Magnetism of Nanocrystallized Amorphous Fe$_{75}$B$_{10}$Si$_{15}$

Arnab Chakraborty

KTH | Tmfy-MSE

Thesis Advisors:
Prof. K. V. Rao
Dr. L. Belova

Dec – 2012

School of Industrial Engineering and Management (ITM)
Department of Material Science and Engineering (MSE)
Royal Institute of Technology (KTH)
SE-100 44 Stockholm
The loom of time and space works the most astonishing transformations of matter.

Carl E. Sagan
“Cosmos” (1980)

From a long view of the history of mankind there can be little doubt that the most significant event of the nineteenth century will be judged as Maxwell’s discovery of the laws of electrodynamics.

Richard P. Feynman
“The Feynman Lectures in Physics” (1964)
Magnetism of Nanocrystallized Amorphous Fe$_{75}$B$_{10}$Si$_{15}$

Arnab Chakraborty
Acknowledgments

This thesis work has been performed at the Department of Materials Science and Engineering, Tmfy-MSE, at the Royal Institute of Technology in Stockholm, Sweden; under the supervision of Prof. K.V. Rao and Dr. L. Belova.

I thank Prof. Rao for this opportunity, and his guidance - firm at all times, was what helped me understand and learn. He has always demanded the highest quality of understanding and work, which I respect. I thank Dr. Belova for her support despite her busy schedule, and for training me in technique and theory of Scanning Electron Microscopy (SEM). It is not every day that one has the opportunity to work with scientists of such calibre - and this, has been an honor.

I thank Dr. Ansar Masood, for always guiding me; with his wealth of experience - I benefited greatly in my work. He taught me, with utmost patience, all the experimental techniques necessary for this work: Arc-remelting, Rapid Quenching, X-Ray Diffraction, Vibrating Sample Magnetometry, and Magneto-thermogravimetry. This work would go nowhere without his support and expertise.

I thank Sreekanth K.M., for his unflinching support in every aspect of my work in the Lab. I have had discussions on magnetism, thin-films, and even politics with him. He has been a friend, and a brother.

I thank Dr. Välter Ström, for his fluid grasp of instruments, for introducing the technique of Annealing to me, and for the highly constructive discussions - which he fostered.

I thank my colleagues at the Lab, Maryam Beyghazhi, Dr. Zhiyong Quan, Dr. Sandeep Nagar, Anastasiia Riazanova, Venkatesan Dhanasekharan, and Dr. Fang Mei for making the Laboratory a place where work was always fun.

I also must mention Dr. Pavel Korzhavyi, Dr. Anders Elliason, and Prof. Pär Jönsson - who have indirectly contributed to my academic achievements, in numerous ways.

I thank my friends and benefactors, especially Vikram Asher, Sumit Kumar and Pankaj Bhat.

I thank my family - my mother Ila Chakraborty and my sister Amrita Chakraborty, they have raised me, sacrificed for me, and loved me at all times - much of what I have done, is possible due to them.

I especially thank Neetu Sharma; without her unwavering love, and without her assistance - I’d not have reached here. To her, I am indebted.

I thank Shuchita Soman. In my short stroll between birth and quietus - she is bliss.

This effort is dedicated to these four remarkable individuals.

“Don’t let the sun go down without saying thank you to someone, and without admitting to yourself that absolutely no one gets this far alone.”
— Stephen King
Magnetism of Nanocrystallized Amorphous Fe$_{75}$B$_{10}$Si$_{15}$

Abstract

Amorphous ribbons of alloy composition Fe$_{75}$B$_{10}$Si$_{15}$ are cast by melt spinning and annealed to partially nanocrystalline states. The magnetic properties are investigated by VSM and MTGA. Structure is examined using XRD and SEM. Results obtained show nanostructured material with excellent soft magnetism in samples annealed at temperatures below the crystallization temperature as well as enhancement of magnetic hardness for annealing at high temperatures. This validates Herzer’s Random Anisotropy model of magnetism in nanostructured materials and provides basis for further inquiry into tweaking alloy compositions and/or manipulating annealing parameters. Also, increase of Curie temperature is noted with respect to increasing annealing temperatures arising from stress relaxation, validating a study on the relationship between the two.

**keywords:** amorphous metals, nanocrystalline materials, magnetism, soft magnetic material

arnab chakraborty [arnab@kth.se]
# Contents

Acknowledgments vi
Abstract vii
Contents ix
Preface 1

1. Introduction 3
   1.1 Magnetism
      - Mechanism of magnetism
      - Types of Magnetism and their properties
      - Types and properties of ferromagnetic materials
      - Models explaining ferromagnetism in materials
   1.2 Amorphous Alloys 10
      - History: 1960 to present
      - Basic classification, science
      - Preparation and properties
      - Applications: Scope, in general
      - Applications: Magnetic & Electrical
   1.3 Nanocrystalline Materials 19
      - History and Research on nanocrystalline materials
      - Fe-based soft-magnetic nanostructured alloys

2. Experimental Work 24
   2.1 Characterization Techniques
      - X-Ray Diffractometer (XRD)
      - Scanning Electron Microscope (SEM)
      - Vibrating Sample Magnetometer (VSM)
      - Magneto-Thermogravimetric Analyzer (MTGA)
   2.2 Fabrication and Experiments 30
      - Ingot Preparation using the DC Arc Remelter (DCR)
      - Melt Spinning using the Controlled Rapid Quenching Machine (CRQM)
      - Annealing using the Mini Infrared Lamp Annealer (MILA)
      - Experimental Parameters

3. Results and Discussions 34
   3.1 Analysis
      - XRD Analysis
      - SEM Analysis
      - VSM Analysis
      - MTGA Analysis
   3.2 Conclusion 41
      - Summary of Results
      - Future Scope

Bibliography XLV
Magnetism of Nanocrystallized Amorphous Fe$_{75}$B$_{15}$Si$_{15}$
Preface

Amorphous metallic alloys are unique in having no long range atomic order and thus are a new class of solids. The absence of crystalline defects and grain boundaries, allows for study of such materials for novel properties, viz. short range order, soft magnetism, high material strength, etc. It also opens up greater possibilities in applications in the fields of low corrosion materials, biomaterials, electronics and electrical engineering.

Recently, nanostructured materials derived from amorphous precursors have been of interest due to their magnetic properties. Especially from the applications point of view of voltage transformers, where low magnetostriction, higher resistivity and soft-magnetism are important, and such materials offer technological interest. The benefit of low coercivity offered by amorphous materials is offset by the loss of the extent of magnetization in such materials due to the lowered content of the ferromagnetic component: e.g. Iron.

Nanocrystallization offers an increase in the net saturation magnetization while keeping the coercivity low. For such tailoring of properties, an understanding of the nanostructured materials is a must. The purpose of this thesis is to study and understand the magnetic properties of such nanostructured alloy systems with respect to annealing parameters, the grain size and the crystalline volume fraction.

Of all amorphous alloys developed, Fe-based materials display high saturation magnetization, and excellent soft magnetic properties. It is expected that soft-magnetic properties first improve and then rapidly deteriorate upon nanocrystallization, as coercivity and remanence is enhanced.

For experimental work, we chose FeBSi was selected with a composition of – 75 at.% Fe, 10 at.% B, and 15 at.% Si. Melt-spun ribbons were produced and batches of samples were annealed and also fully devitrified. All samples were characterized for structural and magnetic properties.

This thesis is divided into three parts: Introduction, Experimental Work, and Results and Discussions. The Introduction discusses Magnetism, Amorphous Materials, and Nanostructured Materials.

"I embarked on this paper with the object of obtaining a general view of the nature of the metallic state. In the course of it, it was forced on me that the confusion which exists in this field is quite as much due to lack of systematic experimentation as to the intrinsic difficulties of theory."

- J. D. Bernal

[DOI: 10.1039/tf9292500367]
1. Introduction

1.1 Magnetism

*Mechanism of magnetism*

Modern technological devices rely on magnetism and magnetic materials; which include electrical power generators and transformers, electric motors, radio, television, telephones, computers, and components of sound and video reproduction systems. Iron, certain steels, and the naturally occurring mineral lodestone are well-known examples of materials that exhibit magnetic properties.

There have been great discoveries and experiments in Magnetism. From Zheng Gongliang and Shen Kua in 9th century China using the lodestone; Gilbert propounding that the Earth was itself a magnet and Descartes showing that magnetism was a purely physical phenomenon and not metaphysical; Bernoulli’s horseshoe magnet; Oersted and Ampère connecting electricity with magnetism; to Faraday’s conceptualization of fields in the 19th century. All of this finally led to the revolutionary equations of Maxwell – which unified electricity, magnetism and light.

All matter is influenced in varying degrees by the presence of a magnetic field. Magnetism is described best by the field generated by a moving electric charge and the building block of magnetism is the magnetic dipole thus formed. The simplest magnet therefore, is an electron with its intrinsic spin. Similarly, the orbital motion of an electron around its nucleus also contributes to the magnetic behavior of materials. The magnetic moment of an electron due to its spin, and directed along it, is given by the Bohr magneton \( \mu_B = e\hbar/2m_e \), where \( e \) is the charge of an electron, \( m_e \) is its mass and \( \hbar \) is the reduced Planck’s constant. It should be noted that due to spin, even the nucleus has a net magnetic moment – but being many orders of magnitude lesser than the moment due to electrons, it is generally disregarded.

Magnetic field is denoted by \( H \) and it induces magnetic flux; this magnetic induction is given by \( B \). They are related by \( B = \mu H \), where \( \mu \) is the permeability of the material in consideration. Permeability can be said to be the readiness of the material to carry magnetic flux and can be compared with the base value of permeability of free space \( \mu_0 \).

Magnetization \( M \), on the other hand, is the field a material generates by itself under the influence of the external field and therefore contributes to the induction. These terms are related by the relationship \( B = \mu H + \mu M \). Magnetization \( M \) is proportional to the field by the relation \( \chi_m = M/H \). Where \( \chi_m \) is the susceptibility – a unitless parameter related to permeability as \( \mu/\mu_0 = 1 + \chi_m \). Both permeability \( \mu \) and susceptibility \( \chi_m \) are dependent on the magnetic field \( H \).
Magnetism: types and properties

Since all matter is composed of atoms containing electrons, they all display magnetic characteristics. These can be classified into the following types:

Diamagnetism: In most matter, the spin and orbital motion get cancelled for pairs of electrons. Therefore, in individual atoms with fully filled electron shells or subshells, the total moment is zero – like in inert gases (e.g. Xenon - 5s² 4d¹⁰ 5p⁶). This arrangement is due to the Pauli Exclusion Principle, which forbids any sub atomic particle to have the same quantum state. This allows for a weak form of magnetism called Diamagnetism – in which the material generates an opposing field when subjected to an external field \( H \) as a manifestation of Lenz’s Law. This happens due to all dipoles in the material opposing the external magnetic field. For such materials, the relative permeability \( \mu_r \) given by \( \mu/\mu_0 \), is slightly less than one, and hence susceptibility \( \chi_m \) is negative. The diamagnetic response is present in all materials, but since it is very weak – it is detected only in the absence of other forms of magnetism.

Paramagnetism: When materials have unpaired electrons, a net magnetic moment due to the electron spin is associated with each atom (e.g. Aluminium - 3s² 3p² and Tantalum - 4f¹⁴ 6s² 5d³). When such a material is placed in a magnetic field \( H \), these moments align – causing a small positive magnetization \( M \), showing linear dependence. This is achieved at large fields, because these dipoles do not interact and no magnetization is retained. For such materials, the relative permeability \( \mu_r \) given by \( \mu/\mu_0 \), is one, or slightly more than one, and hence susceptibility \( \chi_m \) is positive.

---

† It should be noted that in certain materials, the atoms may have unpaired electrons in the s- or p- subshells (e.g. Bismuth - 5d¹⁰ 6s² 6p³ & Gold - 5d¹⁰ 6s¹). In such ‘solids’, the electrons are highly delocalized and hence the prevailing response is still diamagnetic – due to the phenomenon of ‘quenching’ – i.e. the diamagnetic response of the nearly highly localized d- subshell outweighing the paramagnetic response due to the valence electrons.†³
Ferromagnetism: Certain metallic materials possess a permanent magnetic moment in the absence of an external field, and manifest very large and permanent magnetization $M$. Relative permeability $\mu_r$ given by $\mu/\mu_0$, as well as susceptibility $\chi_m$ have large positive values dependent on the field $H$. This class of magnetism originates due to the un-cancelled electron spins with the valance electrons in the highly localized d- and f- subshells. It is thus observed in certain transition metals (Iron - 4s$^2$ 3d$^6$, Cobalt - 4s$^2$ 3d$^7$, Nickel - 4s$^2$ 3d$^8$) and in some rare-earth metals (e.g. Gadolinium - 4f$^7$ 5d$^1$ 6s$^2$, Dysprosium - 4f$^{10}$ 6s$^2$). At the level of the atom, increased stability of the atom is given by the lowest energy states, therefore unpaired electrons reside in different orbitals with parallel spins before pairing up with opposing spins – this is as per the Hund’s rule of maximum multiplicity. This results in the adding up of the dipole moments to give a net atomic magnetic moment. Ferromagnetic materials exhibit a long-range ordering at the atomic level that causes the unpaired electron spins to line up parallel with each other in a region called a domain. In the bulk of the solid, such domains are usually randomly oriented, in the absence of external magnetic fields to result in a null net-magnetization. In the presence of an external field $H$, these domains align themselves with the field and the material becomes ‘magnetized’. The maximum extent of such magnetization $M$ is called saturation magnetization $M_s$ and upon removal of the external field, the magnetization that is remembered by the material is called remnant magnetization $M_r$. This ‘memory’ is available only above a particular value of external field $H$, given by coercivity $H_c$. These three values, i.e. $M_s$, $M_r$, and $H_c$ are properties of the material. Such a property of retaining the magnetic history is called hysteresis.

The long-range order discussed here, is due to the interaction of the dipole moments of neighboring atoms. This expectation of symmetry is called the exchange interaction $J_{ex}$ dependent on the vector product of the atomic moments and an exchange constant $J$. It can be calculated as per different approximations or models. For ferromagnetic materials, the

---

1 Ferromagnetism is not just dependent on the chemistry of a material, but also on its crystalline structure and microscopic arrangement. There exist ferromagnetic metal alloys whose constituents are not ferromagnetic, called Heusler alloys, named after Fritz Heusler. Converse to that, there are non-magnetic alloys, such as certain stainless steels, that are composed almost entirely of ferromagnetic metallic materials. 5
value of the exchange constant $J$ (and therefore the interaction) is positive, and thus, the moments line up parallel.

The ordering of ferromagnetic materials is also dependent on temperature. Above a certain temperature, called the Curie temperature $T_C$, the long-range order abruptly ceases to exist. This temperature (related closely to the melting point) is where the thermal energy, given by $k_B T$ ($k_B$ is the Boltzmann constant) contributes to sufficient atomic agitation to counteract the exchange between adjacent atomic dipoles. Thus, above $T_C$, the material shows paramagnetic response. From this, it can also be deduced, that at $T = 0K$, saturation magnetization $M_s$ will be at its theoretical highest – due to a total lack of thermal agitation.

Antiferromagnetism: When the exchange constant $J$ and the vector product leading to the exchange interaction $J_{ex}$ discussed above has a negative value, the tendency of every atom is to align its magnetic moment anti-parallel to its neighboring atom. This gives rise to a null net magnetic moment within the material (e.g. Terbium - $4f^9 6s^2$ below 300K, Neodymium - $4f^4 6s^2$ below 20K).

Such materials also have an ordering temperature, above which the material shows paramagnetic response, this is called the Néel temperature $T_N$ and is analogous to the Curie temperature $T_C$.

Ferrimagnetism: Certain ceramic materials exhibit a permanent magnetization that is characterized by a lower positive relative permeability $\mu_r$ and distinct source of the net magnetic moment. This is similar to the case of antiferromagnetism, where the exchange constant $J$ is negative, except for the fact that the different constituent atoms of the material have unequal magnetic moments. In the lattice, one set of magnetic ions may align with, when another set of magnetic ions opposes an external field. This creates layers of opposing magnetization, which do not entirely cancel out. This results in a relatively smaller net magnetization $M$. These materials show the same dependence on temperature as ferromagnetic materials, and above the Curie temperature $T_C$, they show paramagnetic response. Also, being good insulators, they are attractive in high-frequency applications.

An example of a ferrimagnetic material is Magnetite Fe$^{2+}$O$^2−$ – (Fe$^{3+})_2 (O^2−)_3$, which is observed freely in nature and has an inverse-spinel crystal structure. Here, the Fe$^{2+}$ cations at octahedral sites are fully responsible for the net magnetic moment of the material as all the Fe$^{3+}$ cations at octahedral and tetrahedral sites have their individual moments arranged anti-parallel to each other.

Superparamagnetism: If the grain size of a ferro- or ferri- magnetic material drops below a certain size, the individual grains show a paramagnetic response. This size depends on the material e.g. 3-5nm for Magnetite Fe$_3$O$_4$ and 7-8nm for BCC $\alpha$-Fe (Iron) particles (isolated). This happens, as the entire grain itself has a single, aligned, large net magnetic moment, and thus the thermal energy of such a grain or the particle becomes comparable to the energy required by it to flip its single magnetic moment. Therefore, even at a temperature well
below the material’s Curie temperature $T_C$, the material shows a response similar to paramagnetism. This flipping of the moment has a time period of $t_N$, called the Néel relaxation time, which is dependent on the size and the temperature – for a given material. For a standard test time (say, $t_m$), if the particle size is kept constant, then at a particular temperature, called the blocking temperature $T_B$, the $t_N$ value becomes equal to $t_m$. Below this blocking temperature $T_B$, for the standard test time $t_m$, the measured magnetization is the spontaneous magnetization of the particle – and the particle appears to be blocked in its initial state. Above this blocking temperature $T_B$ however, the magnetization of the particle will flip several times during the standard test time $t_m$, and the measured magnetization will average to zero.

Superparamagnetism differs from paramagnetism, in that the material still has the very high susceptibility of the ferro- or ferri- magnetic material. This, and the properties discussed above lead to various applications in heat-assisted magnetic recording, ferrofluids, and even various biomedical applications.

![Fig. 3 (a) Bloch walls as places where magnetization changes (b) Change in domain structure with respect to applied field, showing magnetization](image)

In a discussion of magnetism, its properties of interest are Curie temperature, Hysteresis, Domain structure, Magnetic anisotropy energy, and Magnetostriction. Of these, Curie temperature $T_C$ and Hysteresis have been discussed above, in detail under ferromagnetism. Additionally, domain structure can be discussed in light of hysteresis. In all ferro- and ferri-magnetic materials below their Curie temperature $T_C$, there exists regions of tiny volumes with aligned magnetic dipole moments. These regions are called domains. Without an external field, all domains are oriented randomly in a way that reduces the total energy (magnetostatic) of the system – by closing flux-circuits within the bulk of the material. Therefore, macroscopically, the net magnetization of ferro- and ferri- magnetic materials is zero. The boundary between domains is called the Bloch walls. These are very narrow zones, where the direction of magnetization changes from one to another. With the application of an external field, domains align themselves to the applied field $H$, and show a net
magnetization $M$ depending on the field. This behavior is represented in the hysteresis loop – which is plotted as shown in the image above – with respect to domain structure. It has been postulated that the magnetization grows at the expense of neighboring domains via the movement of Bloch walls, and saturation $M_s$ is achieved when the entire material becomes a single domain and finally, that domain aligns with the applied field. The most remarkable proof of this is noted in tiny jumps in the hysteresis loop, called the Barkhausen effect, these jumps signify the movement of the Bloch wall past crystal imperfections, like inclusions and grain boundaries.

Magnetic anisotropy energy $K_u$ is the energy associated with ferro- and ferri- magnetic materials when their magnetization points in a particular crystallographic direction. This direction is called the easy axis, and rotating individual dipole moments from these preferred orientations leads to the orbital charge distribution of the atoms to assume a less compatible form with respect to the crystal structure. Therefore, saturation magnetization $M_s$ is achieved at lower coercivity $H_c$, when the applied field is parallel to the easy axis. This energy is lower in a cubic structure like BCC (e.g. $\alpha$-Fe, Iron), and higher in a uniaxial crystal structure, like HCP (e.g. $\alpha$-Co, Cobalt).

Magnetostriction $\lambda_s$ is the strain that is developed by certain materials when their magnetic state is changed; i.e. when the polarity of their magnetization is varied. This strain can be positive or negative (causing length increase or decrease respectively) along a particular crystallographic orientation and is closely related to the anisotropy – it is explained to be the strain that causes lowering of the magnetocrystalline anisotropy energy $K_u$.

**Types and properties of ferromagnetic materials**

Ferromagnetic materials can be broadly classified into soft and hard magnetic materials based on the hysteresis behavior exhibited by these materials. The key property that decides either soft or hard magnetic characteristic of the material is the magnetocrystalline anisotropy energy $K_u$, related to work done $E_a$ for orienting the magnetization vector from the easy axis, to the direction of applied field by an angle $\theta$, in the relationship given by $E_a = K_u \sin^2 \theta$. 

![Fig. 4 (a) Hysteresis of soft and hard magnetic materials (b) Various magnetic materials classified as per their softness/hardness](image-url)
In case of soft magnetic materials it is desirable to have minimum anisotropy whereas reverse is applicable for hard magnetic materials. Soft magnetic materials exhibit high initial permeability and low coercivity with high saturation in a hysteresis loop.\cite{1} In these materials, the area under the hysteresis curve representing the hysteresis loss $BH_{\text{max}}$ must be as low as possible as the sample can be magnetized and demagnetized at relatively low fields. Alloy systems, which exhibit soft magnetic characteristics, include pure Iron, Nickel, Cobalt, Fe-Si, Fe-Co, Fe-Ni alloys etc.\cite{7} These find application in magnetic shielding and largely in power transmission and AC appliances.

On the other hand, hard magnetic materials possess high coercivity $H_c$ with the remanence $M_r$ almost same as saturation $M_s$ in a hysteresis loop. Their high magnetic anisotropy energy $K_u$ prevents them from being demagnetized easily. These make for permanent ‘magnets’. For these materials, the area under the hysteresis curve $BH_{\text{max}}$, which also represents the magnetic energy that the material can store – is as high as possible. Alnico, Sm-Co, NdFeB alloy systems are few examples of hard magnetic materials.\cite{1} Among these materials, sintered NdFeB magnets are reported to have the highest energy product $BH_{\text{max}}$, to date \{ > 400 kJ/m$^3$\}. These materials find wide range of applications in automobiles, electrical and telecommunication appliances, motor industry, magnetic resonance imaging (MRI) devices, etc.\cite{8}

The market trends of magnetic materials and their evolution throughout history can be understood in the images below.

\begin{itemize}
  \item Fig. 5 Market share of Magnetic Materials (lighter shade represents hard magnets)\cite{1}
  \item Fig. 6 Trends in the development of magnetic materials and methods over time\cite{1}
\end{itemize}
1.2 Amorphous Alloys

History: 1960 to present

Glassy and amorphous metals and their alloys were first fabricated by metal vapor-deposition at cryogenic temperatures with thin films of germanium and bismuth. After largely unsuccessful attempts at a more generic amorphous metallic state, it was found in 1960, at Caltech, by Duwez, et al.9,10, that when a liquid metallic alloy is cooled at very high cooling rates of the order of magnitude of $10^6$ K/sec – the disordered structure of the liquid can be maintained. This was first noted with a binary Au$_{75}$Si$_{25}$ system.9 During the experiment, the liquidus point was seen lowered to 970K (from 1336K) and on quenching against a copper plates, amorphous flakes were formed by the rapid-solidification technique. Since then many alloy systems have been studied and have led to the development of bulk glassy alloys with enhanced desirable properties. The restriction naturally faced due to a high cooling rate is a small form-factor of about 0.01 to 0.1 mm thickness and diameter for ribbons, wires and powders. However lower cooling rates of about 0.067 K/sec are possible with certain alloy systems. These have led to ingots as bulky as 75 - 80 mm in diameter in Pd-Cu-Ni-P alloys. However, there are certain rules that are universally observed in these systems. It was shown and subsequently patented by Chen and Polk 11 that a thermally stable amorphous metal alloys have roughly a composition of $M_a Y_b Z_c$. Where M is one or more metals from the group consisting of iron, nickel, cobalt, vanadium, and chromium; Y represents elements from the group consisting of phosphorus, boron, and carbon; and Z represents aluminium, silicon, tin, antimony, germanium, indium, and beryllium; and $a$, $b$, and $c$ are in atomic percent.12 They range from 60 to 90, 10 to 30 and 0.1 to 15, respectively. The component Y is the necessary glass former, and it contributes greatly to the atomic confusion which results in an amorphous solid state. It was seen that a large negative heat of mixing was a critical requirement as well. And what seems most important is the presence of a eutectic point with the lowest ‘liquidus’ temperature. With these considerations, developing new alloy systems with favourable properties is possible – by careful selection of alloy ingredients.12,13

Fig. 7 (a) Inoue’s empirical rules (b) Amorphous transition adapted from 12,14
Further on, it was the research led by Inoue, et al. that has led to the finding of a large no. of multicomponent alloy systems. The table in the figure below represents the glassy alloy states that have been reported till date.\textsuperscript{12}

<table>
<thead>
<tr>
<th>1. Non-ferromagnetic alloy systems</th>
<th>Year</th>
<th>2. Ferromagnetic alloy systems</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Ln-M (Ln = lanthanide metal, M = Ni, Cu, Zn)</td>
<td>1988</td>
<td>Fe (Al,Ga) (P,C,B,Ni,Ge)</td>
<td>1995</td>
</tr>
<tr>
<td>Ln-Al-TM (TM = Fe, Co, Ni, Cu)</td>
<td>1989</td>
<td>Fe (Nb,Mo) (Al,Ga) (P,B,Si)</td>
<td>1995</td>
</tr>
<tr>
<td>Ln-Ga-TM</td>
<td>1989</td>
<td>Co (Al,Ga) (P,B,Si)</td>
<td>1996</td>
</tr>
<tr>
<td>Zr-Al-TM</td>
<td>1990</td>
<td>Fe (Zr,Hf,Nb)-B</td>
<td>1996</td>
</tr>
<tr>
<td>Zr-Ti-TM-Re</td>
<td>1993</td>
<td>Fe-Ga-(Cr,Mo)-(P,C,B)</td>
<td>1999</td>
</tr>
<tr>
<td>Zr-Ti,Nb,Pd-Al-TM</td>
<td>1995</td>
<td>Fe-(Cr,Mo)-(C,B)</td>
<td>1999</td>
</tr>
<tr>
<td>Pd-Cu-Ni-P</td>
<td>1996</td>
<td>Ni (Nb,Cr,Mo)-(P,B)</td>
<td>1999</td>
</tr>
<tr>
<td>Pd-Ni-Fe-P</td>
<td>1996</td>
<td>Co-Ta-B</td>
<td>1999</td>
</tr>
<tr>
<td>Ti-Ni-Co-Sn</td>
<td>1998</td>
<td>Fe-Ga-(P,B)</td>
<td>2000</td>
</tr>
<tr>
<td>Cu-Cu-Ag-Mg</td>
<td>2000</td>
<td>Ni-Zr-Ti-Sn-Si</td>
<td>2001</td>
</tr>
<tr>
<td>Cu-Zr-Cu-Hf</td>
<td>2001</td>
<td>Ni (Nb,Ta)-Zr-Ti</td>
<td>2002</td>
</tr>
<tr>
<td>Cu-(Zr,Hf)-Ti</td>
<td>2001</td>
<td>Fe-Si-B-Nb</td>
<td>2002</td>
</tr>
<tr>
<td>Cu-(Zr,Hf)-Al</td>
<td>2003</td>
<td>Co-Fe-Si-B-Nb</td>
<td>2002</td>
</tr>
<tr>
<td>Cu-(Zr,Hf)-Al-(Ag,Pd)</td>
<td>2004</td>
<td>Ni-Nb-Sn</td>
<td>2003</td>
</tr>
<tr>
<td>Pt-Co-Ni-P</td>
<td>2004</td>
<td>Co-Fe-Ta-B-Si</td>
<td>2003</td>
</tr>
<tr>
<td>Ti-Co-(Zr,Hf)-(Co,Ni)</td>
<td>2004</td>
<td>Ni-Pd-P</td>
<td>2004</td>
</tr>
<tr>
<td>Ag-Pr-Pd-Cu-Si</td>
<td>2005</td>
<td>Fe-(Cr,Mo)-(C,B)-Ln (Ln = Y, Er, Yb)</td>
<td>2004</td>
</tr>
<tr>
<td>Ce-Fe-Al-Si-Fe</td>
<td>2005</td>
<td>Co-(Cr,Mo)-(C,B)-Ln (Ln = Y, Er, Yb)</td>
<td>2005</td>
</tr>
<tr>
<td>Cu-(Zr,Hf)-Ag</td>
<td>2005</td>
<td>Ni (Nb,Ta)-Zr-Pd</td>
<td>2006</td>
</tr>
<tr>
<td>Pd-Pr-Cu-P</td>
<td>2007</td>
<td>Ni-Pd-P-B</td>
<td>2009</td>
</tr>
<tr>
<td>Zr-Co-Al-Ag-Pd</td>
<td>2007</td>
<td>Fe-(Nb,Co)-(P,B,Si)</td>
<td>2010</td>
</tr>
<tr>
<td>Ti-Zr-Co-Pd</td>
<td>2007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-Zr-Co-Pd-Sn</td>
<td>2007</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 8 Typical bulk glassy alloy systems reported up to 2010**\textsuperscript{12}

**Basic classification, science**

It can be seen that in writing, the term 'bulk metallic glasses' is most commonly seen. Also, the terms 'bulk glassy alloys', 'glassy metals', 'amorphous alloys', 'vitreous metals', and various permutations of them are loosely used to refer to this class of materials. It is important to note that the word 'bulk' always refers to the larger form-factors of amorphous metals. The word 'glassy' or 'glass' indicates a vitreous or amorphous nature that is observed in such material, where it attains a supercooled liquid state without instantly recrystallizing as the temperature rises... this is different from the property of normal amorphous metals in which continuous heating results in direct transformation to the crystalline phase without any glass-transition.\textsuperscript{12} Thus, for bulk glassy metals, the glass forming range $\Delta T_x$ is given by $(T_x - T_g)$, where $T_x$ is the crystallization temperature and $T_g$ is the glass-transition temperature - is large. Also, the reduced glass transition temperature $T_r$ - given by the ratio $(T_g/T_m)$ is quite large, where $T_m$ is the melting temperature. This can be understood very simply - it means, that if an sample of bulk glassy metals was annealed, it will remain vitreous up to $T_o$, and if the difference between $T_o$ and $T_g$ is large, the material can be heated up, worked on and then returned to its original glassy state. It also means that a particular alloy system will easily form a bulk glassy state when the difference between the melting point and the glass transition temperate is lesser. To put these rules forth systematically, it can be said that while amorphous metals are formed - guided by atomic confusion and these three empirical guidelines (noted in Fig. 7.): \textsuperscript{12,13}
a) Multicomponent systems with three or more constituents
b) Different atomic size ratios, typically with difference exceeding 12 ~ 13%
c) Negative heats of mixing amongst all components

This can be understood via thermodynamics and the kinetics of crystallization as per the Kolmogorov-Johnson-Mehl-Avrami equation.\textsuperscript{15–19} The equation states

Thermodynamically, high glass forming ability is obtained with low free energy for crystallization \( \Delta G = \Delta H_f - T \Delta S_f \). For this low free energy value, entropy of fusion \( \Delta S_f \) is expected to be large due to the large number of disordered states possible in a multiple component alloy, and the enthalpy of fusion \( \Delta H_f \) is expected to be low due to dense random packing that causes increase in the liquid-solid interfacial energy. These values can be used in turn in viewing glass forming from the point of view of crystallization kinetics, where homogeneous nucleation \( I \) depends directly on the solid-liquid interface energy \( \sigma \), the enthalpy of fusion \( \Delta S_f \) and inversely on enthalpy of fusion \( \Delta H_f \), the viscosity \( \eta \) and glass transition temperature \( T_r \). The growth factor \( U \) again directly depends on the enthalpy of fusion \( \Delta H_f \) and inversely on viscosity \( \eta \) and glass transition temperature \( T_r \). This is consistent with and validates the empirical rules and the need for a deep eutectic point, as stated earlier.\textsuperscript{†}

The table in the following figure relates liquid alloy properties with the role that a particular property plays in glass-forming:

![Table I. Characteristic Properties of Bulk Glass-Forming Metallic Liquids](image)

**Fig. 9** Generic properties involved in glass forming ability and their role in glass formation\textsuperscript{20}

\[ I = 10^{30}/\eta \exp \left[ -\beta \sigma \right] \left( T_1 - T_0 \right)^2 \text{ (in cm}^3\text{ s}^{-1}) \text{ and } U = \left[ 1 - \exp \left\{ -\beta \Delta T/T \left( T/T_0 \right) \right\} \right] 10^5 \eta \text{ (in cm} \text{s}^{-1}) \]

\[ \alpha = (N V)^{1/2} \sigma / \Delta H_f, \text{ and } \beta = \Delta S_f / R \text{ given, } \eta \text{ is the viscosity, } f \text{ is the fraction of nucleus sites at the growth interface and finally, } \alpha \text{ and } \beta \text{ are dimensionless parameters related to the solid-liquid interfacial energy (} \sigma \text{), } N_0 \text{ is the Avogadro number, } V \text{ is the atomic volume and } R \text{ is the gas constant.} \]
The following image presents a graphical look at the relationship between the minimum critical cooling rate for glass transformation $R_c$, the maximum sample thickness $t_{\text{max}}$, and the reduced glass transition temperature ($T_g/T_m$) or the temperature interval of supercooled liquid region $\Delta T_x (= T_x - T_g)$ for a few of the newer multicomponent amorphous metals; and also with respect to time-temperature transformation.

Fig. 10 (a) The typical values for nominal alloys: $R_c$ is the cooling rate, $d_{\text{max}}$ is the maximum sample thickness plotted versus $T_g/T_m$. (b) TTT curve versus showing crystallization (adapted from 12)

Models that elucidate the structure of glassy metals are successful only in part, given the highly random nature of the materials. Most notable are Bernal’s model (1959) based on Dense Random Packing of Hard Spheres, which, as the name suggests, is modeling of most dense configurations possible with the constituent atoms considered as hard-spheres. It was further developed by Finney (1970). Equally successful is the Free Volume model developed by Cohen and Turnbull (1960) which postulates that molecular transport happens only when voids of a volume greater than critical volume are available. This can be restated simply as saying that to flow, molecules need space and if a liquid becomes too dense during cooling, its properties are that of a solid. More detail on the model was provided by Fox and Flory. Other models are based on kinetics and include microcrystalline and local icosahedral short range order models (by Miracle), as well as chemical short range order in amorphous alloys. The models successfully predict the short range order (SRO) and the middle range order (MRO) found in most multicomponent alloy systems.

Fig. 11 (a) An approximate view of single crystal versus polycrystalline and amorphous structures. (b) Amorphous state stabilizing short-range structures detected in BMG alloys (adapted from 12)
**Preparation and properties**

The preparation of amorphous metals involves two steps; namely: casting the ingot, which will contain all the desired elements of the multicomponent system, and then the remelting and immediate rapid cooling. The first step may involve vacuum arc remelting to attain homogenous distribution of the alloying components. Rapid quenching has mostly been done via melt-spinning... as it offers unparalleled flexibility and choice for the product.\(^{15,23,25}\) This involves cooling the molten liquid on a highly conducting substrate, namely a copper wheel. Today, the technology has been automated and has evolved; it is more common to use copper blocks or most usually a spinning copper wheel, which results in melt-spun ribbons of amorphous metals with thickness in the range of 40 microns and a width of about 1mm.

Other methods of preparation include mechanical milling, vacuum deposition, electrodeposition, sputtering, and plasma spraying.

![Fig. 12 A close look at melt-spinning and its schematic](adapted from 7, amorphousmetals.com)

And on the topic of properties; amorphous metals excel in almost every way when it comes to mechanical, chemical, electrical, and magnetic properties.
In terms of mechanical properties, glassy materials excel most sharply in terms of the structural strength - as can be seen in the graphs from the figure above. Amorphous metals display excellent surface properties too, due to the absence of any defects, imperfections, irregularities, and dislocations... for the same reason - they have attractive optical and auditory properties. They have high compressive strength and large values of hardness due to absence of any defects internally from where rupture can easily occur via creep – this also leads to large values of coefficient of restitution CoR. It is because of the ability to take strain without yielding, that they do not undergo severe catastrophic failure as often as crystalline material.\textsuperscript{12,26} Such properties also enable glassy metals to be extruded, shaped, and formed without the presence of any internally stressed zones. The table in the figure below gives a quick look at the mechanical properties of bulk amorphous alloys, compared to conventional engineering metals along with costs and manufacturing processes:
Chemically, amorphous metals are very resistant to corrosion, pitting, and other degrading processes due to their lack of surface defects. These can be useful as catalysts and can also be useful in the study of the inherent chemical short-range order in amorphous metals.

Electrically and magnetically amorphous metals are very attractive too. Most amorphous alloy compositions show a very desirable low conductance, in that they are less conducting than regular metallic conductors due to their dense packing and presence of many solute components, which reduces the mean free path of electrons.\textsuperscript{1,13} Due to the absence of grains and dislocations, Bloch wall motion is easy and allows low coercivity $H_c$ in these materials. However, due to the lessened amount, i.e. atomic percentage, of magnetic component (e.g. Fe), the net magnetization can be lower. Susceptibility $\chi$ is large in ferromagnetic amorphous metals and the properties - coercivity ($H$) and magnetization ($M$) are highly tunable. It can be said, that in most cases, ferromagnetic amorphous metals show excellent soft-magnetic characteristics.
In the interest of the focal point of this report, it must be stated, that the more desirable property, of high thermal stability in Fe based ferromagnetic amorphous alloy systems was also studied and expounded by Inoue, et al. into three distinct contributions: 27,28

1. More efficient dense random packing of constituents with significantly different atomic sizes, especially among P, C, and B.
2. Higher energy barriers for the precipitation of Fe-M compounds due to strong interactions between P, C, and/or B and Al.
3. Higher barriers to formation of Fe-B and Fe-C compounds due to Ga additions which are soluble in Fe but immiscible with B or C.

More recent works by Koshiba, et al. has resulted in ferromagnetic amorphous alloys with higher $\Delta T_x$ ($60K$) in in the melt-spun alloys $\text{Fe}_{56}\text{Co}_{7}\text{Ni}_{7}\text{Zr}_2\text{Nb}_8\text{B}_{20}$ and $\text{Fe}_{56}\text{Co}_{7}\text{Ni}_{7}\text{Zr}_2\text{Ta}_8\text{B}_{20}$; and Inoue et al. have last reported $\Delta T_x = 85 K$ in the melt-spun alloy $\text{Fe}_{56}\text{Co}_{7}\text{Ni}_{7}\text{Zr}_8\text{Nb}_2\text{B}_{20}$.27,29,30

These show that further research can result in optimization of glass-transition, with enhanced magnetic properties.

*Applications: Scope, in general* 13,20,26,31–33

The applications of amorphous metals ranges from those in everyday life, like cookware, sporting goods, and protective surface coats; to the more esoteric, like in precision sensors used in Coriolis flow-meters, in anti-reflection coatings, in biomedical applications - to make prosthetic hip or wrist joints and where hyperthermia is to be induced or transcutaneous signal-delivery is needed. Amorphous metals find their way into casings and ornamental covers and even into musical instruments. A more exotic new field is its use as catalytic storage for fuel cells.

*Fig. 16 A collage of amorphous materials already in use* various sources | internet

The table in the image below represents a fair commercial share of what amorphous metals (and derived nanostructured materials) are capable of use in, in the field of engineering.
Applications: Magnetic & Electrical

As can be conjectured from the first half of the table presented in the image above - a very large number of applications await the use of amorphous metals in the magnetic, electrical, and the electronics industry. In the field of electronics, amorphous metals are already in use in power conditioning, in power inductors, and other needs of telecommunication. They are extensively used in remote temperature sensing, remote stress and strain sensing and in highly specialized accelerometers. Recently, they have found application in micro-geared motors as small as 0.9mm total diameter.

However, the greatest promise of amorphous metals is in the field of heavy electrical and power applications. Specifically, soft-magnetic amorphous metals seem to hold promise of properties that can be excellent for transformer cores. It has been shown, that cores made of soft-magnetic amorphous glassy materials can display high efficiency and extremely low losses due to low remnant magnetization $M_r$, high saturation induction and magnetization $B_s$, $M_s$ and higher resistivity $\rho$. Some factors, like stress relief, magnetostriction $\lambda$ and even lower magnetization are only a matter of further research.
1.3 Nanocrystalline Materials

**History and Research on nanocrystalline materials**

Nanocrystalline materials have been of interest only more recently. Research in nanocrystalline materials and especially metallic alloys, have recently increased in the mid-1950s. However, research on metallic nanocrystalline materials spiked around 1970 with independent studies by Gleiter, Birringer, and Suryanarayan. A new journal – “Nanostructured Materials” was introduced by Pergammon Press in 1992 and conferences followed the review by Andres et al. stating that novel science and applications awaited the study of nanostructured materials.

Polycrystalline solids with grain size less than 100 nm are called nanocrystalline materials and can be produced using various methods and different starting phase: vapor (inert gas condensation, sputtering, plasma processing, and vapor deposition), liquid (electrodeposition, rapid solidification) or solid (mechanical alloying, severe plastic deformation, spark erosion). Most of the methods offer two possibilities for creation of nanocrystalline structure: directly in one process or indirectly through an amorphous precursor. Nanocrystallization of metallic glasses is an example of the second procedure. In this case, nanocrystalline material is produced in two steps: (1) formation of amorphous state by quenching of liquid alloy and (2) partial or complete crystallization of the amorphous alloy by annealing. Three important groups of nanocrystalline materials produced from metallic glasses can be distinguished: constructional Al-based alloys, magnetically soft and magnetically hard Fe-based alloys.

(Tadeusz Kulik, 2001)

The quote above is a broad definition for nanocrystalline materials. It also hints at the techniques of preparation of nanostructured materials from amorphous precursors – by annealing. It should also be noted that the definition remarks on only the size of the crystallites $d$, for nanostructured materials derived from amorphous precursors, the crystalline volume fraction is of interest. This can range from low percentages to high ones, and it directly affects the amount of crystalline interfaces available. Thus, nanostructured materials can be considered to consist of two distinct structural components: the nanocrystalline phase with truncated long-range order, and the network of intercrystalline regions the structure of which may change over the material and is the interfacial component.

Nanostructured materials made from amorphous precursors, by devitrification, display about 75% to 90% of the density of their polycrystalline counterparts, and the percentage increases with increasing crystalline volume fraction. With a crystalline atomistic structure when compared to glassy and polycrystalline materials of equivalent composition, the structure-dependent properties vary too. Most notably, for Fe-rich nanostructured alloy systems, magnetism shows interesting properties depending on the crystalline volume fraction and the average grain size.
The image below represents the schematic cross-section through a nano-crystalline material, where the filled circles represent the crystals and the open circles represent the boundary/core material – which will relax into distinct atomic arrangements as per available space.

![Image](image_url)

Fig. 18 (a) A 2D model of a nanostructured material, showing crystalline regions in blackened circles and the boundary/core material is shown with open circles. (b) Similar model in 3D.

**Fe-based magnetic nanostructured alloys**

Alloy composition and controlled annealing can be used to tailor the magnetic properties of the nanostructured biphasic system. The magnetic softness, as explained by Herzer, is related to the ratio of the exchange correlation length (or domain wall thickness) $L_{ex}$, to the orientation fluctuation length $\ell_s$ of randomly distributed local easy axes, which in this case is the average crystallite size. For $L_{ex} \gg \ell_s$, as is the case in Fe-rich alloy systems, the effective magnetic anisotropy $K_{eff}$ averages out and the domain wall can move without hindrances. Moreover, for a critical crystallized volume fraction $x$, the average magnetostriction $\lambda$ vanishes; thus, magnetoelastic contributions to the macroscopic anisotropy also become negligible.

This is understood better by Herzer’s model of random anisotropy (RAM), which is very successful in predicting the coercivity $H_c$ of nanostructured (as well as amorphous) soft-magnetic alloy systems. The model considers a characteristic volume of sides equal to the exchange correlation length $L_{ex}$ – this length is proportional to $(A/K_{eff})^{1/2}$, where $A$ is the exchange stiffness and $K$ is the magnetic anisotropy. A random-walk through $N$ grains with random easy axes, within the considered volume of $L_{ex}$, will be exchange coupled. Since the axes are randomly oriented, the walk over $N$ grains leads to a reduction of the effective

---

1 The random-walk model was formally introduced for ferromagnets with random-axis uniaxial anisotropy, by Alben et al. and it carried the same idea that Harris et al. described in their work using an exchange interaction model that agrees qualitatively with experimental data.
anisotropy by a factor of $(1/N)^{1/2}$ from the individual grain anisotropy $K$. The corresponding proportional change in $K_{\text{eff}}$ is therefore given by $(K/N^{1/2})$. Since the number of grains $N$ is given as $(L_{\text{ex}}/D)^3$, where $D$ is the average diameter of individual grains, the equivalent proportional change in the effective anisotropy $K_{\text{eff}}$ value can be re-written to be proportional to $K(D/L_{\text{ex}})^{3/2}$. Consistently solving for $K_{\text{eff}}$ allows us to get $K_{\text{eff}}^4 = (K^4 D^6 K_{\text{eff}}^3)/A^3$ or simply, $K_{\text{eff}}$ is shown to be proportional to $D^6$. Since coercivity $H_c$ is directly proportional to effective anisotropy $K_{\text{eff}}$, Herzer’s model predicts that coercivity $H_c$ increases proportional to the 6th power of grain size $D$. It is of utmost importance to see that this is applicable only for values of $D$ between 10 to 100 nm. Above that, the exchange length $L_{\text{ex}}$ is comparable to the grain size $D$ and coercivity $H_c$ shows a linear inversely proportional relationship. At such sizes, stiffness is enhanced, and spring-magnetic behavior can be seen with high coercivities $H_c$ and high remanence $M_r$.

This is graphed in part (a) of the figure below which is formally called the Herzer diagram for showing the relationship between grain size $d$, and coercivity $H_c$, and the area of topical interest is the part in the rectangle showing scaling between 10 to 100 nm. Part (b) of the figure shows a 2-D schematic of $N$ nanocrystalline grains of size $D$ in a volume of sides $L_{\text{ex}}$.

![Herzer Diagram](image-url)

**Fig. 19** (a) Herzer Diagram plotting coercivity $H_c$ against average grain size $D$ for some alloys
(b) 2-D schematic of $N$ nanocrystalline grains of size $D$ in a volume of sides $L_{\text{ex}}$ with anisotropy $K$

There have been reports of coercivity $H_c$ depending on grain size $D$ with a $D^n$ power law, and such cases have been explained by Suzuki et al. as an extension of Herzer’s Model. The model is restrictive in application to biphasic systems and is especially successful in METGLAS (Fe-B-Si) type alloys where the exchange stiffness $A$ for the amorphous phase is comparable to that of the crystalline phase. The other property of interest, i.e. magnetostriction, denoted by $\lambda_s$, has also been explained by Herzer with a simple two-phase model of $\lambda_s^{cr} < 0$ and $\lambda_s^{am} > 0$, which interact as per the rule of mixture of the magnetostrictions of the nanocrystalline and amorphous phases, respectively. Also of interest is the fact that annealing of amorphous materials induces anisotropies due
not only to mechanical alignment and structural relaxation, but also atomic pairing – which results in directional order. This is noticeable in Si-Fe systems. 

It has been studied by Moerup et al., that if the nanostructured material has sufficiently small nanocrystals, with enough intercrystalline material to nullify any coupling, then the observed response is superparamagnetic. With increasing nanocrystalline volume fraction, the magnetic exchange interaction increases. This suppresses the superparamagnetic fluctuations of any uncoupled magnetic regions. The effects of annealing and crystallization on the overall magnetic response \{M_s, M_r, T_c, etc.\} and coercivity \(H_c\) have been reported in detail, by Salwska-Waniewska et al., Rao et al., Mazaleyrat et al., and especially for METGLAS (FeBSi) type alloys, by Hernando et al.

Change in soft-magnetic properties is noted for BCC \(\alpha\)-Fe(Si) rich nanocrystals in METGLAS (Fe-B-Si) type alloys of size below 7nm, embedded in the surrounding amorphous matrix. The saturation magnetization \(M_s\) for such nanostructured material drops to about 40% of the bulk polycrystalline saturation magnetization compared to a theoretical 2% drop for amorphous iron. The overall magnetization is attributed to the exchange coupling between the slightly harder nanocrystals, with the surrounding soft amorphous matrix. There is a reduction in the magnetoelastic energy due to reduction of both internal stresses and effective magnetostriction \(\lambda_s\). It has been shown by Yoshizawa (US Patent: 4881989) that for reduction of coercivity \(H_c\) and increment of saturation magnetization \(M_s\), Copper plays an indispensable role, along with the necessity of Niobium, Molybdenum, Tungsten, Tantalum, Titanuim, Zirconium, etc. The Copper plays the all-important role of facilitating segregation and reducing the formation of Fe-metalloid compounds. Along with Copper, the other rare-earth metal helps increase the crystallization temperature and hinders growth of the BCC \(\alpha\)-Fe grains. The patent describes the narrow-range of atomic percentages that must be maintained for optimum soft magnetic properties. This is explained by the decrease of the total magnetic anisotropy \(K\) with reduced grain-size and a lower magnetostriction \(\lambda_s\) along with the enhanced exchange interaction \(J_{ex}\) of the nanoparticles. Inoue et al. have shown that in the absence of Copper and Silicon, it is Niobium and Zirconium in very controlled amount (≈ 7 at. %) with Boron, that leads to lowered coercivity and magnetostriction, with high permeability. Yet, coercivity values as low as those shown by Yoshizawa have not been matched.

To summarize, the coercivity is expected to scale with effective magnetic anisotropy \(K_{eff}\), and it will be less than the effective anisotropy field given by \(2K_{eff}/M_s\). Hence, coercivity \(H_c\) can be made vanishingly small, and the permeability \(\mu\) can be very large in systems with randomly oriented exchange coupled nanocrystals embedded in a soft-magnetic amorphous matrix.
For systems with BCC $\alpha$-Fe as the dominant nanocrystalline phase, Hernando et al. have defined intergranular spacing as $\Lambda = d((1/X)^{1/3} - 1)$, where $d$ is the average grain size and $X$ is the crystalline volume fraction; and exchange correlation length coefficient as $ye = \exp(-\Lambda / \text{Lam})$, where $\text{Lam}$ is the exchange length for the amorphous phase. With these, three important relationships were found: 7,44

1. The first of these is a modified exchange correlation length $L^*$, expressed as a function of the exchange correlation length coefficient:

$$L^* = \left( L_{ex} y_{ex}^2 \right) / X$$

...where $L_{ex}$ is the single-phase exchange correlation length originally proposed by Herzer. The dependence of $L^*$ on $X$ profoundly modifies the $D^6$ dependence of $H_c$.

2. The second of these is a new parameterization of the Magnetocrystalline anisotropy that is also a strong function of the exchange correlation length coefficient:

$$k^* = K_0 X^2 / y_{ex}^2$$

...where $K_0$ represents the macroscopic anisotropy and $k^*$ represents the structural anisotropy. Again, this expression reduces to Herzer's model for $y_{ex} = 1$.

3. Finally, the third relationship describes critical size of crystallites $\delta^*$, below which a reduction in coercivity due to random anisotropy will be observed. It is:

$$\delta^* = \delta_0 \left( y_{ex} / X^{2/3} \right)$$

...where $\delta_0$ is the maximum size of crystallites. In the Herzer model, where $\delta < \delta_0$ then the critical size is independent of the amount of crystalline phase at any temperature. However, in the two-phase model, since $\delta$ grows to exceed $\delta_0$ (by either increasing temperature or decreasing volume fraction of crystalline material) a variety of experimental results can be explained (e.g. magnetic hardening, etc.). (McHenry et al., 1998) 7

Fig. 20 Graphs plotting the unique benefits of nanostructured (and amorphous) materials 12,14,26,28
2. Experimental Work

2.1 Characterization Techniques

**X-ray Diffractometer (XRD)**

X-ray diffraction technique is a versatile and non-destructive method of identification and quantitative analysis of the various crystalline of nanomaterials, bulk and films. The unknown samples are identified by comparing the obtained diffraction pattern with international recognized database containing reference patterns.

A lattice in crystal structure is a regular array of atoms in space. The atoms are arranged to make a series of parallel-planes that are separated from each other by a distance $d$, which usually varies from material to material. Any crystal planes oriented in different direction has different $d_{hkl}$ spacing, where $h, k, \ell$, represent the miller indices of the direction under observation.

X-rays are electromagnetic radiation with wavelengths in the range 0.5-2.5 Å (1nm = 10 Å). Since this is of the same order of magnitude as the interatomic distances in solids, X-rays used to study the internal (crystalline) structure of materials. An X-ray beam impinging on a crystal will be elastically scattered in all directions by the atoms of the crystal. In some directions, an increased intensity is observed due to the constructive interference of the scattered waves. The conditions for constructive interference are easily derived from the simple geometrical picture for the scattering of an X-ray beam by planes of atoms in a crystal, as shown in the figure below. One can consider X-ray beam of wavelength $\lambda$, incident on the crystal at an angle $\theta$ with respect to equidistant $hkl$ lattice- with interplanar distance $d_{hkl}$. Constructive interference will be observed for X-rays that are reflected from the lattice planes at the specular angle, if the path length difference between X-rays scattered from different $hkl$-planes is an integer times the wavelength. This condition is summarized in the Bragg law as $n\lambda = 2 d_{hkl} \sin(\theta)$.

![Fig. 21 (a) X-ray beam of wavelength $\lambda$, incident on the crystal at angle $\theta$ with respect to equidistant $hkl$ lattice-planes, with interplanar distance $d_{hkl}$. (b) Various planes and their miller indices](kuleuven.be)

![Various planes and their miller indices](ethz.ch)
The diffraction analysis can be done by either varying the wavelength $\lambda$ or the angle $\theta$. The former is called the Laue diffraction method, which is faster, but requires synchrotron X-ray sources. By varying $\theta$ however, Monochromatic diffraction is recorded, the goniometer setup used, is called the Bragg-Brentano geometry. This is common in laboratories, with a fixed source. X-rays are produced whenever highly energetic electrons collide with a metal target. The emission of X-rays happens when excited electrons in the target relax down to their most favored (ground) state and this emission is highly specific for all materials. Most common target materials are Copper (Cu $K\alpha_{\text{avg}} = 1.542$ Å) and Molybdenum (Mo $K\alpha = 0.711$ Å). The intensity of reflection is plotted in terms of ‘counts’, against the $2\theta$ angle. A record of diffraction is called the diffractogram, is a combination of signal, noise and a background. The ways to amplify signal is to increase counting time, or even repeat counts; noise can be reduced with shorter wavelengths, or with higher intensity beams.

The analysis of X-ray diffractograms is done by finding the peaks in it, and as per the constituent atoms of the structure under investigation, matching against a database or literature. The peak position on the $2\theta$ scale, gives the lattice parameters and the d-spacing that is being observed. The peak height, which is an approximation for the area under the peak – gives phase amount in the sample. The integral breadth of the peak, or the width of the peak at half its height (called FWHM) allows the very important calculation of crystallite size by the Scherer’s formula, given as $B_{\text{FWHM}} = K\lambda/(t \cos(\theta_{\text{FWHM}}))$, where FWHM is the preferred method. $K$ is the constant of proportionality, usually 0.94, and $t$ is the volume averaged crystal size ($\bar{\theta}$) of the sample. $\theta$ is the angle of reflection for diffraction at the recorded peak, taken in radians. $t$ therefore gives us the average size of the crystallites at the test area. Care should be taken to discard instrumental errors, like broadening and profile from the final diffractogram.

The underlying physics of the computation of grain size by the Scherer’s formula and the X-ray analysis of BCC $\alpha$-Fe nanocrystallites embedded in an amorphous matrix has been discussed by Patterson and Birringer et al. Recently, Mudryi et al. have shown simple qualitative methods to also calculate volume fraction of a crystalline phase $C_{cr}$ in an amorphous matrix, using the peak heights $S_{am}$ and $S_{cr}$ for the first maxima of the amorphous precursors and the Gaussian peak of the nanostructured resultant sample, respectively. The formulation rests on the fact that the structure factor, which dictates the crystalline volume fraction of any phase, is dependent on the peak intensity (with relevant corrections). An additional correction factor $\alpha_c$ is added to account for chemical short-range order, variable relaxation rates, and the free vol., of different amorphous materials. The relationship is written as $C_{cr} = S_{cr} / (S_{cr} + \alpha_c S_{am})$.

For the purposes of this work, a Bruker D2 Phaser (image below) with wavelength Cu $K\alpha_{\text{avg}} = 1.542$ Å, and beam power 300W was used for all samples. The instrument has a FWHM resolution $B_{\text{FWHM}}$ of 0.05° at $30° < 2\theta < 50°$. All diffractograms have been smoothed using a 150 step second order Savitzky-Golay least-sq. operation on the signal. Also, instrumental profile has been renormalized (baseline subtracted) using a 5th order polynomial function.
Scanning Electron Microscope (SEM)

In a scanning electron microscope, images of the sample surface are produced by probing the specimen with high-energy electron beam. As the electron beam impinges on the surface of the sample, signals are produced, which includes secondary electrons SEs, back scattered electrons BSEs and characteristics X-rays. The SEs are electrons that are ejected from the surface of the sample due to inelastic scattering – these mainly help map the surface topography. The BSEs are the electrons, which are elastically scattered and reflected back from the specimen. BSEs are used to detect contrast in areas with different composition since heavy elements backscatter the electrons more strongly compared to light elements.

A working model of SEM is shown in the figure below, along with a schematic of simulation of electron beam penetration into a sample of choice – giving the specimen interaction volume.
To simplify, an SEM consists of a source (electron gun), for the electron beam which is accelerated down the column towards an initial refocusing anode; a series of lenses (condenser and objective) act to control the diameter of the beam as well as to focus the beam on the specimen; a series of apertures (micron-scale holes in metal film) which the beam passes through and is affected by helps reduce divergence. Scanning coils help in rastering, and controls for specimen position, i.e. x,y and z-height and sample orientation (tilt, rotation) is embedded with the stage. High vacuum within the equipment is essential; also a tilt free, vibration free and electromagnetic noise free room is preferred.

The electron gun can be of either thermionic or of field-emission type. Thermionic electron guns work simply by thermionic electron emission; the field-emission electron guns (FEGs) however are more complicated and can be thermally assisted (more common) or cold. The FEG cathode is usually a very sharp bend of tungsten filament, of at most 100nm tip radius, this causes charge build-up and helps emission. A first anode sets up the emission field from the filament, and a second anode sets up the accelerating voltage $V_a$ – which determines the velocity of the electrons and therefore the beam penetration depth. The beam current, on the other hand, determines the number of electrons in the beam and contributes to signal (and noise).

Next, electron lenses in the form of toroidal electromagnets magnify and demagnify the beam to allow precision focusing. Due to lenses, phenomena such as spherical and chromatic aberration or astigmatism may occur – these are corrected by better current control and the use of tertiary coils (stigmator, etc.). Three factors are important in generating image: (1) the beam voltage, an increase in which may decrease aberration, cause specimen charging and even obscure surface detail; (2) emission current, an increase in which may cause specimen charging and even damage; and (3) probe-diameter, which is controlled by different apertures and helps enhance resolution of surface detail by decreasing current and aberration and also allows finer control of probe diameter and probe convergence angle. Of high importance is also the working distance, i.e. z-height of the sample from the electron gun (muzzle) – an increase in working distance betters the depth of field, but deteriorates the resolution and vice versa. The process is elegant in its simplicity, and the underlying principles can be gleaned from the excellent collection of articles compiled and edited by Kazmiruk.64

For the purposes of this work, a Hitachi S3000 SEM (image above) with a cold tungsten FEG, was used for the experiments. Images were collected using synced Quartz PCI software.

**Vibrating Sample Magnetometer (VSM)**

A vibrating sample magnetometer (called Foner balance) measures magnetic properties, invented in 1955 by Simon Foner at Lincoln Laboratory MIT.1,65 In this, a sample is placed inside a uniform magnetic field to obtain a magnetic response from the sample. The sample is then physically vibrated sinusoidally, typically via a linear actuator. The induced voltage $V$ in the pickup coil is proportional to the sample's magnetic moment under the applied...
coercive field by the relationship $Vdt = -n\mu_0 a M$, for a pickup coil of $n$ turns of wire of cross sectional area $a$. The coil arrangement depends on whether the applied field is vertical, as with a superconducting solenoid, or horizontal, as with an electromagnet. The coils are also oppositely wound so that the emf induced in them by the vibrating sample add up. Two pairs of coils are used in a four-pole configuration for the horizontal applied field to create a saddle point around which the sensitivity is independent of sample position. In a typical setup, the induced voltage is measured through the use of a lock-in amplifier using the piezoelectric signal as its reference signal in an arrangement as shown below. By measuring in the field of an external electromagnet, it is possible to obtain the hysteresis curve of a material, by the principles of Faraday’s induction law.\(^1\,\text{65}\)

![Fig. 24 Vibrating Sample Magnetometer schematic](image)

The vibration frequency of the sample is typically in the range 10–100 Hz and the vibration amplitude of a few tenths of a millimeter – all of which is controlled by a feedback loop. The sensitivity of a well-designed VSM can be better than $10^{-8}$ Am$^2$. The response is usually computed from a plot of induction $B$ versus the coercive field $H$. On this plot, the Magnetization values for remanence $M_r$ is the zero-field intercept and saturation $M_s$ is noted on the y-axis when $\mu \approx 1$, or to paraphrase, when the value of $M$ no longer responds to field $H$. This is the hysteresis loop of the material, and is one of the most important and distinguishing features of any magnetic material.

For the purposes of this work, an EG&G PARC Princeton Applied Research Model-155 VSM with LakeShore 7300 controller (image below) was used in standard and low-field scan modes, for every sample.
Magnetism of Nanocrystallized Amorphous Fe_{75}B_{10}Si_{15}

Arnab Chakraborty

Magneto-Thermogravimetric Analyzer (MTGA)

The root technique of thermogravimetry is of thermal analysis, and is mostly for proof of concept. The sample is introduced to one side of a highly sensitive microbalance arrangement, and is heated at desired rates in an atmosphere of choice. The instrument records change in weight as a percentage of the original weight, thereby providing information about weight change (due to phase change, oxidation, dehydration and relaxation), and more importantly – weight change rate can be sharply noted via a derivative weight-loss curve, which tells us the point at which weight-loss is most apparent.

An MTGA is a magnetic extension of the same experimental idea for analysis of phase change in magnetic materials. Here, instead of the gravitational weight being the reference, an arbitrary magnetic pull is used to create a weight analog and the force (along axis Z) on the sample, is given by \( F_z = \text{grad}_z (m.B) \) where \( m \) is the magnetic moment induced in the sample.
sample under the field $B$. The system is then heated at desired heating profiles with accurate documenting of the change in weight percentage. In a multiphasic material, or a material which undergoes phase change (with corresponding change in magnetic response), the plot of temperature versus magnetic weight shows change. A sharp drop in weight will be seen whenever the Curie temperature $T_c$ of a magnetic phase, proportional to the fraction of the phase in the sample. Equivalent to that, a rise in the weight percentage can be seen whenever the system enters a magnetic phase from a non-magnetic or a less magnetic system. The two phenomena stated above are seen during magneto-thermogravimetric analysis of amorphous metallic samples. For amorphous materials, it is known that upon heating, onset of crystallization occurs at $T_{crys}$; also, the Curie temperature $T_c^{am}$ of the amorphous phase is less than that of its crystalline counterpart. Therefore, during analysis, at a distinct temperature, the amorphous phase crosses its Curie temperature $T_c$ and its magnetic weight becomes zero. Upon continuing to higher temperature, the material of the sample starts to crystallize and starts to show a magnetic response again until the Curie temperature of the crystalline phase $T_c^{cr}$ is reached.

For the purposes of this work, a Perkin Elmer TGS-2 Thermal Analysis station (penultimate image above) was used in standard scan modes, for every sample.

2.2. Fabrication and Experiments

*Ingot Preparation using Vacuum Arc Remelter (VAR)*

Ingots weighing 3g each of Fe75B10Si15 were prepared, for the purpose of melt-spinning. The weight 3g was selected due to the ease with which 3g ingots fit into the quartz tube used during melt-spinning. The atomic percentages at% were converted into weight percentage wt%, giving Fe – 88.778 %, B – 2.292 %, Si – 8.930 %. Compositions equivalent to 3g weight were consequently weighed out from > 99.9% pure Fe, B and Si on a Kern ABJ digital microbalance with 0.1mg least-count. Next, the components were arc-melt on a water-cooled remelter setup, with a Centorr Reed STA Tri-arc furnace, in an Argon atmosphere and in the presence of fresh titanium getters. All ingots were re-melt 10 times, alternately on each side to ensure homogeneity.
The ingot, which showed the greatest parity with the combined weight of the original components, was selected for the next step.

**Melt Spinning using the Controlled Rapid Quenching Machine (CRQM)**

Melt spinning is a very versatile technique to fabricate and even continuously cast amorphous ribbons. The ejection of melt from the quartz tube is the central step of melt spinning and for the axial controls of XY with the induction heater, and the Z-height from the wheel surface, a set of translators is used. A copper RF range induction heating coil is built to accommodate quartz tubes of choice and is cooled by water flow through the coil. The coil produces induction heating of the alloy in the quartz tube to the point of causing turbulence in it. To avoid oxidation, this is done after spinning chamber has been evacuated to an ambient pressure of first $10^{-1}$ Pa using a rotary pump, and then $\sim 10^{-3}$ Pa using a diffusion pump. As mentioned earlier, the ingot size, material type and coupling (between coil and alloy) are factors to be considered beforehand. Schematic diagram and image of the Makabe R&D Co. Ltd. (Jp) CRQM-T-20 used, is shown below.

![Fig. 28 Schematic and image of Makabe R&D Co. Ltd. (Japan) CRQM-T-20 at KTH](kth.se)

The ingot selected from the previous step was used in the Controlled Rapid Quenching Machine (CRQM), in a quartz ejection tube with a 0.5mm sanded aperture. Clearance was set at 0.2mm and it was ensured that the wheel is ground free of any roughness. Ejection pressure was set at 0.3 Pa (argon), with a wheel speed of 3400 rpm, translating to $\sim 34$ m/s (for $\varphi_{\text{wheel}} = 19.1$ cm). This resulted in a significant quantity of smooth ribbons with average thickness of approximately 20μm and width 1mm. Variations in these dimensions is entirely random. The ribbons acquired in this step are used for the rest of the experiment.
Annealing using the Mini Infrared Lamp Annealer (MILA)

The Mini Infrared Lamp Annealer used for this work is a ULVAC RIKO MILA-5000, which uses an OMRON microcontroller. The mini lamp annealer works by focusing near infrared rays using a parabolic reflector onto a quartz sample stage of 20mm x 20mm. It has a wide range of available heating rates, and depending on the type of thermocouple used, it can be used for annealing up to 1200°C. The accompanying OMRON microcontroller allows for very detailed temperature ramps and soak-times and also allows tuning PID parameters for fine control on the process values of the heating profile.

Ribbons acquired from the CRQM were annealed in separate batches with 45min soaking time at the temperatures of 425°C to 625°C in intervals of 25°C. One extra batch was annealed at 950°C to have a fully crystalline comparison. A linear 40°C/min profile was used in all cases, in an argon atmosphere, with programs ending in natural cooling.

![MILA-5000 Image](ulvac.co.jp, ulvac.com)

**Experimental Parameters**

Apart from what has been mentioned for every experimental technique above, care was taken to ensure that at all times, all samples were handled with antistatic and non-magnetic tweezers and ceramic scissors was used for cutting sample-pieces. For magnetic measurements especially, non-magnetic tape and soda-straws were used. All equipment and sample handling was done with the use of powder-free latex gloves.

- All XRD results are from a double-run, with 0.02°/step, and 10steps/sec – from 2θ angles ranging from 25° to 75° for all samples. Samples were made on Labora 1mm thick glass slides, using thin double-sided tape, such that the shiny side of the ribbons were facing up and ribbons were lined up parallel to each other without spaces.
- SEM was used only to understand the surface morphology of the various annealed ribbons; sample was mounted using double-sided conductive carbon tape. Further imaging details are available on the image themselves.

- The samples for VSM were prepared on small pieces of 0.2mm thickness VWR borosilicate glass coverslips to maintain flatness of the ribbon. Every ribbon piece (< 5mm long) was carefully weighed to enable calculation of magnetization in terms of mass $M_0$. Special non-magnetic tape was used at all times. The samples were degaussed with a 5.9 kOe field. Scans for hysteresis were run for 100 data points. Every point was repeated twice at a distance of 200ms and time spent per point was 4000ms, keeping Hall probe field range at 6000Oe. Scans for low field coercivity measurement were run as per file presets (0.01A/step) with 100 points, and a Hall probe field range of 2000e.

- Measurements using MTGA were done carefully and with minimum disturbance to the sample pan (material: Pt) – to ensure error free microbalance response. For the sake of accuracy, measurement runs were repeated at least twice in all cases. The heating rate was a constant 40°C and natural air cooling was used at the end of the programs.
3. Results and Discussions

3.1 Analysis

**XRD Analysis**

The results from the X-ray diffraction are presented below - a diffuse halo is observed at the beginning of the diffractograms, which is an artifact of the measurement process. For the amorphous ribbons, a broad hump (diffuse halo) is noticed at about $2\theta = 45^\circ$, which is the rough vicinity of a BCC $\alpha$-Fe(Si) signal. This hump corresponds to a crystallite size less than 1Å, and is thus considered fully amorphous. Annealing between temperatures of 425°C to 500°C shows a unique peak at $2\theta$ values of 50° - corresponding to stoichiometric Fe$_3$Si DO3 superlattice with a broad hump at $2\theta = 45^\circ$. Upon annealing at 525°C, peaks are observed at $2\theta$ values of 27°, 31°, 45°, 56°, and 66° - of which, the peak at 45° is most pronounced. Increasing the temperature of annealing to 550°C shows, in addition to the peaks above, small peaks are added at 43° and 50°. Annealing at 575°C and above shows greater crystallization for all peaks with small extra peaks at 24°, 32°, 57°, 73° and 79°. These are marked for their constituent signatures in the graph below.

![Cascaded view of XRD results showing all constituent phases developed and peak heights.](Image)

As can be seen from the graph above, the dominant phases precipitated are $\alpha$-Fe(Si), Fe$_3$Si, Fe$_2$B and Fe$_5$(SiB$_2$). Out of these, Fe$_2$B and Fe$_5$(SiB$_2$) are formed mostly at higher annealing temperatures. The results are in agreement with literature, which outlines the crystallization mechanism for Fe alloys with particular percentages of Si and B. In the case of Fe$_{75}$B$_{10}$Si$_{15}$,
the crystallization follows the following order: Amorphous $\rightarrow$ $\alpha$-Fe(Si) + Fe$_3$Si $\rightarrow$ Fe$_2$B. In the image below, the phases with the most X-ray signature are marked, with their structure and orientation. It can be noted, that the phases dominating in samples annealed up to 550°C are mainly only $\alpha$-Fe(Si) and Fe$_3$Si. This is shown in the image below, and is relevant to the magnetic response that is observed in the annealed samples.

![Graph showing the peaks having greatest intensity, their constituent phases and crystal parameters.](image)

Fig. 31 Graph showing the peaks having greatest intensity, their constituent phases and crystal parameters.
By using the formulations mentioned earlier (by Scherrer and by Mudryi et al.), crystalline grain size $t$ and volume fraction $C_{cr}$ of most prominent phases can be computed. The results are tabulated below:

<table>
<thead>
<tr>
<th>Samples</th>
<th>Phases</th>
<th>$\alpha$-FeSi</th>
<th>$\alpha$-FeSi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$t$ bcc (111)</td>
<td>$C_{cr}$</td>
<td>$t$ bcc (110)</td>
</tr>
<tr>
<td>Ribbon Anl. at 425°C</td>
<td>2.4 nm</td>
<td>0.66</td>
<td>--</td>
</tr>
<tr>
<td>Ribbon Anl. at 450°C</td>
<td>2.4 nm</td>
<td>0.71</td>
<td>--</td>
</tr>
<tr>
<td>Ribbon Anl. at 475°C</td>
<td>2.2 nm</td>
<td>0.68</td>
<td>--</td>
</tr>
<tr>
<td>Ribbon Anl. at 500°C</td>
<td>3.1 nm</td>
<td>0.71</td>
<td>--</td>
</tr>
<tr>
<td>Ribbon Anl. at 525°C</td>
<td>20.4 nm</td>
<td>0.83</td>
<td>36.4 nm</td>
</tr>
<tr>
<td>Ribbon Anl. at 550°C</td>
<td>20.1 nm</td>
<td>0.88</td>
<td>33.1 nm</td>
</tr>
<tr>
<td>Ribbon Anl. at 575°C</td>
<td>23 nm</td>
<td>0.92</td>
<td>40.3 nm</td>
</tr>
<tr>
<td>Ribbon Anl. at 600°C</td>
<td>28.5 nm</td>
<td>0.93</td>
<td>33.2 nm</td>
</tr>
<tr>
<td>Ribbon Anl. at 625°C</td>
<td>32.7 nm</td>
<td>0.93</td>
<td>39.3 nm</td>
</tr>
</tbody>
</table>

Fig. 32 Table of crystallite size $d$ and volume fraction $C_{cr}$ of various phases observed in annealed samples

**SEM Analysis**

The images from the Scanning Electron Microscope, for some of the samples are shown below, in particular, the images for samples annealed at 525°C and 550°C are of interest, as they are temperatures above the crystallization temperature $T_{cryst}$ of the alloy, with significant crystalline volume fraction.

Fig. 33 On the left, is sample annealed at 525°C showing the rough wheel side; inhomogeneity such as the one seen here is common all over the surface. On the right, is sample annealed at 550°C showing the smooth side exposed to air during flow-casting. Literature suggests that light areas denote low Si concentration.

As is seen in the image above, the surface for annealed ribbons are more or less featureless. This is also evidenced in the micrograph of the as-quenched ribbon samples, shown below.
Fig. 34 Featureless smooth side of the as-quenched ribbon, showing soft scratches on the surface.

The only other micrograph of interest comes from annealing at 950°C, which shows ferritic segregation at the surface (Widmanstätten ferrite), as it is seen without etching. This is shown below, at low magnification.

Fig. 35 Plates of Widmanstätten ferrite, seen in the sample annealed at 950°C
VSM Analysis

The results from Vibrating Sample Magnetometer are shown here. A combined graph of all BH curves shows the difference between magnetization of the annealed sample versus the as quenched ribbons. The observed behavior is noted extensively in literature, and is in perfect agreement with theory. The curves for the annealed samples show varying values for saturation magnetization $M_s$ represented in terms of mass magnetization $M_o$, and these values are highest for the sample annealed at 500°C (227.54 emu/g), followed by the sample annealed at 450°C (195.46 emu/g). Saturation magnetization $M_s$ values for the fully amorphous ribbon was higher (171.44 emu/g) than the fully crystalline sample (166.2 emu/g).

Also, from the graphs, an interesting trend was noticed – that of the remnant magnetization $M_r$, also represented in terms of mass magnetization $M_o$. The samples annealed at 625°C (104.91 emu/g) and 525°C (99.42 emu/g) show the greatest values for $M_r$ – much higher than those for fully amorphous (44.98 emu/g) or even the fully crystalline (104.91 emu/g) samples. Remanence $M_r$ is low also, for sample annealed at 475°C (43.8 emu/g).

Low field measurement led to very accurate values for coercivity $H_c$ and here, as per Herzer’s model discussed earlier and in agreement with literature (see Fig. 19), the coercivity $H_c$ is reduced for samples annealed at temperatures lower than the crystallization temperature $T_{cryst}$, and is enhanced greatly for samples annealed above it, by a more than two orders of magnitude.

The values obtained have been tabulated below;

<table>
<thead>
<tr>
<th>Sample</th>
<th>Properties</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-quenched ribbon</td>
<td></td>
<td>171.44</td>
<td>28.91</td>
<td>0.44</td>
</tr>
<tr>
<td>Ribbon Anl. at 425°C</td>
<td></td>
<td>182.61</td>
<td>61.7</td>
<td>0.31</td>
</tr>
<tr>
<td>Ribbon Anl. at 450°C</td>
<td></td>
<td>195.46</td>
<td>59.1</td>
<td>0.32</td>
</tr>
<tr>
<td>Ribbon Anl. at 475°C</td>
<td></td>
<td>183.79</td>
<td>43.8</td>
<td>0.19</td>
</tr>
<tr>
<td>Ribbon Anl. at 500°C</td>
<td></td>
<td>227.54</td>
<td>51.3</td>
<td>0.26</td>
</tr>
<tr>
<td>Ribbon Anl. at 525°C</td>
<td></td>
<td>158.3</td>
<td>99.42</td>
<td>107.38</td>
</tr>
<tr>
<td>Ribbon Anl. at 550°C</td>
<td></td>
<td>160.56</td>
<td>86.34</td>
<td>82.66</td>
</tr>
<tr>
<td>Ribbon Anl. at 575°C</td>
<td></td>
<td>160.37</td>
<td>92.5</td>
<td>86.42</td>
</tr>
<tr>
<td>Ribbon Anl. at 600°C</td>
<td></td>
<td>157.99</td>
<td>88.2</td>
<td>85.93</td>
</tr>
<tr>
<td>Ribbon Anl. at 625°C</td>
<td></td>
<td>159.38</td>
<td>104.91</td>
<td>112.99</td>
</tr>
<tr>
<td>Anl. at 950°C Crystalline Ribbon</td>
<td></td>
<td>166.2</td>
<td>44.98</td>
<td>19.31</td>
</tr>
</tbody>
</table>

Fig. 36 Table of Coercivity $H_c$ with Saturation and Remnant Magnetization ($M_s$, $M_r$)
The graph of the data obtained are shown below, shows a striking trend which is further discussed in the results. As we can see, the soft magnetic properties are greatly enhanced at annealing temperatures of about 450°C and 500°C. Hardness is greatest for samples annealed at 525°C and 625°C. The graphs in Fig. 37 below, show hysteresis loops — with the saturation and remnant magnetization ($M_s$, $M_r$) values in the inset. In Fig. 38 the coercivity $H_c$ values are plotted on a logarithmic scale, with low-field hysteresis curves in inset.

![Graph showing Hysteresis loops and values of Saturation & Remnant magnetization ($M_s$, $M_r$)](image)

**Fig. 37** Graph showing Hysteresis loops and values of Saturation & Remnant magnetization ($M_s$, $M_r$)

![Coercivity of as-quenched and annealed ribbons](image)

**Fig. 38** Coercivity $H_c$ values versus annealing temperatures, inset shows low-field coercivity $H_c$ loops
**MTGA Analysis**

The plots from Magneto-Thermogravimetric Analyzer all show agreement with theory in their peaks. The graphs are plotted mainly for finding the important structural and thermomagnetic parameters – namely, onset of phase change i.e. crystallization temperature $T_{\text{crys}}$ and the Curie temperature $T_c$. The graphs have been analyzed using a weight derivative curve to precisely point out the transition temperatures visible therein. Although the graphs for as-quenched, and those for the samples annealed at temperatures from 425°C upto 550°C look similar in their profile, there is an important and interesting distinction noticeable with the sample annealed at 550°C, in that it shows a background magnetization even after the Curie temperature of the amorphous phase, $T_{c}^{\text{am}}$ has been reached. This is discussed later on. Also of interest is the steady linear increase – noticed in the Curie temperature $T_c$ for these annealed samples with increasing annealing temperature. The plots for samples annealed at 575°C, 600°C, 625°C show a very peculiar ‘hump’ at the beginning of the heating cycle. This hump denotes an increase in the magnetic weight, and is explained quite simply. The sample annealed at 950°C for comparison, shows a more stable behavior in the beginning, but also displays a small hump at 250°C.

The composite graphs are shown below in batches for ease of viewing. Also included is a graph showing the trend of increasing Curie temperature $T_c$ for higher annealing temperatures.

![MTGA comparison](image)

**Fig. 39** (a) Graphs of as-quenched ribbons and samples annealed to temperatures from 425°C to 550°C (b) Graphs of as-quenched ribbons and samples annealed to temperatures from 575°C to 625°C and 950°C (All insets show plotted weight derivatives of the original curves)
Amorphous ribbons of composition Fe$_{75}$B$_{10}$Si$_{15}$ (METGLAS type) have been fabricated, with thickness of approximately 20µm and width 1mm. The as-quenched ribbons show homogenous amorphous structure. Batches of the amorphous ribbon have been annealed at temperatures from 425°C, 450°C, 475°C, 500°C, 550°C to 575°C, 600°C, and 625°C. For the purposes of comparison, one batch has been annealed at 950°C to allow full crystallization.

Analysis using X-ray diffractometer indicates a well-defined nanostructured material with varying grain sizes and volume fraction of crystallites. The analysis by X-ray is in agreement with studies which predicts the formation of α-Fe(Si) and Fe$_3$Si first due to segregation of Si. α-Fe(Si) has a BCC structure and Fe$_3$Si has a DO3 superlattice which is Heusler like. Further, at annealing temperatures just above the crystallization temperature, Fe$_2$B (with a bct structure) is precipitated, and at even higher temperatures, Fe$_5$SiB$_2$ (also with a bct structure) is formed. The fully crystalline sample shows a lower signature for α-Fe(Si) due to the formation of other stoichiometric phases from a mostly nanocrystalline precursor which is rich in α-Fe(Si) and Fe$_3$Si solid solution. It is noted, that these phases all show a ferromagnetic response in varying degrees. Broad and shifted peaks are observed for annealing at the lower temperatures, and this is due to the residual strain from within the ribbons. The plots for annealing temperatures ranging from 425°C to 500°C show primary...
precipitation of Fe$_3$Si in larger amounts than $\alpha$-Fe(Si), which shows higher precipitation from crystallization temperature $T_{\text{crys}}$ onwards.

The surface morphology of the ribbons has been inspected by scanning electron microscope. The amorphous ribbon shows characteristic surface regularity on side opposite to the wheel-contact. This is due to the absence of any long-range order, and an absence of defects. The wheel-side shows some irregularity, but only in a way, that mimics the wheel surface. The annealed samples show various degrees of inhomogeneity at the small scale. It is conjectured that crystalline volume fraction is quite high at the surface of the ribbons and this is in agreement with literature that also suggests that crystallization temperature decreases with lower Boron content.\textsuperscript{80} Segregation first, of Silicon is seen an at least one micrograph (Anl. at 550°C), which is in agreement with theory.\textsuperscript{54,69,70} Plates of Widmanstätten ferrite are postulated to form due to annealing at high temperature of 950°C, where $\gamma$-Fe is stable and is the precursor to Widmanstätten ferrite.

Striking results have been acquired by characterization of samples using vibrating sample magnetometer. The amorphous phase shows excellent soft magnetic properties, followed by that of the fully crystalline samples.\textsuperscript{7,40,41} The coercivity $H_c$ of the samples annealed above 500°C are very high, by about two orders of magnitude – as shown by low-field measurements. $H_c$ for amorphous ribbons is 0.44 Oe and that for samples annealed at 525°C and 625°C is 107.38 Oe and 112.99 Oe respectively. In comparison, the polycrystalline sample (annealed at 950°C) shows a coercivity $H_c$ of 19.32 Oe. The most interesting and relevant results are acquired for samples annealed between 425°C and 500°C. Superior soft magnetic response is observed, with higher saturation magnetization $M_s$ and lower coercivity $H_c$ – the best of which are $M_s = 227.54$ emu/g ($H_c = 0.26$ Oe) for annealing at 500°C and $H_c = 0.19$ Oe ($M_s = 183.79$ emu/g) for annealing at 475°C. In terms of results, this is expected – to find the most favorable soft-magnetic nanostructured material from an applications point of view, and to explain the science behind the improved properties. Grain size and volume fraction are the factors of correlation in this case, and as noted from the X-ray analysis, the grain size ($\alpha$-Fe(Si) phase) for samples annealed at temperatures from 425°C to 500°C is well below 10nm with volume fraction ranging from 0.65 to 0.75. Concurrently, grain size is above 20nm for samples annealed at temperatures from 525°C to 625°C with volume fractions upward of 0.80. Results are as per the predictions of Herzer’s random anisotropy model, which confirms that coercivity $H_c$ is proportional to the sixth power of grain size, up to about 100nm grains.\textsuperscript{45} Suzuki and Cadogan have, in terms of the intrinsic capability of magnetization of the residual amorphous phase $M_s^{am}$, also explained the dependence of coercivity $H_c$ on crystalline volume fraction; if $M_s^{am} \approx 0$, the coercivity $H_c$ decreases, however, for systems such as the one being studied here – with quite a large $M_s^{am}$ value, the coercivity $H_c$ increases with increasing crystalline volume fraction.\textsuperscript{48,81} Also, the hardening behavior observed here is noted by Škorvánek, et al. for METGLAS like FeBSi alloy systems.\textsuperscript{82} Varga et al. have also extensively investigated this behavior which is in accordance with Herzer’s model.\textsuperscript{42,52}
A peculiar trend was observed with remnant magnetization $M_r$, which is quite high for samples annealed at 525°C and 625°C. This is due to the high volume fraction of $\alpha$-Fe(Si) in both these samples, which couple most strongly. It has also been stated that for ribbons annealed over 600°C, hardening is noticed due to similar exchange between nanograins over a larger crystalline volume fraction. The interesting aspect of the remnant magnetization $M_r$ values, is that they vary in one-to-one proportion with the coercivity $H_c$ with respect to annealing temperatures throughout. This phenomenon has not been noted in literature, for amorphous and nanostructured materials.

Analysis of amorphous and annealed ribbon samples using a magneto-thermogravimetric analyzer shows proof-of-concept results in line with prior work. The scan curves for the amorphous samples was used to determine the range of annealing temperature, with assistance from prior studies. The results acquired during this work led to some interesting phenomenon which are peculiar to the alloy system of choice. For the sample annealed at 550°C, a very small magnetic response (translating to 4wt. %) was noticed even after the Curie temperature for the amorphous phase $T_{c, am}$ was reached. This residual retained magnetization, which was displayed for the entire sample, is as noted in studies which discuss the magnetic response of nanograins at annealing temperatures close to $T_{c, am}$ for FeBSi systems. Also, the samples annealed above 550°C showed a hump at the start of the scans (ca. 250°C). This is easily explained due primarily to the precipitation and growth of newer (magnetic) phases with higher annealing temperatures, and also in part due to structural relaxation offered during the scan, which serves to reduce the structural anisotropy and thus increases magnetic response. This theory is verified by the curve obtained for the sample annealed at 950°C, which also shows the hump even after complete crystallization. This is an aftermath of Joule heating, which does not fully resolve structural stresses.

Of more interest is the steady increase in Curie temperature with respect to annealing between 425°C and 550°C, which is explained by irreversible structural relaxation of internal stresses and removal of microvoids. The gradual increase in the Curie temperature is also evidence of a lack of chemical segregation at these temperatures. The increase is noted to be linear, but further investigation may refine the profile of the observed increase.
To conclude; for the study of high remanence and coercivity ($M_r$, $H_c$) in materials derived from soft-magnetic precursors, this study offers results in a structured format. Excellent soft magnetic properties have been noted for samples annealed at 475°C and 500°C – with coercivity $H_c$ lesser than, and saturation magnetization greater than – both amorphous and polycrystalline ribbons. It has been seen, that magnetic hardness is largest for samples annealed at 550°C and 625°C. This has been attributed to the crystalline volume fraction and grain-size seen in those ribbon samples. Results of interest have been the high remnant magnetization of samples annealed at 525°C and 625°C. Parallel to that, the sample annealed at 550°C shows that magnetization is retained by this sample even at the Curie temperature for the amorphous phase $T_{c,am}$. A one to one relationship between the remnant magnetization $M_r$ and coercivity, for the samples that were annealed up to nanostructured states is seen, which has not been reported for nanostructured materials. Curie temperature has also been shown to increase as suggested by theory – the fit provisionally suggested is linear with respect to increasing annealing temperature.

**Future Scope**

It has been noted in various studies that magnetostriction is greatly reduced for nanostructured systems, and that can be made an inquiry into this simple alloy system. Also, from an application point of view, technology that requires materials of these specific magnetic properties, e.g. for power transformers, nanowires and sensors most notably, may benefit from further studies. Such may include the effects of non-Joule annealing, slight variations of the composition, etc.

From the point of view of Materials Science and Physics, a better understanding of principles, such as Structural properties affecting Magnetism, Evolution of Nanocrystalline Phases, Random Anisotropy, Exchange Mechanisms, etc. can be had.

More immediately, various annealing parameters can be tested – especially the temperature range between 475°C and 500°C at varying annealing periods. This will allow the most optimum annealing conditions to be found, and will provide more data for the study of increase in Curie temperature and the profile of its increase. Transmission Electron microscopy (TEM) and Magnetic Force Microscopy can be carried out for probing the structure and magnetostrictive properties of this material. Low-temperature DC and AC susceptibilities can be carries out using Superconducting Quantum Interference Device (SQUID), and AC Susceptometer – to better resolve the magnetic properties observed herein and investigate superparamagnetic response, if any. In addition, for investigation of the effects of Copper substitution, study with slightly varied alloy compositions can be carried out – to check whether other elemental additions will enhance soft-magnetic properties.
Bibliography


30. Zhang, Y., Hono, K., Inoue, A. & Sakurai, T. 


125. Franco, V., Conde, C. F. & Conde, A. Effect of the Si/B ratio on the magnetic anisotropy distribution of Fe[sub 73.5][Si][sub 22.5-x][B][sub x][Cu][sub 1][Nb][sub 1] (x≤7,9,16) alloys along nanocrystallization. *Journal of Applied Physics* **84**, 5108 (1998). http://dx.doi.org/10.1063/1.368807


