released. The de-airing fitting was unscrewed and the coupling of the gas hose was pulled off. The hood was locked and the mill was run at the preselected speed of 300 revolutions per minute.

Elemental powders (see details in Appendix C) were blended in atomic ratio corresponding to respective compositions in a blender before they were milled. Each starting powder charge of 41.6g was combined with fifty 10 mm diameter tempered steel (1-1.65 wt.% Cr, Fe) milling balls in a powder:ball mass ratio of 1:5. Milled powder specimens were discharged from the mill at selected intervals for analysis. The total milling time was 100 h, interrupted for 4 min every 10 min, in order to minimize excessive temperature rise and to limit adherence of powders to vial walls.

3.2 Annealing of As-Milled Powders

The as-milled powder specimens were transferred to ceramic boats and annealed in a furnace under a vacuum of 1×10^{-5} Pa at various temperatures for different times to study the thermal stability of the alloys. The heating rate for the treatment was 10 K/min. After heat treatment, the heater was turned off, but the vacuum was sustained until the furnace cooled down to room temperature.

3.3 Consolidation of As-Milled Powders

3.3.1 Conventional Cold Compaction and Vacuum Sintering

For conventional cold compaction and vacuum sintering, powders were mixed with 2 wt.% stearic acid as a lubricant and pre-cold compacted in a ring shaped die (outer diameter of 17mm and inner diameter of 11mm) with an uniaxial pressure of 350MPa, as shown in Figure 3-1. The obtained tablets with relative green densities of about 50% and approximately 3 mm in thickness were then sintered in a furnace under a vacuum of 10^{-5} torr at various temperatures in the range 1333-1513 K for 1h. Before heating to that temperature, the furnace was maintained at 723K for 30 min to volatilize the stearic acid. After heat treatment, the heater was turned off, and the samples were cooled under vacuum.

Figure 3-1 A sketch of the die for cold pressing of ring-shaped preform. The left-hand side represents the situation at the starting and the right at the final stage of the deformation process.

3.3.2 Spark Plasma Sintering (SPS)

The Sumitomo Coal Mining (SCM) SPS system Dr Sinter[®] Model 1050 was used for SPS. Powders (~2 g) were placed in a ring shape graphite die (outer diameter of 17mm and inner diameter of 11mm), and the die was placed between the lower and upper electrodes as shown in Figure 3-2. The electrodes apply pressure to the punches while conducting the current. Through application of voltage the powder particles get charged and discharged generating a spark in the space between the particles leading to a high temperature spark discharge/plasma momentarily. The SPS features a very high thermal efficiency because of the direct heating of the sintering graphite mold and stacked powder materials by the large spark pulse current.

Figure 3-2. A schematic diagram of SPS system

Figure 3-3 A schematic of the profile of process variables pressure, temperature and density in SPS.

A typical profile of temperature and pressure used in SPS is shown in Figure 3-3. The SPS system was evacuated to a pressure of 5 Pa, and then an electric current applied through the graphite die. During stage 1, the pressure is applied and increased to 50MPa steadily and maintained throughout stage 2 and 3. At stage 2, the pulse discharge is initiated resulting in some minor heating and plasma formation as the particle surface is activated. It consisted of 30 s pulsed electrical discharge (25 V and 750 A) followed by rapid heating. At stage 3, the pulse plasma is removed, and resistance heating is started to increase the temperature at heating rate 200 K/min to 1103K-1243K and hold for 5 minutes. The actual densification took place during this resistance-sintering step when the high DC current was applied. After soaking the powder at a desired temperature for 5 min, the applied current was reduced, the pressure released, and the specimen cooled down to room temperature in stage 4. After the samples were prepared, density was obtained by measuring the weight and volume of the samples.

3.4 Characterization of As-Milled Powders

3.4.1 Powder Morphology Characterization

Scanning electron microscopy (JSM 5410LV SEM) with accelerating voltage of 20kV was employed to study the particle morphology evolution during ball milling. In order to avoid electron charge build up, ball milled powder samples were scattered on a conductive double-adhesive tape, pasted onto a holder with the other side, and the whole surface of the SEM holder was covered by these tapes to avoid charging.

3.4.2 Characterization of Crystal Size and Structure

3.4.2.1 Characterization by Transmission Electron Microscopy (TEM)

Analyses of grain size and crystal structure were performed using a JEOL 2000 Transmission Electron Microscope with an accelerating voltage of 200kV (wavelength of the electron beam equal to 0.00251 nm). The specimens were prepared by embedding the powders in an epoxy at a powder: epoxy volume ratio of about 1:2, followed by gentle heating and hardening of the resin at 393 K for 15min. Then the powder/resin mixture was dropped into a copper tube, and the tube was cut into pieces of copper ring, manually ground on SiC papers to 100 μm thickness, then dimpled with 3 μm diamond paste to a thickness of 15 μm at the center, and finally ion-milled to perforation.

3.4.2.2 Characterization by Optical Microscopy

The sintered samples were cut cross-sectionally into pieces of 3 mm thickness and mounted on epoxy resin sample holders. These were then first polished mechanically down to a finest carborandum paper (1 μm). After polishing, the specimen was etched with a solution of 10 cm^3 HNO_3 to 90 cm^3 water for about 10 sec, which is essentially an etchant for Fe-Si alloys, and then rinsed in distilled water followed by in ethanol.

The average grain size was determined by observing the etched samples under an Olympus optical microscope the LECO 2001 software. The grain size was estimated using a linear intercept method. Straight lines all the same length are drawn

through several photomicrographs that show the grain structure. The grains intersected by each line segment are counted. The line length is then divided by an average of the number of grains intersected (typically >5), taken over all the line segments. The average grain diameter is found by dividing this result by the linear magnification of the photomicrographs.

3.4.2.3 Characterization by X-ray Diffraction Analysis (XRD)

The powder specimens were analyzed by a Shimadzu X-ray diffractometer, with Cu K α radiation ($\lambda=0.154056$ nm). The diffractometer was operated at 40 kV and 40 mA. The powder was compacted onto a piece of glass holder by pressing the surface with a piece of glass to make the surface smooth and avoid the formation of texture. In order to obtain precise measurements of peak position and half maximum width, a slow scan rate of 0.01 degree/sec and 0.01 degree/step were employed.

3.4.2.3.1 Grain Size and Internal Strain

X-ray diffraction line profiles obtained in a diffractometer are broadened due to instrumental and physical (crystallite size and lattice strains) factors. Therefore, the first indispensable step preparatory to the determination of crystallite size and lattice strain from the recorded XRD scan is determination of the “pure” diffraction line profile for a given reflection whose width depends solely on the physical factors. This “pure” line profile is extracted by removing (deconvoluting) the instrumental broadening factor from the experimental line profile. Only then can the “pure” line profile be used for determining the crystallite size and lattice strain. Simple equations

or graphs based on line profiles of assumed analytical forms can be used for the instrumental broadening correction. In the present work, the instrumental broadening-corrected "pure" line profile breadth of each reflection was calculated from the parabolic approximation correction [Klug, H. P., et al., 1974]:

$$\delta(2\theta) = B \left(1 - \frac{b^2}{B^2} \right) \text{ (rad)} \quad (3-1)$$

where B and b are the widths (in radians) of the same Bragg peak from the XRD scans of the experimental and reference powders, respectively. The reference powder was the same powder of Fe annealed at 1073 K for 24 h to eliminate any broadening due to small crystallite and internal strain. Both B and b were determined by the computer software Origin from the full-widths at half maximum (FWHM) after automatic background removal and $K\alpha$ stripping.

The method was based on the assumption that the crystallite size and strain line profiles are both Cauchy and the appropriate equation for the separation of crystallite size and strain takes the following form [Klug, H. P., et al., 1974]:

$$\delta(2\theta) \cos \theta_o = \frac{0.9\lambda}{L} + 4e \sin \theta_o \quad (3-2)$$

where θ_o is the position of the analyzed peak maximum, λ the X-ray wave length, L the crystallite size and e the "maximum" strain. Any available orders of a given reflection may be used to construct a linear plot of $\sin \theta_o$ against $\delta(2\theta) \cos \theta_o$. The crystallite size L can then be obtained from the intercept and the strain e from the slope. Eq. (3-2) was first proposed by Williamson and Hall [Williamson, G.K., et al., 1953] and is customarily referred to as the "Williamson-Hall method" [Gayle, F. W., et al., 1995; Szenczak, E., et al., 1997].

3.4.2.3.2 Lattice Parameter

It is important to obtain the precise lattice parameter of the Fe-rich phase to understand the dissolution process during mechanical alloying. Some researchers [Farquar, M. C., et al., 1945] have previously measured the lattice parameter of the solid solution of Si in Fe. They concluded that the lattice parameter of the Fe phase decreases with increasing Si content. The smaller atomic size of the Si in comparison with the Fe is responsible for the decrease of the lattice parameter with increase of Si concentration. Therefore, if the lattice parameter of the crystal of the Fe-rich phase decreases during milling process, it would then suggest that Si is dissolving in Fe.

For a crystal of cubic system, the lattice constant “*a*” can be measured from each peak in the spectra using the standard equation.

$$a = \frac{\lambda}{2} \frac{\sqrt{h^2 + k^2 + l^2}}{\sin \theta} \quad (3-3)$$

where,

θ : Bragg Angle

λ : X-ray Wavelength

h, k, l : Miller Indices

Cullity [Cullity, B. D., 1978] reported that the largest single source of error in diffractometers is the displacement of the specimen from the diffractometer axis. The error can be written

$$\frac{\Delta a}{a} = -\frac{D \cos^2 \theta}{R \sin \theta} \quad (3-4)$$

where D is the specimen displacement parallel to the reflecting-plane normal and R is the diffractometer radius. This function is not truly linear in $\cos^2\theta/\sin\theta$, but for $\theta > 60^\circ$ it is sufficiently linear to justify a straight-line extrapolation procedure.

In order to determine the lattice parameter of the iron-rich phase in the powder samples, they were scanned by X-ray diffraction. The lattice parameters of Fe peaks, 15 h, 25 h, 40 h, 60 h, 80 h, 100 h samples were measured. By multiplying the d_{hkl} by $\sqrt{h^2 + k^2 + l^2}$ the lattice parameter is obtained. Then the lattice parameter (y-axis) is plotted against $\cos^2\theta/\sin\theta$ (x-axis) and extrapolated to obtain the intercept on the y-axis. This is the precise lattice parameter. Detailed calculations are described in Section 4.1.2.1.

3.4.2.3.3 Long Range Ordering

The relative long-range order parameter, LRO , was determined by a comparison of the relative intensities of superlattice—fundamental pairs of peaks of the ball-milled powders (assumed to be partially disordered) with respect to the homogenized reference specimen, according to the equation given by Bakker et al. [Bakker, H., et al., 1995]

$$LRO = \sqrt{\frac{(I_S/I_F)_{dis}}{(I_S/I_F)_{hr}}} \quad (3-5)$$

where $(I_S/I_F)_{dis}$ and $(I_S/I_F)_{hr}$ are the intensities of the superlattice reflection taken relative to the fundamental line for the disordered (dis) and homogenized reference (hr) powder, respectively.

3.5 Magnetic Property Measurements

Magnetic property measurements were carried out with an AMH-20 Soft Hysteresisgrapher under a maximum applied field of about 3000 A/m. Figure 3-4 and Figure 3-5 show the system and typical configuration for measuring the hysteresis loop of magnetically soft materials. The system consists of a magnetizing power source, an exciting current controller, an electronic flux integrator, and a data recorder. A ring shape specimen is wound with an exciting winding (the primary) and a search coil (the secondary) for measuring the change in flux. When an exciting current, I , is applied to the primary winding, a magnetic field, H , is produced in the coil, and this in turn produces magnetic flux in the specimen. In uniform specimens, such as ring samples, all of the exciting current is used to magnetize the specimen, and H is proportional to I in accordance with the following equation:

$$H = \frac{\pi N_p I}{2.5L} \quad (3-6)$$

where N_p = 10 is the number of primary turns, I = 10A is the primary current, L is the path length in cm,

$$L = \pi \cdot \frac{Ln \frac{Do}{Di}}{\frac{1}{Di} - \frac{1}{Do}} \quad (3-7)$$

where Do and Di are the outer and inner diameter of the ring. Then the total flux B induced in the test sample by the driving magnetic field is obtained from the output voltage from the secondary coils. The system plots the B-H curve based on the above relationship. The frequency used for this study was 0.01 Hz, which is typical for DC magnetic property measurement. All the measurements were carried out according to ASTM A773 standard:

- 1) Before beginning the test, thicknesses, outer and inner diameters of the specimen were measured using micrometer.
- 2) There was a minimum warm-up period of 10 min for all apparatus and instrumentation.
- 3) Connect the specimen.
- 4) Before test, demagnetize the specimen through the coil by establishing a magnetic field strength sufficiently large to reach a point well above the knee of the magnetization curve. Then, while continuously cycling the magnetization, slowly reduce the magnetizing current to zero.

Figure 3-4 AMH-20 hysteresisgraph system.

Figure 3-5 Typical configuration for measuring the hysteresis loop of magnetically soft materials.

4 RESULTS

4.1 Evolution of Powders during Ball Milling

4.1.1 Particle Morphology Evolution

- Morphology of starting powders

The morphology of the initial Fe, Si and Al powders is given in Figure 4-1 (a), (b) and (c) respectively. The Fe and Si powder particles have irregular shape. The Al particle morphology is rounded and elongated. Therefore the starting powders of both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ had an irregular morphology and their size distribution was also inhomogeneous.

Figure 4-1 SEM morphology of powders before milling: (a) Fe; (b) Si; (c) Al.

- Particle morphology evolution of $\text{Fe}_{75}\text{Si}_{25}$

Figure 4-2 (a)-(f) show the progressive morphology of the powder particles of $\text{Fe}_{75}\text{Si}_{25}$ after milling for 15–100 h.

Figure 4-2 SEM morphology of $\text{Fe}_{75}\text{Si}_{25}$ powders after milling times of (a) 15h; (b) 25h; (c) 40h; (d) 60h; (e) 80h; (f) 100h.

Scanning electron microscopy shows a wide range of particle sizes present at the early stage of milling, $t < 15$ h, as shown in Fig 4-2 (a). At this stage, the powder particles are deformed or fractured by the compressive forces due to the collision of the balls. The milling time is far too short to achieve a homogenous distribution of particle size and shape.

At the next stage of milling, $25\text{h} < t < 40\text{h}$, as shown in Fig 4-2 (b)-(c), the particles became more uniformly shaped, and large particles were gradually broken into smaller pieces. At this stage, the force due to the collision of balls plastically deforms the particles leading to work hardening. When a certain hardness is achieved the hard particles are fractured by a fatigue failure mechanism and/or by fragmentation, leading to size refinement of particles. Therefore, particle size gradually decreases with the increase of milling time.

At the final stage of milling, $60\text{h} < t < 100\text{h}$, as shown in Fig 4-2 (d)-(f), the presence of a high number of small fragmented particles is clearly observed. Most of the particles were fragmented and refined in size. Further mechanical alloying beyond this stage does not physically refine the particle further.

• **Particle morphology evolution of $\text{Fe}_{75}\text{Si}_{25}\text{Al}_{10}$**

Figure 4-3 show progressive morphology of the powder particles of $\text{Fe}_{75}\text{Si}_{25}\text{Al}_{10}$ after milling for 5–100 h.

Figure 4-3 SEM morphology of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ powders after milling times of (a) 15h; (b) 25h; (c) 40h; (d) 60h; (e) 80h; (f) 100h.

The particle morphology evolution of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ was similar to that of $\text{Fe}_{75}\text{Si}_{25}$. After 15 h of milling, as shown in Fig. 4-3 (a), the powder particles exhibited wide range in size distribution and irregular shapes. With continued deformation, the particles became more refined in size as shown in Fig 4-3 (b). After 40 h of milling most of the particles were fragmented and refined in size. No visible further morphology evolution is observed after 40h of milling, as shown in Fig 4-3 (c), (d), (e) and (f). The Al addition did not show obvious influence on the evolution of particle morphology during milling.

4.1.2 Crystal Structure Evolution

The crystal structure evolution with time was monitored using XRD. The patterns obtained in $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ are given in Figure 4-4 (a) and (b) respectively. All constituents were identified by matching with the JCPDS Database installed in the computer [see Appendix A].

Figure 4-4 X-ray diffraction (XRD) patterns of (a) $\text{Fe}_{75}\text{Si}_{25}$ and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ powders after different milling times (0–100h).

Figure 4-4 shows the powder X-ray diffractograms of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ for different milling times. The X-ray diffraction of the samples for different milling times gave a clear indication of the changes that occur in the material. The powder mixture before milling showed peaks of all the elements but, after 15 h, only the bcc-Fe peaks were exhibited. The Si and Al peaks in both alloys were absent. This shows that there had been no detectable reactions during the milling to produce any intermetallic compounds and that Si and Al have dissolved in the Fe matrix.

The Fe Bragg peaks of both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ were also broadened with milling durations. The width of the Fe peaks increases with increase of milling time indicating the development of refined and internally strained grains. Furthermore, there were measurable shifts in the Bragg angles 2θ indicating lattice parameter changes with milling time, which may be attributed to the dissolution of solute atoms into the Fe matrix.

All these changes of X-ray patterns during milling indicate some structural evolutions during milling, which may be grain size refinement, strain accumulation and formation of solid solutions. The determination of grain size, strain and lattice parameters from the X-ray pattern are described and discussed in the following sections in detail.

4.1.2.1 Determination of Grain Size, Internal Strain and Lattice Parameter from XRD Patterns

- **Determination of grain size and internal strain**

The Williamson-Hall method (Eqn. 3-2.) was used to separate the effects of grain size and strain broadening. According to Eqn. 3-2, $\delta(2\theta)\cos\theta_o = \frac{0.9\lambda}{L} + 4e\sin\theta_o$. Thus, we can construct a linear plot of $\delta(2\theta)\cos\theta_o$ against $\sin\theta_o$, and the grain size L and internal strain e can be determined from the intercept $0.9\lambda/L$ and slope $4e$ respectively. The θ_o is the Bragg angle from the diffractogram. The $\delta(2\theta)$ is the “pure” line profile breadth of each reflection obtained by using Eqn. 3-1, $\delta(2\theta) = B\left(1 - \frac{b^2}{B^2}\right)$, where B and b are the full-widths at half maximum height (FWHM) of the Bragg peaks in XRD scans of the experimental powder and the reference powder respectively. Both B and b are determined by the computer software Origin as schematically shown in Figure 4-5.

Figure 4-5 A schematic diagram of FWHM.

Below is an example of the determination of grain size and internal strain for $\text{Fe}_{75}\text{Si}_{25}$ powder milled for 60 h., whose XRD data is summarized in Table 4-1. The $\sin\theta_0$ and $\cos\theta_0$ are determined from the Bragg angles (θ_0) of the diffractogram. The $\delta(2\theta)$ is determined using Eqn. 3-1. Thus we can plot Figure 4-6, taking $y=\delta(2\theta)\cos\theta_0$ against $x=\sin\theta_0$. A straight line is then fitted through these data points to get the slope and intercept. In accordance with Equation 3-2, we can obtain $\text{slope}=4e=0.0243$ and $\text{intercept}=0.9\lambda/L=0.00965$. We used Cu K_α incident radiation in the XRD for which $\lambda=0.154056$ nm. From these the grain size (L) and internal strain (e) are determined, which gives the strain $e=0.0061$ and mean grain size $L= 14.4$ nm. The grain sizes determined in this manner are average values for the samples. The errors of strain and grain size are determined from the errors of slope (a) and intercept (b) of the fitted line.

Table 4-1 $\delta(2\theta)\cos\theta_0$ and $\sin\theta_0$ calculation according to the Williamson-Hall for $\text{Fe}_{75}\text{Si}_{25}$ powder milled for 60 h

(h k l)	$2\theta_0$	B (degree)	b (degree)	$\delta(2\theta_0)$ (rad)	$\sin\theta_0$	$\delta(2\theta_0)\cos\theta_0$ (rad)
110	45.072	1.18	0.1497	0.01508	0.38326	0.01872
211	83.19	1.97	0.1498	0.01706	0.66386	0.02556
200	65.617	1.6	0.1501	0.02062	0.54183	0.02326
310	117.879	3.376	0.1502	0.02592	0.85662	0.03034
220	100.101	2.54	0.1499	0.03471	0.76661	0.02837

Figure 4-6 Crystallite size/strain separation calculation according to the Williamson-Hall approximation given by Eq. (3-2) using the instrumental broadening-corrected "pure" profile breadth, $\delta(2\theta)$, which also calculated from Eq. (3-1). ($\text{Fe}_{75}\text{Si}_{25}$ powder milled for 60 h).

• **Determination of lattice parameter**

Below is an example for the determination of lattice parameter for $\text{Fe}_{75}\text{Si}_{25}$ powder milled for 60 h. Equation 3-4 shows that the error in lattice parameter $\Delta a \approx 0$ when $\cos^2 \theta / \sin \theta$ approaches 0. Therefore, to determine the lattice parameter accurately, it was calculated for Bragg reflections of planes (110), (211), (200), (310) and (220) and was plotted against $\cos^2 \theta / \sin \theta$. This plot is shown in Figure 4-7. A straight line was fitted to the data points and was extrapolated to $\cos^2 \theta / \sin \theta = 0$. The intercept value of lattice parameter at this point is taken as the true lattice parameter of the sample.

Figure 4-7 Lattice parameter calculation according to the Cullity approximation. ($\text{Fe}_{75}\text{Si}_{25}$ powder milled for 60 h).

4.1.2.2 Evolution of Grain Size, Strain and Lattice Parameter during Milling

- Evolution of grain size

The grain sizes of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ obtained from the Williamson-Hall method are plotted against milling time in Figure 4-8. It is clear that the grain sizes of both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ reduced to approximately 26 and 17 nm respectively after 15 h of milling. The grain size of $\text{Fe}_{75}\text{Si}_{25}$ decreased steadily to about 15 nm after 60 hours and remained unchanged thereafter. In comparison, the grain size of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ reached 17 nm in 15 hours and further decreased to a stable size of about 13 nm in 40 hours.

Figure 4-8 Crystalline size of Fe₇₅Si₂₅ and Fe₇₅Si₁₅Al₁₀ powders as a function of milling time.

- **Evolution of lattice strain**

Figure 4-9 shows that the strain increases sharply to a maximum value at 25 h. After reaching the maximum value, it gradually decreases till 80 h and reaches almost a constant value of about 0.6% at 100 h. During the same period, as shown in Figure 4-8, grain size decreases sharply to some value close to its minimum value. This may be explained by a work hardening and softening mechanism. Deformation and work hardening leads to an increase in deformation dislocation density. This increases the internal strain level. Subsequent softening by rearrangement of the dislocations results in subgrain boundary formation. Continued hardening and softening will increase the mismatch angle of subgrain boundaries, ultimately reaching that of a high angle grain boundary. Grain refinement is achieved by this mechanism where strain is relaxed

during re-ordering of the dislocations into the grain boundaries. This increases the incipient hardness of the material which resists further plastic deformation. Consequently, at some point, further deformation is resisted to prevent grain refinement. Further grain refinement may require increased energy input in the form of higher density of grinding balls, higher speed, etc. This aspect was not investigated in this project.

Figure 4-9 Strain of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ powders as a function of milling time.

- **Lattice parameter evolution during milling**

The lattice parameter of $\text{Fe}_{75}\text{Si}_{25}$ decreased from 0.2866 nm to about 0.2843 nm after 40 h of milling, as shown in Figure 4-10. This could be due to the dissolution of smaller Si atoms, whose atomic radius is 0.118 nm [Tennent, R. M., 1971], into the Fe (0.123 nm) matrix, resulting in a reduction of the lattice parameter. Silicon in the Fe(Si) solid solution is a substitutional solute in Fe solvent [Heikinheimo, E., et al., 1998], therefore the smaller solute Si atoms replace the Fe atoms, causing the

shrinkage of lattice matrix. The lattice parameter decreased with milling time and reached a minimum value of about 0.2843 nm after 60 h of milling, which is much higher than that for 25at.% Fe-Si alloy (0.2827 nm) [Farquar, M. C., et al., 1945]. Based on the relationship of lattice parameter value and solute concentration reported by Farquar, M. C. et al. [Farquar, M. C., et al., 1945], about 17at.% Fe-Si alloy was achieved. It indicates that not all the Si atoms have dissolved into the Fe matrix, and some may have dissolved into the grain boundaries also, which does not contribute to a decrease of lattice parameter. This will be further discussed in Section 5.3.

Figure 4-10 Lattice parameter of powders as a function of milling time.

For Fe₇₅Si₁₅Al₁₀, $t < 15$ h, the lattice parameter increased slightly with milling time. A value of about 0.2871 nm was obtained after ball-milling for about 15 h, which is higher than the initial value of that for Fe. The increase in the lattice parameter clearly shows that Al atoms, with a larger atomic radius of 0.142 nm [Tennent, R. M., 1971], dissolved into Fe lattice, with a smaller atomic radius of 0.123 nm [Tennent, R. M., 1971], as a consequence of a lattice parameter increase. At

the same time Si should also be dissolving into Fe, but the increase of lattice parameter indicates the dissolution of Al is predominant at this initial stage. Si dissolution becomes predominant only during $15\text{h} < t < 40\text{h}$ ball milling. After that, the lattice parameter is pretty stable, indicating the Fe matrix has become saturated with Si and Al.

4.2 Thermal Stabilities at Elevated Temperatures

4.2.1 Effects of Addition of Al on the Thermal Stability of $\text{Fe}_{75}\text{Si}_{25}$

Figure 4-11 shows a plot of grain size against annealing temperature for $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloys annealed for 0.5 h. The nanocrystals in $\text{Fe}_{75}\text{Si}_{25}$ appeared to be stable up to 673 K and thereafter grew rapidly. In comparison, crystals in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ did not grow to any significant extent up to 873 K. Thus, the ternary addition of Al appears to inhibit grain growth compared to the parent binary alloy $\text{Fe}_{75}\text{Si}_{25}$, which is probably due to the segregation of Al atoms in the grain boundary even upon ordering transition. The effect of Al on inhibiting grain growth is discussed in detail later in chapter 5. Annealing at temperatures above 773 K brought about several changes in the structure also. In alloys $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, ordering to DO_3 structure was exhibited by means of the appearance of the superlattice peaks corresponding to DO_3 crystal structures in the X-ray diffractograms shown in Figure 4-12. This will be further discussed in Section 5.3.

Figure 4-11. Plots of grain size against annealing temperatures for the two compositions.

Figure 4-12 X-Ray diffractograms of ball milled and annealed powders of (a) $\text{Fe}_{75}\text{Si}_{25}$, and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$. The annealing temperatures are indicated in the figure. Note the appearance of DO_3 superlattice reflections at 773 K and higher temperatures.

4.2.2 Effects of Addition of Nb on the Thermal Stability of $\text{Fe}_{75}\text{Si}_{25}$

The effect of Al on stabilization of the grain growth discussed in Section 4.2.1 indicates that a third element is able to help inhibit the grain growth of the binary alloy. Based on the study of the evolution of grain structure with milling time of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, we estimate 60 h should be enough to reach the stable nanograin structure. Therefore, we prepared $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ with the same milling condition with a milling time of 60 h. The XRD patterns of as-milled $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ after 60 h of milling as well as after annealing at different temperatures are shown in Figure 4-13.

Figure 4-13 X-ray diffraction (XRD) patterns powders after annealing at different temperatures.

Figure 4-14 The bright field TEM micrograph of a $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ specimen milled for 60h with its SAD pattern in inset. The materials has some isolated crystals in an amorphous matrix.

The X-ray diffractogram of the as-milled $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ powders indicates they were mostly in an amorphous state, and the TEM shown in Figure 4-14 proves this XRD observation. Figure 4-14 shows a predominantly amorphous structure with some isolated nanocrystals. The mechanism of amorphization by MA is believed to be related to the destabilization of the crystalline phase resulting from the accumulation of structural defects such as vacancies, dislocations, grain boundaries, and anti-phase boundaries. Significant atomic size difference between the solvent and solute atoms has been used to explain the amorphization phenomenon by MA [Suryanarayana, C., 2001]. Among Nb (0.142 nm), Al (0.142 nm) and Cu (0.128 nm) atoms, Nb and Al atoms have larger atomic radius difference from Fe atom (0.123 nm) than Cu atom does [Tennent, R. M., 1971]. However, $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy has strong ordering tendency and shows DO_3 ordered structure at equilibrium state [Chang, Y.J., 1982]. It indicates that MA may destabilize its long range ordering, but the strong ordering tendency may play a role to prevent it from turning into full amorphous state. That is probably the reason why only Nb caused amorphous matrix in the as-milled condition compared to Al and Cu addition.

However, as the annealing temperature increases the α -Fe peaks become narrower and increase in intensity, and at 873 K the intermetallic Fe_2Nb was detected. Thus the matrix remains a disordered, super saturated solid solution of Si in α -Fe but Nb precipitates out as an intermetallic. Figure 4-15 shows a plot of α -Fe(Si) grain size against annealing temperature for three alloys annealed for 0.5 h. It shows that crystals in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ did not grow to any significant extent up to 873 K. Grain growth in $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ could not be determined until 773 K although crystallization was detected at 573 K, because peak broadening could not be reliably measured. The

grains in this Nb-containing alloy started to grow at higher temperatures in a manner similar to $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$. However, the precipitates present could make the material a poor soft magnet as they will hinder free movement of domain walls. Thus, they are not desirable in soft magnets [McCurrie, R. A., 1994]. This will be further discussed in Section 5.2.

Figure 4-15. Plot of grain size against annealing temperature for annealing time of 30min for three alloys. The rapid grain growth beyond some temperature is evident.

4.2.3 Effects of Addition of Cu on the Thermal Stability of $\text{Fe}_{75}\text{Si}_{25}$

As shown in Fig. 4-16, $\text{Fe}_{75}\text{Si}_{15}\text{Cu}_{10}$ alloy did not show any ordering transformation either but precipitation of Cu was detected after annealing at 773K even in 0.5 h. As the annealing time increases the α -Fe peaks increase in intensity and become stable after 2 h.

A comparison of grain growth behaviour in Al and Cu containing alloys is made in Figure 4-17 against annealing time at 773 K. It is clear that Al has a better grain

growth inhibiting effect than Cu at this temperature. For soft magnets second phase Cu, which will inhibit domain wall movement, is normally not preferred. Therefore, Cu is not a good addition choice to inhibit grain growth either.

Figure 4-16 X-ray diffraction (XRD) patterns of $\text{Fe}_{75}\text{Si}_{15}\text{Cu}_{10}$ powders after annealing at 773K for different times.

Figure 4-17 Plot of grain size against annealing time at 773K for three alloys.

4.3 Grain Growth Kinetics of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$

4.3.1 Grain Growth and Structural Evolution during Annealing

As shown in Figure 4-11 and Figure 4-12 (a), it seems that the ordering and grain growth happened simultaneously at 773K in $\text{Fe}_{75}\text{Si}_{25}$, which indicates they may be somewhat interrelated. Therefore, the phenomena near 773K were studied in detail to find out the root cause behind this coincidence.

Figure 4-18. Plots of grain size of (a) $\text{Fe}_{75}\text{Si}_{25}$, and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing temperature.

While, in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy, the ordering also happened at 773K, no sharp grain growth was observed. Therefore, the grain growth kinetics of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy were also investigated to understand the mechanism of stabilization in this alloy. In Section 4.1.2.2 it was shown that, during ball milling, Si and Al dissolves in Fe to result in a supersaturated, disordered solid solution. Consequently, only bcc-Fe peaks are evident in the as-milled powder. As the powder is annealed, its peak breadth decreases and peak intensity increases. Extra peaks corresponding to the ordered DO_3 superlattice reflections of planes $(1/2\ 1/2\ 1/2)$, $(1\ 0\ 0)$ and $(3/2\ 1/2\ 1/2)$ appear in the XRD patterns of specimens annealed at 773 K and higher (see Figure 4-12), indicating a transformation to the DO_3 ordered structure. The average grain sizes determined from XRD peak broadening are plotted against the annealing temperatures in Figure 4-18 for each annealing time. For $\text{Fe}_{75}\text{Si}_{25}$ two stages can be identified in this figure: a stage of restrained growth for temperatures lower than about 703 K followed by rapid growth at higher temperatures above 773K. It should be noted that the rapid grain growth at temperatures higher than 773 K is accompanied by the ordering transformation. For $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ the ordering was also observed above 773K, while no sharp grain growth was observed, which indicates that Al may somehow inhibit the grains from growing rapidly.

The internal strain calculated using Eqn. 3-2 is shown in Figure 4-19 as a function of annealing time at different temperatures. It is clear that the internal strain reduces sharply in the first 10 minutes to a stable level from the as-milled value of 0.52%. This stable internal strain steadily decreases with increase of annealing temperature. For $\text{Fe}_{75}\text{Si}_{25}$ the strain decreased fast and can almost be eliminated after

annealing at high temperatures 773K-853K, while the strain in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ released slowly and cannot be completely removed even after annealing at 853K for 4 hours.

Figure 4-19. Plots of internal strain of (a) $\text{Fe}_{75}\text{Si}_{25}$ and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing time.

Figure 4-20 shows plots of lattice parameter against the annealing time for different temperatures. For temperatures in the range 577 – 703 K, a slight decrease is observed. This could be attributed to the relaxation of lattice strain. At the higher temperature range of 773 - 853 K where ordering was observed, the lattice parameters

decreased in a few minutes to about 0.2831 nm and remained unchanged over prolonged annealing. This may be mainly related to the absorption of Si atoms from grain boundaries upon ordering. It was reported that lattice parameter might also be influenced by ordering in several other alloys [Cahn, R.W., 1999]. In the Fe-Si system, the lattice parameter was reported to be related only to Si content, not ordering [Miyazaki, M., 1992]. However, the Si is segregation and desegregation during the order-disorder transformation has an effect on lattice parameter.

Figure 4-20. Plots of lattice parameter of (a) Fe₇₅Si₂₅ and (b) Fe₇₅Si₁₅Al₁₀ versus annealing temperature.

The LRO of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing time is plotted in Figure 4-21. Upon annealing at 773K-853K, the ordering transformation was observed in both alloys, and the $\text{Fe}_{75}\text{Si}_{25}$ alloy is able to achieve a high value of LRO of about 0.9 after annealing for 4 h, while $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ only achieved a lower value of about 0.6 after 10 min annealing and remain unchanged during prolonged annealing.

(a)

(b)

Figure 4-21. Plots of LRO of (a) $\text{Fe}_{75}\text{Si}_{25}$, and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing temperature.

4.3.2 Determination of the Activation Energy of Grain Growth

The grain size $D(t)$ of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ is plotted versus the annealing time t in Fig 4-22. They were fitted with Eqn. 2-9, $\frac{D^2(t) - D_{\max}^2}{D^2(0) - D_{\max}^2} = \exp\left[-\frac{2kt}{D_{\max}^2}\right]$, to obtain the rate constant k . For each temperature the curve was fitted using the grain size of as-milled powders as $D(0)$, which are 14.5 nm and 12.5nm for $\text{Fe}_{75}\text{Si}_{25}$.and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ respectively. The value of $D_{\max}$ was taken as the grain size after annealing for 3.456×10^5 s (96 h), as listed in Table-4-2. It can be seen that the curves fit the data very well in Figure 4-22. The parameter k was obtained from the best fit values and are listed in Table 4-2.

Figure 4-22. A plot of grain size of (a) $\text{Fe}_{75}\text{Si}_{25}$, and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ versus annealing time for the different temperatures. Curves are fitted according to Eqn. (2-9) and the fitting k values are tabulated in Table 4-2.

Table 4-2 Maximum grain size and the growth rate constant for different temperatures computed using Eqn. (2-9).

Temperature(K)	Rate Constant k (nm^2s^{-1})		Maximum Grain Size (nm)	
	$\text{Fe}_{75}\text{Si}_{25}$	$\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$	$\text{Fe}_{75}\text{Si}_{25}$	$\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$
573	0.0079	0.0030	20.2	13.0
623	0.0152	0.0069	21.9	13.6
673	0.0205	0.0082	23.1	15.0
703	0.0295	0.0153	25.0	15.2
773	0.0889	0.0250	55.0	15.8
803	0.3093	0.0312	55.2	17.1
833	1.4896	0.0489	56.5	17.3
853	5.3910	0.0550	61.8	18.0

Figure 4-23. Arrhenius plot of $\ln k$ against $1/T$ for the k values in Table 4-2. The activation energies obtained for the two straight lines are also given. Q_1 and Q_2 are the activation energies for $\text{Fe}_{75}\text{Si}_{25}$, and Q_3 and Q_4 are those for $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$.

With the obtained k values for each temperature, the activation energy for grain growth, Q , could now be determined via Eqn. 2-10, $k = k_0 \exp\{-Q/RT\}$. Figure 4-23 shows plots of $\ln k$ versus $10^4/RT$. The activation energy for grain growth, Q , is determined from the slope of the line.

It is evident that two separate straight lines are required to fit the round shaped points for $\text{Fe}_{75}\text{Si}_{25}$ alloy as shown in Figure 4-23. One line fits the round shaped dots below 703 K and another one above 773 K. The activation energies determined from the slopes of the lines are $Q_1=32.3 \text{ kJ mol}^{-1}$ at the low temperature range, and $Q_2=278.9 \text{ kJ mol}^{-1}$ at the higher range respectively. Different activation energies for grain growth in different temperature regimes have also been reported by other workers also in different systems [Malow, T. R., et al. 1997], which indicates that different mechanisms may control the grain growth in different temperature ranges. In the present case, it must be noted that the ordering transformation occurs in the high temperature regime where higher activation energy for grain growth is obtained. In the low temperature regime ($< 703 \text{ K}$), the grains exhibit a slight relaxation in internal strain and limited grain growth with lower activation energy. In the high temperature regime ($> 773 \text{ K}$), rapid grain growth accompanied by ordering and internal strain substantially relaxes. Desegregation of Si from grain boundaries upon ordering transformation is thought to be the reason for the rapid grain growth in $\text{Fe}_{75}\text{Si}_{25}$. This will be discussed in detail in Section 5.3.

In $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy, transformation to DO_3 structure was observed at a temperature similar to that in $\text{Fe}_{75}\text{Si}_{25}$ alloy. Hence, an attempt was made to fit separate lines for the high temperature and low temperature regimes, as for $\text{Fe}_{75}\text{Si}_{25}$.

These fitted lines are in Figure 4-23. The activation energies measured for grain growth are $Q_3=37.2 \text{ kJ mol}^{-1}$ and $Q_4=57.4 \text{ kJ mol}^{-1}$ for the low temperature and high temperature regimes respectively. The grain growth activation energies of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ for these two temperature regimes are comparable. This may be due to the similar grain growth behaviors of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ in these two temperature regimes. In short, Al addition showed a strong effect on stabilizing the binary alloy against grain growth even after ordering transformation. This may be due to the Al atoms, which can remain segregated in the grain boundaries even when ordering occurred. Thus they were able to continue inhibiting grain growth by the solute drag effect. This will also be discussed in detail in Section 5.3.

In summary, the grain growth activation energy which is an indicator of the grain growth mechanism, was consistent in both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ at low temperatures. The activation energy changed at high temperatures when grain growth behavior changed in $\text{Fe}_{75}\text{Si}_{25}$ but remained almost unchanged in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$.

4.4 Sintering Behavior and Magnetic Properties

4.4.1 Sintering Behavior

- **Vacuum sintering**

Figure 4-24 and Figure 4-25 show the microstructures of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloys sintered at 1333K-1453K for 1h in a vacuum furnace. After sintering, the average grain size increased from about 15nm in the as-milled powders, shown in Section 4.1.2.2, to about 4 -5 μm in the bulk as-sintered sample, hence losing the nanostructure. The grain sizes were estimated by using a linear intercept method with these optical micrographs, as described in Section 3.4.2.2. Since the grain sizes of these vacuum sintered samples are already of micron size, which cannot be determined by XRD line broadening (limited to grain size <100nm), optical microscopy was used to characterize the microstructure of the sintered samples.

The micrographs also show a gradual decrease in porosity with increase in sintering temperatures. The density measurements gave relative densities of about 50-80%, which indicated that the vacuum sintering conditions used in this study were not suitable to achieve high density. Some pores are still open and connected with other pores, indicating incomplete sintering.

In summary, these micrographs showed that conventional vacuum sintering could not achieve high density after sintering at temperatures 1333K-1513K for 1 h for both alloys. Further increase in sintering temperature or sintering time may be able to achieve higher density, but it is not desirable, because the grain size will grow even larger. Therefore conventional vacuum sintering is unable to achieve high density and maintain the nanostructure at the same time for these two alloys.

Figure 4-24. Optical Micrograph of Fe₇₅Si₂₅ alloy after sintering at 1333K(a), 1393K(b), 1453K(c) and 1513K(d) for 1h.

Figure 4-25. Optical Micrograph of Fe₇₅Si₁₅Al₁₀ alloy after sintering at 1333K(a), 1393K(b), 1453K(c) and 1513K(d) for 1h.

• SPS sintering

Optical and TEM micrographs of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ after sintering with SPS at 1243K for 5 min are shown in Figure 4-26 (a) and (b) respectively. The optical micrograph shows a high density with closed pores. The density is much higher than those of vacuum sintered samples shown in Figure 4-25. The relative density of this sample is about 95%. Besides, the grain size is too small to be observed by optical microscopy. Therefore, TEM was used, and Figure 4-26 (b) shows that grains are still in the nano-size range with an average grain size of about 86 nm with a DO_3 structure as shown in the inserted SAD pattern.

Figure 4-26. Optical Microscope (a) and Bright field transmission electron micrograph (b) of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy sintered with SPS at 1243K for 5 min with corresponding selection area diffraction pattern as insert.

Figure 4-27 (a) and (b) show the XRD patterns of the bulk $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloys sintered with SPS at various temperatures, respectively. For both alloys, the powder mixture showed additional DO_3 peaks in the XRD pattern after sintering at all three temperatures, which indicates transformation from the nonequilibrium disordered $\alpha\text{-Fe}(\text{Si})$ to the equilibrium DO_3 structure during sintering.

Besides, the peaks became sharper when the sintering temperature increased, due to the grain growth during sintering. The average grain sizes determined with equation 3-2 are shown in Figure 4-28. The average grain size of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy sintered with SPS at 1243K for 5 min determined by peak broadening analysis is about 88 nm, which agrees well with the direct observation of the microstructure by TEM, shown in Figure 4-26 (b).

(a)

(b)

Figure 4-27. X-Ray diffractograms of $\text{Fe}_{75}\text{Si}_{25}$ (a) and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ (b) after SPS at the various temperatures indicated.

Figure 4-28. Plots of relative density and grain size against sintering temperature for $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ after SPS and conventional sintering.

Figure 4-28 shows the evolution of density and grain size with sintering temperatures for both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$. High densities of 86.1 and 94.6% could be achieved at relatively low sintering temperatures of 1103 K-1243 K by SPS, while conventional sintering can only achieve densities of 64.9% and 82.1% even at the highest temperature of 1513 K. Besides the grains grew to the micron size range. These results again showed the major problem with conventional vacuum sintering techniques that the time required for consolidation at high temperature is too long, and coarse microstructures are therefore inevitably formed.

SPS is more promising for the consolidation of nanostructured powders, which achieved much higher density for both alloys and maintained the grain size to less than 100nm. There are several advantages that accrue from using SPS as a consolidation method. Firstly, the resistance heating of particles significantly shortens the high temperature exposure that is essential to achieve sintering. The reason why SPS can sinter parts with the short sintering time is that the plasma environment created by electrical discharge causes the removal of surface oxides on the particles. In contrast to conventional vacuum sintering techniques that can offer only protection against oxidation, SPS leads to consolidation of powders concomitant with the removal of previously formed surface oxides or absorbed gases. Consequently, concentration of heat occurs, and possibly, an activation of the particle surface and rapid neck formation. In the next stage, intense heat is produced at the inter-particle contact zone as direct current flows through the particles. All these advantages enable SPS to achieve high density while minimizing the grain growth.

4.4.2 Magnetic Properties.

Figure 4-29 shows the hysteresis loops of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloys after sintering at various temperatures. The respective magnetic properties for all the sintered samples are obtained from their loops and plotted against sintering temperatures in Figure 4-30. As shown in Figure 4-29 maximum induction increased with increasing sintering temperature, which may be due the higher relative density achieved at higher sintering temperatures. It is also observed that coercivity did not show too much variation with

sintering temperature, which is mainly dependent on internal microstructure such as grain size and porosity during sintering, indicating that the microstructure did not vary too much for these samples during sintering.

Figure 4-29. Hysteresis loops of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloys after conventional sintering at various temperatures.

The magnetic properties for all the samples are summarized and plotted in the Figure 4-30. The grain size and relative density are also plotted in the figure, which is mainly for the convenience of discussion of the relationship between the magnetic properties and those microstructural properties.

Figure 4-30. Plots of density, grain size, maximum induction, maximum permeability and coercivity of Fe₇₅Si₂₅ and Fe₇₅Si₁₅Al₁₀ against sintering temperatures.

The maximum induction B_{max} showed a similar trend with sintering temperature as that of relative density, which indicates that relative density and maximum induction may be interrelated. It seems that higher sintering temperature leads to high relative density and therefore higher maximum induction. Quantitative analysis of this relationship is discussed later in Section 5.4.

The coercivity H_c appears to show similar trends as that of grain size with sintering temperature. For those SPS samples, the grain sizes of which are below 100nm, the H_c of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ increased with increase of sintering temperature as a result of increase of grain size, while that of $\text{Fe}_{75}\text{Si}_{25}$ almost remained unchanged as a result of constant grain size over this sintering temperature range. For nanostructured soft magnets, the grain size needs to be kept as small as possible to achieve low coercivity. For vacuum sintered samples, where grain sizes are in the micron range, the coercivity is expected to decrease with increase of grain size since $H_c \propto D^{-1}$ [Herzer, G., 1997]. For micron grain size magnetic alloys, bigger grain size is preferred for soft magnetic applications $H_c \propto D^6$. As shown in the figure, the grain sizes of both alloys are comparable and did not change significantly with sintering temperature, therefore the coercivity did not show much variation. However, the coercivity of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ showed lower values for all conventionally sintered samples compared to those of $\text{Fe}_{75}\text{Si}_{25}$, which is probably due to the low magnetic anisotropy constant for this composition [Takahashi, M., 1987]. Then only a small applied field is needed to remove the residual induction in the samples, leading to lower coercivity.

The maximum permeability of SPS samples for both alloys showed small change with increasing sintering temperature. $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ showed increments in permeability from 474 to 563 and from 640 to 813 respectively when the sintering temperature was increased from 1103K to 1243K. However, for conventional sintered samples, the maximum permeability showed much stronger variation with sintering temperature, and even achieved a value of about 1989 in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ after sintering at 1513 K for 1h. This is much higher than the maximum value achieved in the SPS samples of about 813 for the $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy after SPS at

1243 K for 5 min. For powder metallurgy magnets, the magnetic permeability is dependent on many factors such as particle exchange coupling and domain wall movement. For these loose compacts obtained by conventional sintering, the grain size does not change with sintering temperature, so the increase of permeability with sintering temperature should be mainly due to the increase in density, which leads to the increase of exchange coupling between particles and therefore to be more sensitive to applied field, resulting in higher permeabilities. Therefore, the maximum permeability of conventionally sintered samples showed a similar trend versus sintering temperatures as those of relative density. Although the SPS samples have density comparably higher than those of conventionally sintered samples, their permeability seems fairly low. This is probably related to the grain boundary pinning effect, because there are lots of nanograins and therefore many grain boundaries, which are bigger than the so-called exchange length, normally less than 30nm. Hence they are not able to take advantage of the nanostructure. During magnetization, those grain boundaries will pin the movement of domain walls and result in a less sensitive response to the applied magnetic field and lower permeabilities.

5 DISCUSSION

5.1 Formation of Nanocrystalline Solid Solutions during MA

5.1.1 Particle Morphology Evolution

The powder morphology evolutions of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ are very similar, as evident in Figures 4-2 and 4-3. At the initial stage of ball milling, $t < 15$ h, the powder particles of both alloys showed a wide range of size distribution. This may be explained by the different nature of the particles. Soft particles can be easily plastically deformed under compressive loading to become irregular in shape. They could be cold-welded to form larger particles. On the other hand, the hard particles tend to resist the attrition and compressive forces. They may fracture into smaller pieces. Note that a high number of small fragmented particles are also clearly visible. The powder mixture contains both ductile (Fe, Al) and brittle (Si) particles in comparable amounts. The hard particles may resist deformation while the ductile particles tend to deform and bind the hard particles together. At this stage the particles could be inhomogeneous in composition with hard Si particles embedded in the Fe/Al matrix. Further, a wide size distribution is common as the hard particles may be fragmented into a small size while the ductile particles may get agglomerated/cold welded into larger particles. The milling time considered at this stage of milling is too short to achieve chemical homogeneity of particles. A more homogenous distribution is expected when ball-milling duration is increased.

At the next stage of milling, $15\text{h} < t < 40\text{h}$, as shown in Figures 4-2 and 4-3, more and more large particles get broken into smaller fragments with the increase of

milling time. The force of the impact plastically deforms the powder particles leading to repeated work hardening. With the increase of hardness, the particles become easier to be fractured by a fatigue failure mechanism and/or by the fragmentation of brittle powders. On the other hand, the tendency of cold welding is reduced with the increase of milling time as the overall hardness increases. Consequently, considerable refinement and reduction in particle size is evident at this stage of the mechanical alloying process. The increase in milling time leads to disintegration of the agglomerated particles and smaller particle diameters. Moreover, the distribution of particle size became more homogeneous and the particle shape became more spherical. In summary, at this stage, the particles get work hardened, so that the tendency to fracture predominates over that to cold welding. The agglomerated particles were fragmented and refined in size in the absence of strong agglomerating forces. Repeated agglomeration and refining forces the elements to get intimately mixed resulting in alloying.

Finally, for $t > 60\text{h}$, as shown in Figures 4-2 and 4-3, the particle sizes for both alloys were observed to be relatively constant and more uniform in shape. No visible microstructural features are observed. At the completion of the mechanical alloying process, the powder particles possess severely deformed, metastable structure. Further mechanical alloying beyond this stage cannot physically improve the alloy distribution or particle size. Homogeneity of the particle size is an outcome of an equilibrium between fracturing and cold welding.

5.1.2 Grain Refinement and Strain Accumulation

Figure 4-8 and Figure 4-9 showed the grain size and strain evolutions during milling for both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$. The grains of both alloys were refined with milling time and reached constant values at around 60 h. Their strains increased sharply to maximum values at 25 h. After reaching the maximum value, strain gradually decreased till 80 h and reached almost a constant value of about 0.6% at 100 h. The grain size and strain evolution during the milling process can be explained by a phenomenological model [Fecht, H. -J., 1995]:

- I. Initially, due to plastic deformation, a high dislocation density is introduced in the very early stages of the process. The creation and movement of dislocations gives rise to deformation and to an increase in the internal strain.
- II. When a critical strain level is reached locally, softening is initiated to reduce the internal strain energy by forming low-energy dislocation structures, resulting in small-angle boundaries. The original crystallites get subdivided into subgrains of smaller size. For such small grain sizes, plastic deformation occurs predominantly by sliding along the grain boundaries.
- III. Further milling converts the whole material into a collection of nanosubgrains. Continued milling causes boundary sliding and migration which convert the small angle boundaries into high angle boundaries by increasing the boundary dislocation density until an optimum grain size is achieved. For prolonged milling (in our case > 60 h), the optimum grain size is approached. The internal strain also remains constant because equilibrium is reached between hardening and softening recovery.

5.1.3 Formation of Solid Solutions

The lattice parameter evolutions during milling of both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ are shown in Figure 4-10. In $\text{Fe}_{75}\text{Si}_{25}$, lattice parameter decreased from 0.2866 nm to about 0.2843 nm after 40 h of milling and thereafter remained constant till 100 h. The decrease of lattice parameter indicates the dissolution of the smaller Si atom (0.118 nm) [Tennent, R. M., 1971] into the Fe (0.123 nm) matrix with increasing milling time which leads to shrinkage of the lattice. The dissolution was not complete until about 60 h. According to the literature [Farquar, M. C., 1945], dissolution of about 17 at.% Si in Fe is sufficient to reduce its lattice parameter value to 0.2843 nm. This indicates that some amount of Si atoms actually did not dissolve into the Fe matrix. The undissolved Si may be segregated in the grain boundaries without contributing to the shrinkage of Fe lattice. The segregation of Si atoms will be quantitatively discussed further in Section 5.3.

In $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, for $t < 15$ h, the lattice parameter increases with milling time as shown in Figure 4-10. This may be attributed to dissolution of the bigger atoms of Al (0.142nm) [Tennent, R. M., 1971] into the Fe matrix, which overcompensates in this period to influence the Si dissolution. For $t > 15$ h, the lattice parameter begins to decrease with milling time which signifies that the dissolution of Al atoms is completed while Si dissolution still continues. This evolution of lattice parameter proves that both Al and Si atoms should have diffused into the Fe matrix and formed $\text{Fe}(\text{SiAl})$ solid solution. Due to the larger size of Al atoms compared to Si atoms, the final lattice parameter of this ternary alloy after 100h of milling is larger than that of the binary alloy.

Alloying normally occurs through atomic diffusion by a vacancy mechanism. Several factors like temperature, density of defects, and crystalline size can strongly affect the diffusion process. Defects generated during milling could accelerate diffusion by providing short circuit diffusion paths. Also, the size of the particle and/or grain is decreased considerably, resulting in a decrease in diffusion distance and/or an increase in relative area of grain boundary, i.e. providing more high diffusivity paths. For the two alloys in this study, $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, the milling conditions should have provided enough energy for the diffusion of solute atoms into the Fe matrix to finally enable complete dissolution. However, the final lattice parameter of $\text{Fe}_{75}\text{Si}_{25}$ shows that not all the Si atoms have diffused into the Fe matrix. Some of which may be segregated in the grain boundaries. Such grain boundary segregated solute could inhibit the grain growth during annealing, which will be discussed in detail later in Section 5.3.

In summary, true solid solution alloys have been formed during MA for both alloys. However, in these metastable nanostructured alloys, not all the atoms have dissolved homogeneously in the lattice to form the intended composition. Some of them could be segregated in the grain boundaries. The quantitative analysis of this effect will be discussed later in Section 5.3.

5.2 The Effects of Al, Nb and Cu on the Thermal Stability of $\text{Fe}_{75}\text{Si}_{25}$ during Annealing

It is clear that addition of Al has a strong grain growth inhibiting effect in Fe-Si system, as evident in Figure 4-11. The effect of Al is believed to be due to the solute drag effect, despite the occurrence of ordering transformation. The segregated Si and Al atoms in the grain boundaries of NC materials could restrain grain boundary migration by a drag effect at low temperatures $<773\text{ K}$ before the ordering transformation occurs. When ordering occurs, much of Si diffuses into the Fe matrix in the binary Fe-Si alloys, with loss of the solute drag effect and consequent sharp grain growth. The sharp decrease shown in the lattice parameter of $\text{Fe}_{75}\text{Si}_{25}$ at temperatures $>773\text{ K}$ is a strong evidence for this hypothesis (see Figure 4-20). Thus the solute concentration of Si in the Fe lattice should have increased from about 17% to 23% upon ordering based on the published relationship between lattice parameter and Si concentration in Fe reported by Farquar, M. C. [Farquar, M. C., 1945]. This sharp increase of Si concentration in the Fe lattice must lead to a depletion of Si atoms in grain boundaries, which results in a decrease of drag force to grain boundary migration, and therefore grain growth. This will be further discussed in Section 5.3. However, in the $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ much of the Al should have remained segregated in the grain boundaries even when ordering transformation occurred. This may be due to the high segregation coefficient of Al in the Fe matrix. High segregation coefficient indicates high tendency to remain in the grain boundary. This enables Al atoms to remain segregated in the grain boundaries even upon ordering transformation and thus retain the thermal stability against grain growth. Besides, no second phase appeared to

have been precipitated during annealing. The quantitative analysis of this effect will be discussed later in Section 5.3.

$\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ also showed equally good resistance to grain growth. This may be attributed to segregated Nb atoms and/or Fe_2Nb intermetallics, both of which may hinder grain boundary migration. Lecaude has reported [Lecaude, N., 1997] that Nb is believed to be the key atom to inhibit grain growth of Fe(Si) crystals in Finemet due to the slow diffusion rate of Nb in the alloy. In addition to the solute drag effect, the second phase Fe_2Nb may also inhibit grain growth as particles can also generate a large pinning force to inhibit grain boundary migration [Randle, V., 1986]. It was reported that Ni_3P precipitates in a crystallized Ni-P amorphous alloy inhibits the grain growth of Ni nanocrystals by pinning the grain boundaries [Boylan, K., 1991]. Actually, both solutes and precipitates can inhibit grain growth by reducing the boundary mobility. However, the formation of Fe_2Nb intermetallics is not desirable for soft magnetic materials. A second phase is known to have a domain wall pinning effect which is deleterious to the soft magnetic properties [Jiles, D., 1991]. The energy of magnetic domain walls is reduced when they intersect second phase particles. The well-known example is cementite (Fe_3C) particles in iron and steels. In steel, the effect of carbide inclusions on the coercivity of iron was described by Dijkstra and Wert [Dijkstra, L., 1950], in which case the energy of magnetic domains is believed to be reduced when cementite content increases in the microstructure of the material. Using a simple elastic membrane model, it has been shown that the energy of domain wall can be reduced 70 times with a 1 μm inclusion in iron [Jiles, D., 1991]. Experimental data are available that show coercivity increases sharply with

the increase of volume fraction of precipitates [Jiles, D., 1991]. Therefore, Nb is not a desirable addition although it also showed some effect of inhibiting grain growth.

In the Cu containing alloy, $\text{Fe}_{75}\text{Si}_{15}\text{Cu}_{10}$, grain growth is also slowed down by Cu addition as compared with $\text{Fe}_{75}\text{Si}_{25}$. However, the effect of Cu is not as strong as that of Al and Nb, which is probably due to the premature precipitation of Cu, that removes the segregated elements from grain boundaries leading to rapid grain growth. In $\text{Fe}_{95}\text{Cu}_5$ alloys synthesized by mechanical alloying it was reported that no appreciable grain growth occurs prior to Cu precipitation [Eckert, J., et al., 1993]. Eckert et al. reported that after Cu precipitation at 870K, grain growth sets in. The grain size in their alloy grew from 5nm in the as-milled condition to about 21 nm, and the strain released to less than 0.1%. The thermal stability against grain growth also disappears after the Cu precipitation was detected.

In summary, all three additions showed some effects of inhibiting grain growth during annealing. The Al addition showed the best effect of inhibition of grain growth without any undesirable precipitation. Therefore Al addition looks to be the most promising ternary addition to the Fe-Si system to retain the nanostructure.

5.3 Grain Growth Kinetics and Ordering Transformation of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$

Ordering and grain growth appear to occur simultaneously at about 773 K in $\text{Fe}_{75}\text{Si}_{25}$, which indicates they may be somewhat interrelated. In $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy also,

the ordering occurred at a similar temperature but no sharp grain growth was observed. We attribute this concurrence to the role of solute segregation to grain boundaries. Below we enter into a semi-quantitative analysis of solute segregation, using published theories, to quantify the extent of segregation in the two alloys.

Before ordering, both alloys showed stability against grain growth, which should be due to the solute drag effect. According to the theory of solute drag controlled grain growth [Cahn, J. W., 1962], GB solute segregation exerts a drag force f proportional to the difference in solute concentration ΔC between the grain boundary (GB), C^{GB} , and the crystal C^{Cry} . Thus,

$$f \propto \Delta C = |C^{GB} - C^{Cry}| \quad (5-1)$$

It could be inferred from Eqn. 5-1 that the drag force will disappear when ΔC approaches zero leading to grain growth. P. Lejcek and O. Schneeweiss reported [Lejcek, P., et al., 2001] that ordering affects the solute GB segregation in Fe-Si system. They observed that ordering transformation results in solute desegregation. Therefore, the concurrence of ordering and rapid grain growth is probably related to the change in ΔC resulting from the ordering transformation. This notion is justified below using GB segregation models available in the literature and an effort is made to quantify ΔC before and after ordering.

5.3.1 Fe₇₅Si₂₅

The Langmuir-McLean segregation isotherm [Hondros, E. D., 1996] can be used to calculate the GB concentration in the as-milled disordered solid solution. This equation is,

$$\frac{C_{disGB}^{GB}}{1 - C_{disGB}^{GB}} = \frac{C^{Bulk}}{1 - C^{Bulk}} \exp\left(-\frac{\Delta H^{GB} - \Delta S^{GB} T}{RT}\right) \quad (5-2)$$

where, C_{disGB}^{GB} is the GB Si concentration when the boundary itself is disordered and C^{Bulk} is the bulk Si concentration. $\Delta H^{GB} = -15900 \text{ J mol}^{-1}$ and $\Delta S^{GB} = 12.1 \text{ J mol}^{-1} \text{ K}^{-1}$ are the segregation enthalpy and entropy of Si at the GB in binary Fe-Si system [Huang, J. Y., 1994]. R is gas constant ($= 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T the absolute temperature. Rewriting Eqn. 5-2 in a convenient form, we obtain

$$C_{disGB}^{GB}(T) = \frac{C^{Bulk}}{1 - C^{Bulk}} \exp\left(-\frac{\Delta H^{GB} - \Delta S^{GB} T}{RT}\right) \left/ \left[1 + \frac{C^{Bulk}}{1 - C^{Bulk}} \exp\left(-\frac{\Delta H^{GB} - \Delta S^{GB} T}{RT}\right) \right] \right. \quad (5-3)$$

The graph of C_{disGB}^{GB} against T may be plotted using Eqn. 5-3 with $C^{Bulk} = 25 \text{ at\%}$, the bulk concentration of Si in the alloy. This is shown in Figure 5-1 (line a).

The concentration of Si in the crystals C^{Cry} can be calculated using the equation of mass conservation condition,

$$C^{Bulk} = C^{GB} \chi^{GB} + C^{Cry} (1 - \chi^{GB}) \quad (5-4)$$

where C^{Bulk} , C^{Cry} and C^{GB} are the concentrations in the bulk, in the crystal and at the GB respectively, and χ^{GB} is the volume fraction of GB regions in the material. Eqn. 5-4 could be re-written for the concentration of Si in the crystal C^{Cry} as,

$$C^{Cry} = \frac{C^{Bulk} - C^{GB} \chi^{GB}}{(1 - \chi^{GB})} \quad (5-5)$$

If we assume that the materials consist of uniform, equiaxed crystals and that the GB region is a thin layer of thickness δ , the volume fraction of GB regions in one crystal is,

$$\chi^{GB} = \frac{A^{GB} (0.5\delta)}{V} \quad (5-6)$$

where, A^{GB} and V are the boundary area and volume of a grain respectively. Further, by assuming a specific shape for the crystals, we can relate χ^{GB} to grain size. For example, for the tetrakaidecahedral shape that is usually applied in polycrystalline material analysis, we can relate A^{GB} and V to grain size D by (see Appendix B)

$$\chi^{GB} = \frac{3.14\delta}{D} \quad (5-7)$$

The average grain size D in the as-milled powder is 14.5 nm. Using this value for D and assuming a typical grain boundary thickness δ of 0.5 nm, $\chi^{GB} = 10.83$ vol% for the as-milled powder. Substituting this into Eqn. 5-5 gives,

$$C^{Cry} = \frac{25at.\% - C^{GB} \times 10.83\%}{89.17\%} \quad (5-8)$$

Eqn. 5-8 represents the concentration of Si within the crystal irrespective of whether it is ordered or not. If we substitute the expression for C_{disGB}^{GB} from Eqn. 5-3 into Eqn. 5-8 for GB concentration, we may obtain C_{disGB}^{cry} as a function T . This substitution assumes that the grain size does not change with temperature, a condition that is reasonably satisfied in the low temperature regime. The curve of C_{disGB}^{cry} versus T is also shown in Figure 5-1 (line b).

The Si concentration calculated by the above procedure within the crystal at room temperature when the GBs are disordered is approximately 16.15 at%. This is substantially lower than the bulk concentration of 25 at%. J. Y. Huang theorized [Huang, J. Y., 1994] that in supersaturated solid solutions, only a part of the solute atoms are dissolved in the lattice of the solvent while the rest are segregated to the GBs. The lattice parameter of the as-milled powder stabilized at 0.2842 nm during

ball milling. A published relationship between lattice parameter and dissolved Si in disordered Fe-Si system [Farquar, M. C., 1945] shows that the Si content corresponding to this lattice parameter is 17 at%. For 25 at% Si, the lattice parameter should be 0.2827 nm. The low value of C_{disGB}^{cr} is due to both, a high GB region volume fraction and GB segregation of Si.

Ordering transformation occurred at high temperatures upon annealing. Ordering could occur not only in the crystal but also at the GBs in some systems [Lejcek, P., 2003] which could lead to a change in Si concentration at GBs. To quantify the Si segregation in a partially ordered GB, we use a phenomenological model proposed by P. Lejcek and O. Schneeweiss [Lejcek, P., 2001]. In this model, a fraction M^{GB} of the GB is assumed to be ordered (GB order parameter) while the balance is disordered. This fraction depends on T according to the relationship,

$$M^{GB} = \left(\frac{T_c^{GB} - T}{T_c^{GB}} \right)^\beta \quad (5-9)$$

where β is a GB exponent, and T_c^{GB} is the ordering temperature of the GB. P. Lejcek and O. Schneeweiss suggest that the ordering temperature of the GB is about 60 K higher than that of the bulk crystal T_c^{Bulk} . Since T_c^{Bulk} for Fe-25 at.%Si is 1493 K [Kubaschewski, O., 1982], we take $T_c^{GB}=1553$ K. Since, the bulk concentration of Si in our material is stoichiometric for the ordered structure, the solute concentration at ordered parts of the GB can be written as [Lejcek, P., 2001],

$$C_{ordGB}^{GB} = C_{disGB}^{GB} [1 - M^{GB}] + C^{Bulk} M^{GB} \quad (5-10)$$

Substituting Eqns. 5-9 and 5-10 into Eqn. 5-3, we can obtain the expression for GB concentration of solute as a function of temperature when the boundaries are partially ordered,

$$C_{ordGB}^{GB}(T) = \frac{\frac{C^{Bulk}}{1 - C^{Bulk}} \exp\left(-\frac{\Delta H^{GB} - \Delta S^{GB}T}{RT}\right)}{1 + \frac{C^{Bulk}}{1 - C^{Bulk}} \exp\left(-\frac{\Delta H^{GB} - \Delta S^{GB}T}{RT}\right)} \times \left[1 - \left(\frac{T_c^{GB} - T}{T_c^{GB}}\right)^\beta\right] + C^{Bulk} \left(\frac{T_c^{GB} - T}{T_c^{GB}}\right)^\beta \quad (5-11)$$

The plot of Eqn. 5-11 is also shown in Fig. 5-1 (line d). With Eqns. 5-11 and 5-8, the crystal concentration and the corresponding concentration difference, ΔC , could also be plotted against the temperature, as shown in Figure 5-1.

The Si concentration difference, ΔC , between the crystal and the GB can now be determined for any temperature for the cases, disordered and partially ordered GB. For the lower temperature range 573 – 703 K when the crystal and the GB are disordered, ΔC calculated using Eqns. 5 and 10 is between 48.95 at% (at 573 K) and 32.69 at.% (at 703 K). At the higher temperature range of 773 – 853 K when the crystal and the GB are ordered, and the corresponding values are 7.51 at % (at 773 K) and 6.36 at.% (at 853 K). These ranges are indicated in Figure 5-1. Thus, there is a reduction by about a factor of 6 in ΔC at the higher temperatures. This deduction implies a greatly reduced GB drag force facilitating grain growth at the high temperature range.

The curves (b) and (e) in Figure 5-1 indicate that the crystal concentrations at room temperature (300 K) are about 16.15 at.% and 24.1 at.% respectively for disordered and ordered GBs. Figure 4-20 shows that annealing in high temperature regime sharply decreases lattice parameter from 0.2842 to 0.2831 nm. This indicates

an increase of Si concentration in the crystals from around 17 at.% to 23 at.% [Kubaschewski, O., 1982]. Thus, our lattice parameter measurements also support the Si concentration calculations. This reduction in lattice parameter could be attributed to desegregation of Si from GBs to the crystal during ordering transformation.

Figure 5-1. The variations of solute concentrations at GBs and in the crystal against temperature for various cases and the corresponding differences between GB and crystal concentration. (a) GB concentration of Si with disordered boundary C_{disGB}^{GB} in $Fe_{75}Si_{25}$ alloys (b) Crystal Si concentration with disordered boundary C_{disGB}^{Cry} in $Fe_{75}Si_{25}$ alloys, (c) ΔC of Si for disordered boundary in $Fe_{75}Si_{25}$ alloys, (d) Si GB concentration with ordered boundary C_{ordGB}^{GB} in $Fe_{75}Si_{25}$ alloys, (e) Si Crystal concentration with ordered boundary C_{ordGB}^{Cry} in $Fe_{75}Si_{25}$ alloys, (f) Si ΔC for ordered boundary. (g) GB concentration of Al with disordered boundary C_{disGB}^{GB} in $Fe_{75}Al_{25}$ alloys. (h) Al GB concentration with ordered boundary C_{ordGB}^{GB} in $Fe_{75}Al_{25}$ alloys, (i) ΔC of Al for disordered boundary in $Fe_{75}Al_{25}$ alloys, (j) Al ΔC for ordered boundary in $Fe_{75}Al_{25}$ alloys. The ΔC regions for the two temperature ranges are shown enclosed in thin rectangles.

5.3.2 Fe₇₅Si₁₅Al₁₀

The ordering in Fe₇₅Si₁₅Al₁₀ did not result in sharp grain growth. This indicates that ordering may not have lead to strong de-segregation as that in the Fe₇₅Si₂₅ alloy. We attempt a quantitative analysis of the grain boundary segregation and solute drag effect in Fe₇₅Si₁₅Al₁₀ ternary alloy also here in order to understand this phenomenon better. However, since the equation of solute segregation (Eqn. 5-2) is valid for binary systems only, the grain boundary segregation and solute drag effect in Fe₇₅Si₁₅Al₁₀ ternary alloy cannot be quantitatively analyzed as those in Fe₇₅Si₂₅ binary alloy. Hence, we compare the solute drag effect in Fe₇₅Si₂₅ alloy with that in binary Fe₇₅Al₂₅ alloy, which may give us some indications of the effect of addition of Al on inhibiting the grain growth.

According to the literature [Hondros, E. D., 1996], the grain boundary segregation enrichment ratio of Al in the Fe-Al system is about 10 times of that of Si in the Fe-Si system, which means the Al atoms have a stronger tendency to stay segregated in the grain boundary than Si atoms. Thus, we may write the following relationship:

$$\frac{C_{Al}^{GB}}{1 - C_{Al}^{GB}} = 10 * \frac{C_{Si}^{GB}}{1 - C_{Si}^{GB}} \quad (5-12)$$

Rewriting Eqn. 5-12 in a convenient form, we obtain

$$C_{Al}^{GB} = \frac{10C_{Si}^{GB}}{1 + 9C_{Si}^{GB}} \quad (5-13)$$

Therefore we can obtain the Al grain boundary concentration in both ordered and disordered Fe₇₅Al₂₅ by substituting Eqn. 5-3 (Si grain boundary concentration in

ordered $\text{Fe}_{75}\text{Si}_{25}$) and Eqn. 5-11 (Si grain boundary concentration in disordered $\text{Fe}_{75}\text{Si}_{25}$) into the Eqn. 5-13 respectively. Thus, we can also plot the grain boundary concentrations against the temperature for both ordered (curve h) and disordered (curve g) $\text{Fe}_{75}\text{Al}_{25}$ alloy, as shown in Figure 5-1. According to the relationship of grain boundary concentration and crystal concentration as described in Eqn. 5-8, the crystal concentrations of Al in both ordered and disordered $\text{Fe}_{75}\text{Al}_{25}$ alloys can also be determined. Then the ΔC can also be determined and plotted against temperature. As shown in Figure 5-1, the curve i is ΔC for disordered $\text{Fe}_{75}\text{Al}_{25}$ alloy, and curve j is that for the ordered one. It shows that concentration difference ΔC in $\text{Fe}_{75}\text{Al}_{25}$ alloy is very high in the disordered alloy, about 70%-75% at temperatures 573 K – 703 K, and it will not decrease too much upon ordering transformation at temperatures 773 K – 853 K, maintaining values of about 60%. Therefore, high ΔC values of about 60% can be maintained in $\text{Fe}_{75}\text{Al}_{25}$ alloys at temperatures 773 K-853 K, which is much higher than the value, about 10%, in the $\text{Fe}_{75}\text{Si}_{25}$ alloy. The ΔC in the ternary $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy may not be as high as that in the binary $\text{Fe}_{75}\text{Al}_{25}$ alloy, but the calculations for $\text{Fe}_{75}\text{Al}_{25}$ alloy showed that it should be higher than that of $\text{Fe}_{75}\text{Si}_{25}$ alloy due to the stronger segregation tendency of Al as compared with that of Si. Therefore, the better thermal stability of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy is most likely due to the substitution of Si by Al, which remains segregated in the grain boundary and provides a drag force for its migration.

This calculation is in agreement with the LRO parameters shown in Figure 4-21. The LRO of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy of about 0.6 is lower than that of $\text{Fe}_{75}\text{Si}_{25}$ alloy (about 0.9), which confirms that most of Al atoms should still be segregated at grain boundaries upon ordering, resulting in a lower degree of ordering in the matrix. In

summary, the replacement of Si by Al should result in a higher concentration of solute atoms in grain boundaries, which does not decrease too much even upon ordering. This helps to inhibit the grain growth.

- **Activation energy for grain growth**

Activation energy of grain growth is an indicator of the grain growth mechanism. As shown in Figure 4-23, the activation energy for grain growth of binary alloy $\text{Fe}_{75}\text{Si}_{25}$ is different in the two temperature regimes. In the higher temperature regime of 773 - 853 K, the crystals attain the equilibrium DO_3 ordered structure, and the activation energy measured for grain growth of $303.8 \text{ kJ mol}^{-1}$ is near to the activation energy of 312 kJ mol^{-1} reported for lattice diffusion of Si in microcrystalline, ordered DO_3 Fe-Si alloys [Shukla, S., 2003]. This implies a “solute dependent grain growth” according to Cahn’s theory for grain growth with solute impediment [Cahn J. W., 1962], indicating that the migration of solute atoms with GBs is the rate controlling mechanism for grain growth. In the lower temperature regime of 573-703 K, the activation energy is only 31.2 kJ mol^{-1} , which is much lower than the reported activation energy of 212 kJ mol^{-1} for lattice diffusion of Si in microcrystalline, disordered bcc-Fe(Si) [Salamon, M., et al., 1999]. Similar small activation energies for grain growth in NC material have been observed by other researchers also [Shukla, S., 2003]. The small grain sizes in NC materials, in which the diffusion distances are short and chemical activities are high, may be a reason for these small values [Averbach, R. S., et al., 1993]. Besides, the large volume fraction of grain boundaries in NC materials and the differences in the local atomic structure

of grain boundaries could also affect atomic diffusivities [Fultz, B., et al., 2000] and consequently the grain growth. The grain growth is related to diffusion. The change of diffusivity due to the local atomic structure [Kornelyuk, L., 1998] may have a strong influence on grain growth behavior. The atomic structures of grain boundaries in NC materials are quite unlike those of conventional materials, especially those in highly strained non-equilibrium balled milled NC alloys. There is some evidence that mechanical alloying creates grain boundaries having a higher energy than annealed high-angle grain boundaries [Fecht, H. J., 1990]. Perhaps the atoms diffuse faster in these severely distorted structural environments which implies that the energy barrier is small. Therefore, the low value of activation energy in the low temperature regime is probably related to the non-equilibrium atomic structure in the MA NC alloys. However, annealing at the high temperature regime may have changed the grain boundary atomic structure and the crystal structure to make it more like equilibrium ones, which lead to a much higher value of activation energy, comparable to that in conventional material.

In the $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy, transformation to the DO_3 structure was observed at a temperature similar to that in the $\text{Fe}_{75}\text{Si}_{25}$ alloy. Hence, an attempt was made to fit separate lines for the high temperature and low temperature regimes, as for $\text{Fe}_{75}\text{Si}_{25}$. These fitted lines are in Figure 4-23. The activation energies measured for grain growth are about 37.2 kJ mol^{-1} and 57.4 kJ mol^{-1} at low temperature and high temperature regime respectively. The activation energies are similar for both temperature regimes. It was observed that the internal strain in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy reached only 0.2% (Figure 4-19) which means that the crystal is not fully relaxed when annealed at high temperature. Even the LRO parameter only reached about 0.6

(Figure 4-21), which means that a high degree of long range ordering is not achieved. Besides, as we discussed in the last chapter, most of the Al atoms should still remain in the grain boundary. The combination of these effects may keep the system staying in metastable nanocrystalline condition, which is not too much different from that of the as-milled state and is far from the equilibrium bulk state. Therefore, the activation energy for grain growth for the high temperature regime is also low and comparable to those typical values of MA nanocrystalline alloys.

In summary, Al showed obvious effect of inhibiting grain growth even upon ordering, which may be due to the higher grain boundary segregation coefficient of Al than that of Si. The activation energy of grain growth of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy did not show much increase upon ordering either, which may have resulted from the incomplete structural changes as compared with those of the $\text{Fe}_{75}\text{Si}_{25}$ alloy.

5.4 Sintering Behaviors of $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$

For both $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, as shown in Figure 4-28, higher density could be achieved at a relatively low sintering temperatures by SPS, besides which the grain sizes were maintained under 100nm. The advantage of the SPS processing technique for achieving high density while retaining fine crystalline structure has been reported by Omori, M. [Omori, M., 2000], which could be due to the high heating rate, plasma assistance and short holding time as compared with conventional sintering. It has been reported that $(\text{Al}+12.5 \text{ at.\%Cu})_3\text{Zr}$ powders prepared by MA could be

consolidated to full density by SPS at 853 K [Lee, S. H., 2003]. The average grain size was 8.9 nm which is one of the smallest grain sizes ever reported for nanocrystalline bulk specimens prepared by various consolidation methods [Lee, S. H., 2003]. Our study shows that high-density nanocrystalline compacts in FeSi-based alloys could also be achieved by SPS.

Under the same sintering condition, the $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ can achieve higher density and smaller grain size as compared with $\text{Fe}_{75}\text{Si}_{25}$, as shown in Figure 4-28. This might be due to the retarded grain growth in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ upon exposure to high temperatures. The smaller grain size of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ could provide more diffusion paths, so that the sintering can be much quicker in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ than that in $\text{Fe}_{75}\text{Si}_{25}$. Many researchers have reported the effects of grain size and grain boundaries on diffusion and sintering both theoretically and experimentally which show that a precursor with fine grain structure can be sintered more efficiently [Koch, C. C., 2002]. For example, it was reported in fully dense cubic Y_2O_3 (melting point, 2,439 °C), with a grain size of 60 nm, that full density could be achieved at temperatures of about 1,000 °C without applied pressure. The successful suppression of grain growth by exploiting the difference in kinetics between grain-boundary diffusion and grain-boundary migration is reportedly the key knob for this study. High diffusion flux was maintained along grain boundaries during sintering by suppression of grain growth [Chen, I. W., 2000] which depends on bulk diffusion.

5.5 Magnetic Properties of Fe₇₅Si₂₅ and Fe₇₅Si₁₅Al₁₀

The maximum induction $B_{\max}$ showed a relationship with density, as shown in Figure 4-30. It seems that higher sintering temperature leads to higher relative density and therefore higher maximum induction. This is because pores tend to set up demagnetization fields in the compacts. The maximum induction has been reported to be directly related to the density/porosity in P/M product [Moyer, K. H., et al., 1980] by the empirical relationship:

$$Bs = Bsn(1 - aP) \quad (5-14)$$

where Bs and Bsn are saturation induction for porous and non-porous materials respectively, P is porosity, a is a constant. This relationship shows higher density/lower porosity leads to higher Bs . The Bs of both conventionally sintered and SPS sintered alloys shown in Figure 4-30 are re-plotted against porosity and fitted with Eqn. 5-14, as shown in Figure 5-2. The triangle shaped dots represent Fe₇₅Si₁₅Al₁₀ alloys, and the diamond dots represent Fe₇₅Si₂₅ alloy. From the equation of the fitted line, we can obtain the Bsn from the intercept with the y-axis. This is about 1.07T and 1.22T respectively for Fe₇₅Si₂₅ and Fe₇₅Si₁₅Al₁₀ alloys. In other words, Fe₇₅Si₂₅ and Fe₇₅Si₁₅Al₁₀ may achieve about 1.07 T and 1.22 T respectively if the porosity=0, which is comparable to the values of Bs for FINEMET (1.0-1.2T) [McHenry, Michael E., 1999]. In summary, Fe₇₅Si₁₅Al₁₀ SPS compacts showed Bs values of about 0.9-1.0T. The predicted Bs values using Eqn. 5-14 indicate that both Fe₇₅Si₂₅ and Fe₇₅Si₁₅Al₁₀ alloys should be able to achieve comparable Bs with that of FINEMET when full density is achieved.

Figure 5-2. Plot of B_s versus Porosity of (a) $\text{Fe}_{75}\text{Si}_{25}$ and (b) $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy. Curves are fitted according to Eqn. (5-14). Triangle dots represent $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, the diamond dots for $\text{Fe}_{75}\text{Si}_{25}$.

It was reported that mean atomic magnetic moment is dependent on the alloy composition [McHenry, M.E., et al., 1999]. For example, the atomic magnetic moment of $\text{Fe}_x\text{Co}_{1-x}$ alloy shows a maximum value at $\text{Fe}_{0.6}\text{Co}_{0.4}$, and a 20% decrease was observed when the Co atomic content is increased to 80%. Besides, several other systems, like Fe-V, Fe-Cr, Ni-Co and Ni-Cu, were also reported to exhibit similar behaviors in this literature. It was also reported that there is a significant change in Fe magnetic moments in the $\text{Fe}_{75}\text{Si}_{25}$ alloy when ternary elements are introduced [Hines, W. A., et al., 1976], which will therefore lead to a change of saturation induction also. Detailed studies have been completed for ternary systems with different additions, such as V, Mn, Ti and Co, but Al appears not to have been investigated. Based on the predicted B_{sn} values in our study, it shows that the substitution of the Si by Al might result in an increase of about 20% in B_s , which may be related to a change in the mean atomic magnetic moment resulting from the ternary addition of Al.

The coercivity H_c of these two alloys $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ showed a strong relationship with grain size, as shown in Figure 4-30. For those SPS samples,

the H_c of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ increased with sintering temperature as a result of increment of grain size, while that of $\text{Fe}_{75}\text{Si}_{25}$ almost remained unchanged as a result of constancy in grain size over this sintering temperature range. The concept of a magnetic exchange length and its relationship to the domain wall width and monodomain size is important in the consideration of magnetic anisotropy in nanocrystalline soft magnetic materials. Herzer shows that, for a large number of grains with random crystallographic easy axes, within a volume to be exchange coupled, that the coercivity should be proportional to D^n ($n>1$), where D is grain size [Herzer, G., 1997]. Therefore, coercivity should increase with increase of grain size in the nanometer range. Our observation of coercivity in this study is in accordance with his prediction, which also increases with the increase of grain size.

In vacuum sintered samples, the grain sizes of both alloys are comparable and did not change significantly with sintering temperature. Therefore the coercivity also did not show much variation. As for the effect of addition of Al on coercivity, the coercivity of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ showed lower values for all conventionally sintered samples when compared with those of $\text{Fe}_{75}\text{Si}_{25}$. This is probably due to the low magnetic anisotropy constant corresponding to this composition [Jiles, D., 1991]. In other words, for this composition, the magnetic domains do not have a strong preference to stay in a certain direction and they are easily rotated by a magnetic field leading to low coercivity. The magnetic anisotropy is highly dependent on alloy chemistry [McHenry, M. E., et al., 1999]. For example, in $\text{Fe}_{1-x}\text{Co}_x$ alloys, the minimum anisotropy occurs near $x=0.5$. Therefore, for those applications that require low anisotropy, the alloy composition will have to be somewhere around FeCo. $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ also may have an optimum composition that shows low coercivity. The

lower coercivity and probably lower magnetocrystalline anisotropy of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ could be beneficial in some applications.

A slight increment of maximum permeability with increase of sintering temperature was observed for both alloys after sintering with SPS. However, for conventionally sintered samples, the maximum permeability showed large variation with sintering temperature, and it achieved a maximum value of about 1989 in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ after sintering at 1513 K for 1 h. The maximum value achieved in conventionally sintered samples was 813, which was achieved in the $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy sintered using SPS at 1243 K for 5 min.

For powder metallurgy magnets, the magnetic permeability is dependent on many factors such as particle exchange coupling and domain wall movement, and they relate to density and grain size respectively. Although for the SPS sample, densities are higher than those of conventionally sintered samples, their permeabilities are fairly low. This is probably related to the small grain size. The grain size in SPS sintered samples are about 90 nm which is larger than the so-called exchange length, normally less than 30 nm [Herzer, G., 1997], resulting in loss of the advantages of nanostructure for magnetic materials. Therefore, the random crystallographic easy axes effect which can cancel the anisotropy of each domain within exchange length is not operative in SPS samples although it is still in the nanometer grain size range. Besides, the small grain size leads to a high volume fraction of grain boundary in the NC material, which will pin the movement of domain walls and may result in lower permeabilities than those of conventionally sintered rings. Therefore, in order to take

advantage of nanostructure, the grain size needs to be controlled within a certain range and to be as small as possible.

As shown in Fig. 4-30, we achieved a highest saturation induction of about 1.0 T in this project. This value is comparable to the saturation induction reported in Finemet, of about 1.2 T [Yoshizawa, Y., et al. 1988]. With respect to coercivity, the nanocrystalline compacts prepared by SPS with grain sizes about 50-90nm showed values of 150-400 A/m, which is within the range of 100-700A/m, reported for nanomagnets (see Fig 2-16) prepared by crystallization of amorphous ribbon with similar grain size. Chaman Lall [Lall, C., 1992] reported that Fe-3%Si commercial materials processed by conventional powder metallurgy, sintered at 1433 K for 45 min, with a mean grain size of about 100 μm , showed a saturate induction of 1.17 T, a permeability of 2900 and a coercivity of 104 A/m. These are again quite comparable to the properties obtained in this study (see Fig. 4-30). Thus, nanocrystalline alloys synthesized via MA in this study have significant potential as soft magnetic materials, and the properties could be further improved by further optimizing the chemistry and process.

5.6 Proposed Material and Process Design for Further Material Optimization and Process Improvement.

This study shows that certain ternary alloying additions, such as Al, can be quite powerful to inhibit grain growth. Besides, the advanced consolidation technique SPS can also be helpful to achieve a high-density nanostructured compact. These

observations give us some indications to further optimize material chemistry and process design for the future.

As discussed in Section 5.2, all three ternary alloying additions showed some effects on inhibiting grain growth during annealing. Al and Nb appeared to have a higher grain growth inhibiting effect than Cu. There should be some more powerful additions that could inhibit the grain growth even more effectively. However, the effects of different elements and concentrations can hardly be systematically studied to determine how to retard grain growth most effectively. Simulations are therefore good options to predict the best element and concentration for a given system to retard grain growth.

Besides material optimization, the sintering process is also critical to retain the nanostructure. Since, it is essential to maintain the nanostructure in the final bulk material, to obtain the right conditions for consolidation of the mechanically milled powder is critical. The dilemma one has to deal with in consolidating nanostructured materials is that we need diffusion to achieve atomic level bonding between particles, but in the meantime, diffusion also causes coarsening of grains and interfacial reactions. It is difficult to define a condition window (the range of temperature and pressure) in which the positive effect of the diffusion is attained, without having the side effects. As shown in Section 4.4.1, SPS shows a good capability of producing high-density nanostructured compacts, compared to conventional sintering. Therefore, some advanced consolidation techniques that can further decrease the consolidation temperature and/or shorten hold time will be more promising. For example, explosive compaction is one of the candidates [Ando, S., 1999]. Explosive compaction produces

high stresses during short time periods, heavily deforming the particles and producing fully dense compacts without any heating.

In summary, the density and nanostructure could be further improved by optimizing material chemistry and process design.

5.7 Scientific Advancements and Technical Accomplishments

This project focused on synthesis, thermal stability, sintering behavior and magnetic properties of nanocrystalline Fe-Si alloys. It was shown that high energy ball milling of elemental powder precursors is a viable technique to synthesize Fe-Si based nanocrystalline, and even amorphous, solid solution alloys. The effects of three ternary alloying elements were assessed, namely Al, Cu and Nb, on the ability to form nanocrystalline structure. All three elements accelerated nanostructure formation compared to the binary Fe-Si. Nb was the most effective. The advantage considered is the avoidance of the more expensive approach which forms nanostructure upon crystallization from the amorphous phase.

The thermal stability of the alloys was also studied, and the relationship between grain growth and ordering transformation was semi-quantatively analyzed. It was proved, using previous theories on grain boundary segregation, that alloying elements-Si in particular-segregate to grain boundaries in the as-milled alloys. This segregation effectively pins the boundaries and retards grain growth at high temperatures until desegregation is brought upon associated with ordering. Annealing

beyond 773K causes desegregation and consequent grain growth. This understanding of the grain growth mechanism is an important contribution made by this project. Besides, the effect of alloying additives Al, Nb and Cu on thermal stability was also assessed and it was shown that Al is the best ternary alloying candidate to restrict grain growth.

Conventional and spark plasma sintering processes were assessed to densify the nanostructured powder and the relationship between processing parameters, structure and magnetic properties was discussed. It is shown that density of the product also has an effect on the magnetic property besides the alloy chemistry and nanostructure. Hence, the aim of the processing step should be to achieve high density while maintaining the nanocrystalline structure to take the advantage of the nanostructure for magnetic applications. The spark plasma sintering technique is promising for consolidation of nanocrystalline powders without excessive grain growth.

6 CONCLUSIONS

6.1 Mechanochemical Activation

Ball milling elemental powder mixtures corresponding to the compositions $\text{Fe}_{75}\text{Si}_{25}$, $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Cu}_{10}$ reduced their grain sizes to the range 12.0-14.5 nm in 60 hours. Ball milling an elemental powder mixture corresponding to the composition $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ produced predominantly amorphous structure with some isolated crystals in 60 hours. The lattice parameters of the alloyed α -Fe changed in accordance with predictions made from the atomic radii of the dissolving elements.

Annealing at high temperatures caused grain growth in all alloys. Grains were resistant to growth up to a specific temperature and thereafter rapid growth occurred. In $\text{Fe}_{75}\text{Si}_{25}$, rapid grain growth began at 773 K in 30 minutes. All three ternary alloying additions inhibited grain growth but Al and Nb appeared to have a higher grain growth inhibiting effect than Cu.

Other transformations that occurred on annealing are:

- Formation of ordered DO_3 structure in $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ (at ≥ 773 K)
- Precipitation of Cu in $\text{Fe}_{75}\text{Si}_{15}\text{Cu}_{10}$ (at ≥ 773 K)
- Precipitation of Fe_2Nb in $\text{Fe}_{75}\text{Si}_{15}\text{Nb}_{10}$ (at ≥ 873 K)

Grain boundary segregation of alloying elements in the milled powders was thought to have produced a drag effect on boundary migration. Removal of this segregation by ordering reactions in the matrix or by second phase precipitation may be the reason for rapid grain growth to occur above an annealing temperature.

6.2 Ordering and De-segregation in $\text{Fe}_{75}\text{Si}_{25}$

The as-milled $\text{Fe}_{75}\text{Si}_{25}$ powder was nanocrystalline with an average grain size of 14.5 nm and lattice parameter of 0.2842 nm. On annealing, several changes were observed. These changes appear to depend on the annealing temperature range.

In the low temperature range of 577 - 703 K:

- grain growth was limited with some relaxation in internal stress;
- crystal structure remained disordered bcc-Fe(Si);
- lattice parameter decreased to about 0.2838 nm;
- activation energy for grain growth was 32.3 kJ mol^{-1} .

In the higher temperature range of 773 - 853K:

- rapid grain growth occurred and internal stress reduced to almost zero;
- crystal structure became DO_3 ordered with LRO parameter reaching 0.9;
- lattice parameter decreased to 0.2831 nm;
- activation energy for grain growth was $303.8 \text{ kJ mol}^{-1}$.

The ordering transformation which occurs at about 773 K caused GB desegregation of Si and triggered grain growth. Our estimation shows that GB solute

concentration reduces by a factor of approximately 4 when ordering occurs thereby relaxing the drag effect on boundaries leading to grain growth.

The as-milled $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ powder was nanocrystalline with an average grain size of about 13 nm and lattice parameter of about 0.2862 nm. On annealing, several changes were observed. These changes appear to depend on the annealing temperature range also.

In the low temperature range of 577 - 703 K:

- grain growth was limited with some relaxation in internal stress;
- crystal structure remained disordered bcc-Fe(Si);
- lattice parameter decreased to about 0.2857 nm;
- activation energy for grain growth was 37.2 kJ mol^{-1} .

In the higher temperature range of 773 - 853K:

- rapid grain growth did not occur;
- internal strain continued to relax
- crystal structure became DO_3 ordered with LRO parameter reaching 0.6;
- lattice parameter decreased to 0.2850 nm;

activation energy for grain growth was 57.4 kJ mol^{-1} .

The activation energy determined using Michel's model of grain growth with impediment, shows that grain growth of $\text{Fe}_{75}\text{Si}_{25}$ after ordering is controlled by lattice diffusion of Si in the ordered DO_3 phase. The low values of activation energies in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ at high and low temperature regimes indicates that the ternary alloy is in a nonequilibrium state even in the high temperature regime, for which it is neither fully relaxed nor highly ordered.

The ordering transformation which occurs at about 773 K in $\text{Fe}_{75}\text{Si}_{25}$ causes GB de-segregation of Si and triggers grain growth. Existing models show that GB solute concentration reduces by a factor of approximately 6 when ordering occurs thereby relaxing the drag effect on boundaries leading to grain growth. However, in $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$, the prediction is a reduced solute de-segregation, even after ordering which continues to inhibit the grain growth even at high temperatures.

6.3 Sintering $\text{Fe}_{75}\text{Si}_{25}$ and $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$

In conventional pressureless sintering in a vacuum furnace for 1 hr in the temperature range 1333 – 1513 K, the grain size increased to 4600 – 4800 nm from the initial size of 15 nm for both compositions although, $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ showed consistently lower grain sizes. In comparison, SPS method resulted in grain sizes in the range 55 – 85 nm.

The grain size of $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ was consistently lower than that of $\text{Fe}_{75}\text{Si}_{25}$ after all sintering treatments. Hence, Al alloying contributes to grain growth inhibition in nanocrystalline $\text{Fe}_{75}\text{Si}_{25}$.

The relative densities of SPS products were in the range 75 -95 % for both compositions while for pressureless vacuum sintering they were 53 – 75 %. The $\text{Fe}_{75}\text{Si}_{15}\text{Al}_{10}$ alloy was consistently about 10% denser than $\text{Fe}_{75}\text{Si}_{25}$ for the same sintering treatment.

6.4 Magnetic Properties of Sintered Products

All products showed ferromagnetic behaviour. In all samples, the saturation induction increased as the sintering temperature increased irrespective of the sintering method. The SPS products always showed higher saturation induction when compared to the pressureless sintered products. This could be attributed to the effect of porosity. As porosity decreased, the saturation induction increased.

The coercivity was nearly constant in the conventionally sintered products but, in SPS products, the coercivity increased with increase of sintering temperature. This is attributed to grain growth effects since the grain sizes of SPS product are significantly smaller and thus the effect is large as coercivity $\propto D^n$.

Overall, the Al addition to $\text{Fe}_{75}\text{Si}_{25}$ has many beneficial effects, namely

- Reduced grain growth during sintering
- Increased sintered density
- Improved saturation induction of sintered products

The magnetic properties could be further optimized by better control of grain growth during sintering. Ideally, the grain size should be smaller than the “exchange length”, which is normally less than 30 nm [Herzer, G., 1997], to take full advantage of nanostructure in magnetic materials. Therefore, the grain size needs to be controlled within this range. This could not be achieved by Al ternary alloying and SPS densification. Alternative possibilities must be investigated.

6.5 Contribution to Fe-Si based Magnetic Materials.

The root cause for the concurrence of ordering and grain growth in $\text{Fe}_{75}\text{Si}_{25}$ was proven to be the removal of the solute drag effect. A semi-quantitative analysis of this effect has been carried out to confirm this hypothesis. The effect of Al addition on inhibiting the grain growth has also been semi-quantitatively analyzed and is probably due to a stronger segregation tendency of Al as compared with that of Si. Some high-density nanostructured compacts with grain size less than 100 nm and relative densities of about 95% were achieved using SPS, which indicates that it is possible to achieve high-density nanostructured bulk materials by controlling grain growth with a suitable addition and by using an advanced sintering process.

PUBLICATIONS

Journal Papers

1. *Production and Annealing of Nanocrystalline Fe-Si and Fe-Si-Al Alloy Powders*, Zuo, B., Saraswati, N., Sritharan, T., Hng, H.H., *Materials Science and Engineering A*, v 371, n 1-2, Apr 25, 2004, p 210-216.
2. *Ordering and Grain Growth in Nanocrystalline Fe₇₅Si₂₅ alloy*, Zuo, B., Sritharan, T., *Acta Materialia*, v 53, n 4, February, 2005, p 1233-1239.
3. *Effects of Ternary Alloying on Mechano-Synthesis and Nano-Crystal Stability of an Iron-Silicon Alloy*, Zuo, B., Sritharan, T., Teo, Y.B. and Damayanti, M., *Journal of Alloys and Compounds*, v 390, n 1-2, Mar 22, 2005, p 82-87.
4. *Production and Grain Stability of Nanocrystalline Fe-Si Powders and the Effects of Aluminum Addition*, Zuo, B., Saraswati, N., Sritharan, T., Hng, H.H., *International Journal of Nanoscience*, v 4, n 4, August, 2005, p 667-676.
5. *Sintering Behaviors and Magnetic Properties of Fe₇₅Si₂₅ and Fe₇₅Si₁₅Al₁₀ Alloys*, Zuo, B., Sritharan, T., in preparation.

Conference Papers

1. *High-Energy Ball Milled Nanostructured Magnetic Materials: A Review*, Zuo Biao, Thirumany Sritharan, Hng Huey Hoon, *1st International Conference on Materials Processing for Properties and Performance (MP3)*, 2002, p302.
2. *Production and Grain Stability of Nanocrystalline Fe-Si Powders and the Effects of Aluminum Addition*, B. Zuo, N. Saraswati, T. Sritharan*, H. H. Hng, *Nanotech 2004 - The 1st International Conference on Nanotechnology*, 2004, p245.
3. *Thermal Behavior of Nanocrystalline Fe₇₅Si₂₅ Alloy Produced by Mechanical Alloying*, Zuo, B. and Sritharan, T., *The Thirteenth International Conference on Processing and Fabrication of Advanced Materials. (PFAM XIII)*, 2004, p465.
4. *Grain Coarsening Behaviour of Nanocrystalline Fe-Si-X Powders*, Sritharan, T., Zuo, B., Hng, H.H., *Powder Metallurgy World Congress & Exhibition (PM2004)*, 2004, p 6.
5. *Grain Growth Study in a Mechanothesized Nanocrystalline Fe₇₅Si₂₅ Alloy*, Sritharan, T., Zuo, B., *Proceedings of an International Conference on Solid-Solid Phase Transformations in Inorganic Materials 2005*, v 2, *Proceedings of an International Conference on Solid-Solid Phase Transformations in Inorganic Materials 2005*, 2005, p 917.

REFERENCES

- Alben, R., Becker, J.J., Chi, M.C., Random anisotropy in amorphous ferromagnets, 1978, J. Appl Phys, **49**, 1653-1658.
- Alben, R., Budnick, J. and Cargill, G.S., in Metallic Glasses. ASM, Metals Park, OH, 1978, p.304.
- Ando, S., Mine, Y., Takashima, K., Itoh, S. and Tonda, H., Explosive compaction of Nd-Fe-B powder , 1999, J. Mater. Proc. Tech., **85**, 142-147.
- Atkinson, H.V., Theories of normal grain growth in pure single phase systems, 1988, Acta Metall. **36**, 469-491.
- Averback, R.S., Hofler, H.J., Tao, R., Processing of nano-grained materials, 1993, Mater. Sci. Eng. A **166**, 169-177.
- Backker, H., Zhou, G.F., Yang, H., Mechanically driven disorder and phase transformations in alloys, 1995, Prog. Mater. Sci., **39**, 159-241.
- Benjamin, J.S., Mechanical alloying: A perspective, 1990, Metal Powder Report, **45**, 122-127.
- Boylan, K., Ostrander, D., Erb, U., Palumbo, G., Aust, K.T., In-situ tem study of the thermal stability of nanocrystalline Ni-P, 1991, Scripta Metall Mater, **25**, 2711-2716.
- Birringer, R., Gleiter, H., Klein, H. -P. and Marquardt, P., Nanocrystalline materials an approach to a novel solid structure with gas-like disorder, 1984, Phys. Lett. **102**, 356-359.
- Burke, J.E., Some factors affecting rate of grain growth in metals, 1949, Am. Inst. Min. Eng., **1**, 881-886.

-
- Buschow, K.H.J., Amorphous alloys, 1985, Journal of the Less Common Metals, **110**, 205-223.
- Cahn, J.W., The impurity-drag effect in grain boundary motion, 1962, Acta Metall., **10**, 789-798.
- Cahn, R.W., Lattice parameter changes on disordering intermetallics, 1999, Intermetallics, **7**, 1089-1094.
- Cao, P., Lu, L., Lai, M.O., Grain growth and kinetics for nanocrystalline magnesium alloy produced by mechanical alloying, 2001, Mater. Res. Bull., **36**, 981-988.
- Chandra, R., Taneja, P., John, J., Ayyub, P., Dey, G.K., Kulshreshtha, S.K., Synthesis and TEM Study of nanoparticles and nanocrystalline thin films of silver by high pressure sputtering, 1999, NanoStruct Mater. **11**, 1171-1179.
- Chang, Y.J., An electron microscopic investigation of order-disorder transformation in a Fe-Si-Al alloy and of its dislocation configurations, 1982, Acta Metall., **30**, 1185-1192.
- Charap, S.H., Lu, P.-L. and He, Y., Thermal stability of recorded information at high densities, 1997, I.E.E.E. Trans. Magn., **33**, 978-983.
- Chen, C.-W., Magnetism and Metallurgy of Soft Magnetic Materials (Dover, New York, 1986), section 4.2.
- Chen, L.C. and Spaepen, F., Calorimetric evidence for the microquasicrystalline structure of 'amorphous' Al/transition metal alloys, 1988, Nature, **336**, 366-368.
- Chen, I.W. and Wang, X.H., Sintering dense nanocrystalline ceramics without final-stage grain growth, 2000, Nature, **404**, 168-71.
- Cullity, B.D., 1978, Elements of X-ray Diffraction, Reading, Mass.: Addison-Wesley Pub. Co.

-
- Dadras, M.M. and Morris, D.G., Mechanical disordering of Fe-28%Al-4%Cr alloy, 1993, Scripta. Metall. Mater. **28**, 1245-1250.
- Dijkstra, L.J. and Wert, C., Effect of inclusions on coercive force of iron, 1950, Phys. Rev., **79**, 979-985.
- Ding, J., Li, Y., Chen, L.F., Deng, C.R., Shi, Y., Chow, Y.S. and Gang, T.B., Microstructure and soft magnetic properties of nanocrystalline Fe-Si powders, 2001, J. Alloys and Comp. **314**, 262-267.
- Eckert, J., Holzer, J.C., Krill, C.E. and Johnson, W.L., Thermal stability and grain growth behavior of mechanically alloyed nanocrystalline Fe-Cu alloys, 1993, J. Appl. Phys. **73**, 131-41.
- Eckert, J., Relationships governing the grain size of nanocrystalline metals and alloys, 1995, NanoStruct. Mater. **6**, 413-416.
- Eckert, J., Holzer, J.C., Krill, C.E. and Johnson, W.L., Structural and thermodynamic properties of nanocrystalline fcc metals prepared by mechanical attrition, 1992, J. Mater. Res. **7**, 1751-1761.
- Erb, U., Electrodeposited nanocrystals: synthesis, properties and industrial applications, 1995, NanoStruct. Mater. **6**, 533-538.
- Farquar, M.C., Lipson, H. and Weill, A.R., 1945, J Iron Steel Inst. **152**, 457.
- Fecht, H.-J., Nanostructure formation by mechanical attrition, 1995, NanoStruct. Mater. **6**, 33-42.
- Fecht, H.J., Hellstern, E., Fu, Z., and Johnson, W.L., Nanocrystalline metals prepared by high-energy ball milling, 1990, Metall. Trans. *A*. **21**, 2333-2337.
- Fultz, B. and Frase, H.N., Grain boundaries of nanocrystalline materials-their widths, compositions and internal structures, 2000, Hyperfine Interactions, **130**, 81-108.

-
- Ganapathi, S.K., Owen, D.M. and Chokshi, A.H., Kinetics of grain growth in nanocrystalline copper, 1991, Scripta Metall. Mater., **25**, 2699-2704.
- Gao, Z. and Fultz, B., The thermal stability of nanocrystalline Fe-Si-Nb prepared by mechanical alloying, 1993, NanoStruct. Mater. **2**, 231-240.
- Gayle, F.W. and Biancaniello, F.S., Stacking faults and crystallite size in mechanically alloyed Cu-Co, 1995, NanoStruct. Mater. **6**, 429-432.
- Gertsman, V.Y. and Birringer, R., On the room-temperature grain growth in nanocrystalline copper, 1994, Scripta Metall. Mater., **30**, 577-581.
- Gibbs, J.W., in The Collected Works of J.W. Gibbs, Vol. I. Longmans, Green, New York, 1928, p. 55.
- Gleiter, H., 1972, Prog. Mater. Sci., **16**, 138.
- Graham, C.D. and Egami, T., Magnetic properties of amorphous alloys, 1980, J. Magn. Magn. Mater., **15-18**, 1325-30.
- Grvaznov, V.G., Polonskv, I.A., Romanov, A.E. and Trusov, L.I., Size effects of dislocation stability in nanocrystals, 1991, Phys. Rev. B, **44**, 42-46.
- Guo, W.H. and Kui, H.W., Bulk nanostructured alloy formation with controllable grain size, 2000, Acta Mater. **48**, 2117-2121.
- Hahn, H., Microstructure and properties of nanostructured oxides, 1993, NanoStruct. Mater. **2**, 251.
- Hahn, H., Logas, J. and Averbach, R.S., Sintering characteristics of nanocrystalline TiO₂, 1990, J. Mater. Res., **5**, 609-614.
- Handwerker, C.A., Blendell, J.E. and Coble, R.L., in Science of Sintering, ed. Uskovic, D.P., Palmour, H. and Spriggs, R.M., Plenum Press, New York, 1989, p. 3.

-
- Heikinheimo, E., Kodentsov, A.A. and Vanloo, F.J.J., Interdiffusion in Ordered and Disordered Fe(Si) Solid Solution, 1998, Scripta Mater., **38**, 1229-1235.
- Herzer, G., Grain Size dependence of coercivity and permeability in nanocrystalline ferromagnets, 1990, I.E.E.E Trans. Magn. **26**, 1397-1402.
- Herzer, G., in Handbook of Magnetic Materials, ed. Buschow, K.H.J., Vol. 10, Chap. 3, Elsevier Science, Amsterdam, 1997, p. 415.
- Hines, W.A., Menotti, A.H., Budnick, J.I., Burch, T.J., Litrenta, T., Niculescu, V. and Raj, K., Magnetization studies of binary and ternary alloys based on Fe₃Si, 1976, Phys. Rev. B, **13**, 4060-4068.
- Hockel, P.G. and Weissmuller, J., Precipitation in nanocrystalline Al-Ag prepared by inert gas condensation and by mechanical alloying, 1996, Scripta Mater. **35**, 647-653.
- Hoefer, H.J. and Averbach, R.S., Grain growth in nanocrystalline TiO₂ and its relation to vickers hardness and fracture toughness, 1990, Scripta Metal, **24**, 2401-2406.
- Hondros, E. D. and Seah, M.P., in Physical Metallurgy, 3rd edn, ed. Cahn, R.W. and Haasen, P., Elsevier, Amsterdam, 1983, p. 855.
- Hondros, E.D., Seah, M.P., Hofmann, S. and Lejček, P., in: Cahn, R.W., Haasen, P. (Eds.), Physical Metallurgy, fourth ed., North-Holland, Amsterdam, 1996, p. 1201.
- Hondros, E.D., Seah, M.P., Hofmann, S. and Lejček, P., in: Cahn, R.W., Haasen, P. (Eds.), Physical Metallurgy, fourth ed., North-Holland, Amsterdam, 1996, p. 1284.

-
- Huang, J.Y., Wu, Y.K., He, A.Q. and Ye, H.Q., Direct evidence of nanocrystal enhanced complete mutual solubility in mechanically alloyed Co---Cu powders, 1994, Nanostruct. Mater., **4**, 293-302.
- Iordache, M.C., Whang, S.H., Jiao, Z., and Wang, Z.M., Grain growth kinetics in nanostructured nickel, 1999, NanoStruct. Mater. **11**, 1343-1349.
- Isonishi, K. and Okazaki, K., Grain growth in nanocrystalline NbAl₃ prepared by mechanical alloying, 1993, J. Mater. Sci., **28**, 3829-34.
- Jiang, H.G., Hu, H.M. and Lavernia, E.J., Synthesis of Fe-rich Fe-Al nanocrystalline solid solutions using ball milling, 1999, J. Mater. Res., **14**, 1760-1770.
- Jiang, J.Z., Anomalous grain growth in nanocrystalline Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉ alloys, 1997, NanoStruct. Mater. **9**, 245-248.
- Jiles, D., Introduction to magnetism and magnetic materials. London: Chapman & Hall, 1991, P. 185.
- Johnson, D.L., Rusin, R.P. and Hansen, J.D., Application of a new sintering model, 1992, Advances in Powder Metallurgy. **3**, 17-24.
- Jung, Y.G., Ha, C.G., Shin, J.H., Hur, S.K. and Paik, U., Fabrication of functionally graded ZrO₂/NiCrAlY composites by plasma activated sintering using tape casting and it's thermal barrier property, 2002, Mater. Sci. Eng. A. **323**, 110-118.
- Kawanishi, S., Isonishi, K. and Okazaki, K., Grain growth and its kinetics of nanophase niobium aluminide produced by mechanical alloying, 1993, Mat. Trans. JIM, **34**, 49-53.
- Kear, B.H., and Strutt, P.R., Chemical processing and applications for nanostructured material, 1995, NanoStruct. Mater. **6**, 227-236.
- Kittel, C., Physical theory of ferromagnetic domains, 1949, Rev. Mod. Phys., **21**, 541-591.

-
- Klug, H.P., Alexander, L., X-ray diffraction procedures for polycrystalline and amorphous materials. 2nd ed. New York: John Wiley & Sons, 1974, [chapter 9]. P. 618-708.
- Knauth, P., Charai, A. and Gas, P., Grain growth of pure nickel and of a Ni-Si solid solution studied by differential scanning calorimetry on nanometer-sized crystals, 1993, Scripta Metal. Mater. **28**, 325-330.
- Koch, C.C., The synthesis and structure of nanocrystalline materials produced by mechanical attrition: a review, 1993, NanoStruct. Mater. **2**, 109-129.
- Koch, C.C., Synthesis of nanostructured materials by mechanical milling: problems and opportunities, 1997, NanoStruct. Mater. **9**, 13-22.
- Koch, C.C., Nanostructured materials: processing, properties and potential applications, 2002, Noyes Publications, Norwich, NY.
- Kojima, A., Ogiwara, F., Makino, A., Inoue, A. and Masumoto, T., Microstructure of nanocrystalline Fe-Nd-Pr-B alloys produced by crystallization of amorphous phase, 1997, Mater. Sci. Eng. A **226-228**, 520-525.
- Kornelyuk, L., Lozovoi, A.Y. and Razumovskii, I.M., Enhancement of diffusion in deformation-induced non-equilibrium grain boundaries, 1998, Philosophical Magazine A, **77**, 465-474.
- Krill, C.E., Klein, R., Janes, S. and Birringer, R., Thermodynamic stabilization of grain boundaries in nanocrystalline alloys, 1995, Mater. Sci. Forum, **179-181**, 443-448.
- Kubaschewski, O., Iron-Binary Phase Diagrams. Springer-Verlag. NY. 1982. p. 136.
- Kuhrt, C. and Schultz, L., Formation and magnetic properties of nanocrystalline mechanically alloyed Fe-Co and Fe-Ni, 1993, J. Appl. Phys. **73**, 6588-6590.

-
- Kuhrt, C. and Schultz, L., Formation and magnetic properties of nanocrystalline mechanically alloyed Fe-Co, 1991, *J. Appl. Phys.* **71**, 1896-1900.
- Kumpmann, A., Guenther, B. and Kunze, H.-D., Thermal stability of ultrafine-grained metals and alloys, 1993, *Mater. Sci. Eng. A* **168**, 165-169.
- Lai, M.O. and Lu, L., *Mechanical alloying*, Kluwer Academic Publishers, Boston, MA (1998).
- Lall, C., *Soft Magnetism*, Metal Powder Industries Federation, Princeton, New Jersey (1992).
- Lecaude, N. and Perron, J.C., Nanocrystallization mechanisms in Finemet-type alloys from calorimetric studies, 1997, *Mater. Sci. Eng. A* **226-228**, 581-585.
- Lee, S.H., Moon, K.I., Hong, H.S. and Lee, K.S., Microstructural and mechanical properties of nanocrystalline (Al + 12.5 at.%Cu)₃Zr alloys synthesized by planetary ball milling and spark plasma sintering, 2003, *Intermetallics*, **11**, 1039-1045.
- Lee, P.Y., Yang, J.L. and Lin, H.M., Amorphization behaviour in mechanically alloyed Ni-Ta powders, 1998, *J. Mater. Sci.* **33**, 235-239.
- Lejček, P. and Schneeweiss, O., Solute segregation at ordered grain boundaries, 2001, *Surf. Sci.*, **487**, 210-222.
- Lejček, P. and Fraczkiewicz, A., Boron segregation in intermetallics: on the possible origins of a low-level intergranular segregation, 2003, *Intermetallics*, **11**, 1053.
- Liu, K.W. and Mucklich, F., Thermal stability of nano-RuAl produced by mechanical alloying, 2001, *Acta Mater.*, **49**, 395-403.
- Lu, K., 1993, The thermal instability of nanocrystalline Ni-P materials with different grain sizes, *Nanostruct. Mater.*, **2**, 643-652.

-
- Lu, P.-L. and Charp, S.H., Thermal instability at 10 Gbit/in² magnetic recording, 1994, I.E.E.E. Trans. Magn., **30**, 4230-4232.
- Makino, A., Inoue, A. and Masumoto, T., Nanocrystalline soft magnetic Fe-M-B (M = Zr, Hf, Nb) alloys produced by crystallization of amorphous phase (overview), 1995, Mat. Trans. JIM, **36**, 924-938.
- Malow, T.R. and Koch, C.C., Grain growth in nanocrystalline iron prepared by mechanical attrition, 1997, Acta Mater, **45**, 2177-2186.
- Marlow, T.R. and Koch, C.C., in Synth. and Proc. of Nanocryst. Mat., ed. D. L. Bourell. TMS, Warrendale, PA, 1996, p. 33.
- Maurice, D and Courtney, T.H., Milling dynamics: Part III. Integration of local and global modeling of mechanical alloying devices, 1996, *Metall. Mater. Trans.*, **A27**, 1981-1986.
- Mayo, M.J., Hague, D.C. and Chen, D.-J., Processing nanocrystalline ceramics for applications in superplasticity, 1993, Mater. Sci. Eng. A **166**, 145-159.
- McCurrie, R.A., Ferromagnetic Materials Structure and Properties, ACADEMIC PRESS INC, San Diego, CA, 1994, p. 35.
- McHenry, M.E., Willard, M.A. and Laughlin, D.E., Amorphous and nanocrystalline materials for applications as soft magnets, 1999, Prog. Mater. Sci., **44**, 291-433.
- Meyers, M.A., Benson, D.J. and Fu, H.H., in: Advanced Materials for the 21st century, The Minerals, Metals, and Materials Society, Warrendale, PA, 1999, p. 499.
- Michels, A., Krill, C.E., Ehrhard, H., Birringer, R. and Wu, D.T., Modelling the influence of grain-size-dependent solute drag on the kinetics of grain growth in nanocrystalline materials, 1999, Acta Mater., **47**, 2143-2152.

-
- Michels, A., Krill, C.E., Natter, H. and Birringer, R., in Grain growth in polycrystalline materials III, ed. H. Weiland, B. L. Adams and A. D. Rollett. The Minerals, Metals and Materials Society, Warrendale, PA, 1998, p. 449-454.
- Miyazaki, M., Ichikawa, M., Komatsu, T. and Matusita, K., Formation and electronic state of DO₃-type ordered structure in sputtered Fe-Si thin films, 1992, J. Appl. Phys., **71**, 2368-2374.
- Moyer, K.H., McDermott, M.J., Topolski, M.J. and Kearney, D.F., "Magnetic properties of Iron Alloys", Magnetic and Electrical P/M Seminar, Metal Powder Industries Federation, Princeton, NJ, 1980, pp. 37.
- Murty, B.S., Joardar, J. and Pabi, S.K., Influence of Fe and Cr on the disordering behavior of mechanically alloyed NiAl, 1996, Nanostruct. Mater., **7**, 691-697.
- Nave, R., 2001, <http://hyperphysics.phy-astr.gsu.edu/hbase/solids/magpr.html>.
- Nieh, T.G. and Wadsworth, J., Hall-Petch relation in nanocrystalline solids, 1991, Scripta Metal. Mater. **25**, 955-958.
- Omori, M., Sintering, consolidation, reaction and crystal growth by the spark plasma system (SPS), 2000, Mater. Sci. Eng. A, **287**, 183-188.
- Pochet, P., Tominez, E., Charon, L. and Martin, G., Order-disorder transformation in Fe-Al under ball milling, 1995, Phys. Rev. B, **52**, 4006-4017.
- Randle, V. and Ralph, B., Interactions of grain boundaries with coherent precipitates during grain growth, 1986, Acta Metall., **34**, 891-898.
- Ryu, J.R., Moon, K.I., Lee, K.S., Microstructure and mechanical properties of nanocrystalline Al-Ti alloys consolidated by plasma activated sintering, 2000, J. Alloys and Comp. **296**, 157-165.
- Salamon, D., Shen, Z.J. and Šajgalík, P., 2007, Journal of the European Ceramic Society, **27**, 2541-2547.

-
- Salamon, M. and Mehrer, H., Diffusion in the B20-type phase FeSi, 1999, Philosophical Magazine A, **79**, 2137-2155.
- Schwarz, R.B., Desch, P.B., Srinivasan, S., Nash, P., Synthesis and properties of trialuminides with ultrafine microstructures, 1992, NanoStruct. Mater. **1**, 37.
- Shukla, S., Seal, S., Vij, R. and Bandyopadhyay, S., 2003, Nano Letters, **3**, 397.
- Skandan, G., Processing of nanostructured zirconia ceramics, 1995, NanoStruct. Mater. **5**, 111-126.
- Smith, C.S., 1948, Trans. Am. Inst. Min. Engrs, **175**, 15.
- Spassov, T., Koster, U., Grain-growth in nanocrystalline zirconium-based alloys, 1993, J. Mater. Sci., **28**, 2789-2794.
- Suryanarayana, C. and Froes, F.H., 1990, *J. Mater. Res*, **5**, 1880–1886.
- Suryanarayana, C., Chen, G.H. and Froes, F.H., 1992, *Scripta Metall. Mater*, **26**, 1727–1732.
- Suryanarayana, C., 2001, Mechanical alloying and milling, *Prog. Mater Sci.* **46**, 1-184.
- Szewczak, E., Paszula, J., Leonov, A.V., Matyja, H., Explosive consolidation of mechanically alloyed Ti-Al alloys, 1997, *Mater Sci. Eng. A* **226-228**, 115-118.
- Takahashi, M., Arai, H. and Wakivarna, T., Magnetostriction constants for Fe-Al-Si (senducst) single crystals with DO3 ordered structure, 1987, *I.E.E.E. Trans. Magn.*, **23**, 3523-3525.
- Tennent, R.M., Science data book, Oliver&Boyd, Hong Kong, 1971,.
- Tenwick, M. J. and Davies, H. A., 1984, *Int. J. Rapid. Sol.* **1**, 143-155.
- Terwilliger, C.D. and Chiang, Y.-M., Effect of calcium segregation on grain growth in nanocrystalline TiO₂, 1994, *NanoStruct. Mater.* **4**, 651-661.
- Terwilliger, C.D. and Chiang, Y.-M., Size-dependent solute segregation and total solubility in ultrafine polycrystals: Ca IN TiO₂, 1995, *Acta Metall.*, **43**, 319-328.

-
- Thompson, J.R. and Politis, C., Formation of amorphous Ti-Pd alloys by mechanical alloying methods, 1987, *Europhysics Letters*, **3**, 199-205.
- Trudeau, M., Nanocrystalline Fe and Fe-riched Fe-Ni through electrodepositon, 1999, *NanoStruct. Mater.* **12**, 55-60.
- Veprek, S., Nesladek, P., Niederhofer, A., Maennling, H. and Jilnek, M., TMS Annual Meeting 1999, San Diego, CA, February/March 1999, Invited Paper.
- Weissmueller, J., in *Synthesis and Processing of Nanocrystalline Powder*, ed. D. L. Bourell. TMS, Warrendale, PA, 1996, p. 3.
- Weissmueller, J., Krauss, W., Haubold, T., Birringer, R. and Gleiter, H., Atomic structure and thermal stability of nanostructured Y-Fe alloys, 1992, *Nanostruct. Mater.*, **1**, 439.
- Weissmueller, J., Some basic notions on nanostructured solids, 1994, *Mater Sci. Eng. A* **179-180**, 102-107.
- Wiechert, W., Mournier, H. and Hoppe, D., 2nd IMACS Symposium on Mathematical Modeling MATHMOD 2, Vienna, Feb. 2-4, 2000, pp. 685-690.
- Williamson, G.K., Hall, W.H., 1953, *Acta Metall.*, **1**, 22-31.
- Wissmueller, J., Alloy effects in nanostructures, 1993, *Nanostruct. Mater.*, **3**, 261.
- Yamazaki, K., Risbud, S. H., Aoyama, H. and Shoda K., 1996, *J. Mater. Proc. Tech.*, **56**, 955-965.
- Yoshizawa, Y., Oguma, S., and Yamauchi, K., New Fe-based soft magnetic alloys composed of ultrafine grain structure, 1988, *J. Appl. Phys.*, **64**, 6044-6046.

APPENDICES

Appendix A

X-ray diffraction profiles in JCPDS Database:

Card No : 60696
Elements : Fe
Mineral name : Iron
Crystal system : Cubic
Lattice constants : a = 2.8664 Ang

Peak	h	k	l	Indensity	Cu
1	1	1	0	100	44.671
2	2	1	1	30	82.329
3	2	0	0	20	65.018
4	3	1	0	12	116.378
5	2	2	0	10	98.94
6	2	2	2	6	137.125

(A1)

Card No : 271402
 Elements : Si
 Mineral name : Silicon
 Crystal system : Cubic
 Lattice constants : $a = 5.43088 \text{ \AA}$

Peak	h	k	l	Intensity	Cu
1	1	1	1	100	28.441
2	2	2	0	55	47.3
3	3	1	1	30	56.118
4	4	2	2	12	88.022
5	3	3	1	11	76.374
6	6	2	0	8	127.532
7	5	3	1	7	114.08
8	4	0	0	6	69.127
9	5	1	1	6	94.943
10	4	4	0	3	106.709
11	5	3	3	3	136.879

(A2)

Card No : 40787
Elements : Al
Mineral name : Aluminum
Crystal system : Cubic
Lattice constants : $a = 4.0494 \text{ \AA}$

Peak	h	k	l	Intensity	Cu
1	1	1	1	100	38.471
2	2	0	0	47	44.737
3	3	1	1	24	78.224
4	2	2	0	22	65.131
5	3	3	1	8	112.035
6	4	2	0	8	116.562
7	4	2	2	8	137.444
8	2	2	2	7	82.432
9	4	0	0	2	99.072

(A3)

Appendix B

The volume V and surface area A^{GB} of a tetrakaidecahedral crystal are

$$V = 8\sqrt{2}a^3 \quad (A1)$$

and

$$A^{GB} = (6 + 12\sqrt{3})a^2 \quad (A2)$$

where a is the edge length of the tetrakaidecahedron. In polycrystalline materials, the edge length

$$a = 0.592\langle L \rangle \quad (A3)$$

where $\langle L \rangle$ is the mean intercept length in space, and it can be expressed in spatial diameter (grain size) as:

$$\langle L \rangle = \frac{2}{\pi}D \quad (A4)$$

Substituting Eqn. A4 into A3, we obtain

$$a = 0.377D \quad (A5)$$

Therefore, the volume V and surface area A^{GB} in terms of the grain size D are:

$$V = 8\sqrt{2}(0.377D)^3 = 0.606D^3 \quad (A6)$$

$$A^{GB} = (6 + 12\sqrt{3})(0.377D)^2 = 3.807D^2 \quad (A7)$$

Substituting Eqns. A6 and A7 into Eqn. 16, we get

$$\chi^{GB} = \frac{3.14\delta}{D}$$

Appendix C

The powders below from “American Elements” were used for this project:

Fe (99.9 wt.%, -100 mesh, <149 micron)

Si (99.95 wt.%, -325 mesh, <44 micron)

Al (99.95 wt.%, -325 mesh, <44 micron)

Cu (99.95 wt.%, -100 mesh, <149 micron)

Nb (99.9 wt.%, -100 mesh, <149 micron)