

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

MAGNETIC AND STRUCTURAL PROPERTIES OF
Fe/CEMENTITE NANOPARTICLES PRODUCED
BY SOLID STATE PYROLYSIS

AYDAN AKYILDIZ MERT

A THESIS OF MASTER OF SCIENCE
PHYSICS DEPARTMENT

Prof. Dr. MEVLÜT KARABULUT

FEBRUARY 2024

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL

MAGNETIC AND STRUCTURAL PROPERTIES OF
Fe/CEMENTITE NANOPARTICLES PRODUCED
BY SOLID STATE PYROLYSIS

AYDAN AKYILDIZ MERT

A THESIS OF MASTER OF SCIENCE
PHYSICS DEPARTMENT

PROF. DR. MEVLÜT KARABULUT

FEBRUARY 2024

T.C.
GEBZE TEKNİK ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

KATI HAL PİROLOZİS YÖNTEMİ İLE ÜRETİLEN
Fe/CEMENTİTE NANOPARÇACIKLARIN MANYETİK
VE YAPISAL ÖZELLİKLERİ

AYDAN AKYILDIZ MERT

YÜKSEK LİSANS TEZİ
FİZİK ANABİLİM DALI

PROF. DR. MEVLÜT KARABULUT

ŞUBAT 2024

YÜKSEK LİSANS JÜRİ ONAY FORMU

GTÜ Lisansüstü Eğitim Enstitüsü Yönetim Kurulunun 05/02/2024 tarih ve 2024/10 sayılı kararıyla oluşturulan jüri tarafından 16/02/2024 tarihinde tez savunma sınavı yapılan Aydan Akyıldız Mert'in tez çalışması Fizik Anabilim Dalında Fizik Programında YÜKSEK LİSANS tezi olarak kabul edilmiştir.

JÜRİ

ÜYE

(TEZ DANIŞMANI) : Prof. Dr. Mevlüt Karabulut

ÜYE

: Prof. Dr. Eyüp Duman

ÜYE

: Prof. Dr. Osman Öztürk

ONAY

Gebze Teknik Üniversitesi Lisansüstü Eğitim Enstitüsü Yönetim Kurulunun

...../...../..... tarih ve/..... sayılı kararı.

İMZA/MÜHÜR

ABSTRACT

Carbon-encapsulated iron-cementite magnetic nanoparticles (MNPs) have attracted great attention in the scientific community due to their wide range of applications and ease of production. The production of cementite nanoparticles is mostly done by the chemical vapor deposition (CVD) method in the literature. Unlike this method, studies have begun to be carried out with the pyrolysis method because it is simple, fast, and repeatable. This study aims to perform the structural and magnetic characterization of Fe/Fe₃C structures produced at different temperatures using solid-state pyrolysis. With this method, 6 different samples were produced in 45 minutes at 700-750-800-850-900 and 1000 °C. The production of Fe/Fe₃C nanoparticles could not be achieved with a proper crystal structure at 700°C and 750°C but, at higher pyrolysis temperatures, appropriate structuring occurred, and carbon nanotubes decorated with Fe/Fe₃C particles were formed. Phase analyses were performed by XRD and Rietveld Refinement, and iron oxide structures were observed at 700 °C and 750 °C. Magnetization measurements were first made using magnetic field-dependent magnetization measurement, and hysteresis curves compatible with ferromagnetic nanoparticles were recorded with a SQUID magnetometer. In the temperature dependent magnetization measurement, in addition to Curie Temperature effect, the decomposition of Fe₃C and phase formation took a role in magnetization changes. Magnetization originating separately from iron and cementite was analyzed, and mass ratios were calculated. It was seen that the mass ratios calculated from magnetization and the mass ratios calculated with XRD were compatible with each other.

Keywords: Fe, Cementite, Solid State Pyrolysis Method, SQUID, Ferromagnetism

ÖZET

Demir-Sementit içelikli karbon kapsüllü manyetik nanoparçacıklar (MNP'ler), geniş uygulama alanları ve üretim kolaylıkları nedeniyle bilim dünyasında büyük ilgi görmüştür. Literatürde Sementit nanoparçacıklarının üretimi çoğunlukla kimyasal buhar biriktirme (CVD) yöntemi ile yapılmaktadır. Bu yöntemin aksine, basit, hızlı ve tekrarlanabilir olması nedeniyle piroliz yöntemi ile çalışmalar yapılmaya başlanmıştır. Bu çalışmanın amacı, katı hal pirolizi kullanılarak farklı sıcaklıklarda üretilen Fe/Fe₃C yapılarının yapısal ve manyetik karakterizasyonunu gerçekleştirmektir. Bu yöntemle, 700-750-800-850-900 ve 1000 °C sıcaklıklarında 45 dakikada 6 farklı örnek üretildi. Fe/Fe₃C nanoparçacıklarının 700°C ve 750°C'de uygun kristal yapı ile üretimi gerçekleştirilemedi. Bunun yanı sıra, daha yüksek piroliz sıcaklıklarında uygun yapılanma meydana geldi ve Fe/Fe₃C parçacıkları ile çevrelenmiş karbon nanotüpler oluştu. Faz analizleri, X-ışını kırınımı (XRD) ve Rietveld Analiz yöntemleri kullanılarak yapıldı ve 700°C ve 750°C'de demir oksit yapıları gözlemlendi. Manyetizasyon ölçümleri, ilk olarak manyetik alana bağlı manyetizasyon ölçümü kullanılarak yapıldı ve Süperiletken Kuantum Girişim Cihazı (SQUID) manyetometresi ile ferromanyetik nanoparçacıklara uygun histerezis eğrileri kaydedildi. Sıcaklığa bağlı manyetizasyon ölçümünde, Curie Sıcaklığı etkisinin yanı sıra, Fe₃C'nin Fe ve C'a ayrışması ve yeni bir faz oluşumu manyetizasyon değişikliklerinde rol oynadı. Demir ve Sementit 'den elde edilen manyetizasyon değerli ayrı ayrı analiz ediliğ kütle oranları hesaplandı. Manyetizasyondan hesaplanan kütle oranları ile XRD ile hesaplanan kütle oranlarının birbiriyle uyumlu olduğı görüldü.

Anahtar Kelimeler: Fe, Sementit, Katı hal piroliz, SQUID, Ferromanyetizma

ACKNOWLEDGEMENTS

I would like to express my deep and sincere gratitude to my supervisors, Prof. Dr. Mevlüt Karabulut from Gebze Technical University, Turkey, Prof. Dr. Mehmet Acet, Prof. Dr. Michael Farle and Dr. Marina Spasova from University Duisburg-Essen, Germany who not only shared their profound scientific knowledge with me but also taught me great lessons of life. Their support, suggestions and encouragement gave me the drive and will to complete this work.

European Union's Horizon 2020 research and innovation programme under grant agreement No 857502 (MaNaCa) has my gratitude to support this work.

I wish to express my warm and sincere thanks to AG Farle Team from University Duisburg-Essen, Germany and H. Gyulasaryan, G. Chilingaryan, A. Gnoyan and A.Manukyan from Institute for Physical Research of National Academy of Science (IPR-NAS), Armenia for their collaboration to this research.

I am grateful to my brother Arda Akyıldız, my mother Nuray Bekiroglu Akyıldız, my father Ayhan Akyıldız and my husband Dr. Alican Mert for their love and support.

Finally, I want to thank, Mustafa Kemal Atatürk who is the founding father of the Republic of Turkey, gave the education opportunity and equality to Turkish women and Republic of Turkey, that celebrates the 100th years of Republic in 2023.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	v
ÖZET	vi
ACKNOWLEDGEMENTS	vii
TABLE OF CONTENTS	viii
LIST OF SYMBOLS AND ABBREVIATIONS	ix
LIST OF FIGURES	x
LIST OF TABLES	xi
1. INTRODUCTION	1
1.1. Magnetic Materials	3
1.2. Hysteresis Curve	5
1.3. Cementite	6
1.4. Solid State Pyrolysis Method	8
1.5. Transmission Electron Microscopy	9
1.6. X-RAY Diffraction	10
1.7. Rietveld Analysis	10
1.8. Superconducting Quantum Interference Device Magnetometer	11
2. SYNTHESIS OF Fe/Fe ₃ C MAGNETIC NANOPARTICLES	15
3. MORPHOLOGICAL ANALYSIS AND SIZE DISTRIBUTION	17
4. STRUCTURAL ANALYSIS	22
5. MAGNETIC PROPERTIES OF Fe/Fe ₃ C NANOPARTICLES	29
6. STRUCTURAL DIFFERENTIATION CAUSED BY MAGNETIZATION	37
7. CURIE TEMPERATURE CALCULATION	39
8. MAGNETIZATION ANALYSIS	41
9. CONCLUSION	44
REFERENCES	48
BIOGRAPHY	53
PRESENTATIONS FROM THE THESIS	54
APPENDICES	55

LIST OF SYMBOLS AND ABBREVIATIONS

°	: Degree
°C	: Centigrade
λ	: Wavelength
Å	: Ångström
Am ² /kg	: Ampere meter square per kilogram
C	: Carbon
emu	: Emu
Fe	: Iron
Fe ₃ C	: Cementite
Fe ₃ O ₄	: Magnetite
γ -Fe ₂ O ₃	: Maghemite
g	: Gram
G	: Gauss
H	: Applied magnetic field
H _c	: Coercive field
K	: Kelvin
kA/m	: Kiloampere per meter
kV	: Kilovolt
min	: Minute
M	: Magnetization
M _s	: Saturation magnetization
M _{rem}	: Remanence magnetization
nm	: Nanometer
Pa	: Pascal
T	: Tesla
T _c	: Curie Temperature
F700-45	: Sample prepared at 700°C Pyrolysis temperature by 45 minutes
F750-45	: Sample prepared at 750°C Pyrolysis temperature by 45 minutes
F800-45	: Sample prepared at 800°C Pyrolysis temperature by 45 minutes
F850-45	: Sample prepared at 850°C Pyrolysis temperature by 45 minutes
F900-45	: Sample prepared at 900°C Pyrolysis temperature by 45 minutes
F1000-45	: Sample prepared at 1000°C Pyrolysis temperature by 45 minutes
HT	: High temperature
LT	: Low temperature
MNPs	: Magnetic Nanoparticles
NPs	: Nanoparticles
SQUID	: Superconducting Quantum Interference Device
TEM	: Transmission Electron Microscopy
XRD	: X-Ray Diffraction
ZFCF	: Zero Field Cooled Field

LIST OF FIGURES

	<u>Page</u>
Figure 1.1.a.: Schematic of carbon encapsulated Fe/Fe ₃ C Magnetic Nanoparticles.	2
Figure 1.1.b: Carbon encapsulated Fe/Fe ₃ C Magnetic Nanoparticles.	2
Figure 1.2: Moment alignment and behavior of the magnetic materials.	4
Figure 1.3: M-H hysteresis loops of a ferromagnetic.	5
Figure 1.4: The metastable equilibrium of Fe + Fe ₃ C phase diagram.	7
Figure 1.5: Structure of Fe ₃ C cell.	8
Figure 1.6: Schematic of Solid-State Pyrolysis Method's furnace.	8
Figure 1.7: Schematic of Transmission Electron Microscope (TEM).	9
Figure 1.8: Bragg's Law's schematic illustration.	10
Figure 1.9: Schematic of the Superconducting Quantum Interference Device (SQUID)	12
Figure 2.1: Powder cementite.	15
Figure 3.1: TEM device.	17
Figure 3.2: TEM images of A. F700-45, B. F750-45, C. F800-45, D. F850-45, E. F900-45, F. F100-45	18
Figure 3.3: High-resolution TEM images of F700-45.	19
Figure 3.4: Size distribution of the samples measured with ImageJ software.	20
Figure 3.5: The size distribution of all samples with standard deviation according to solid state pyrolysis temperature.	21
Figure 4.1: X'Pert Panalytical Diffractometer.	22
Figure 4.2: Jana and Maud software's' interface.	23
Figure 4.3: Observed and Calculated XRD patterns of the samples.	25
Figure 4.4: XRD Patterns of Cementite-Iron-Carbon nanocomposites.	26
Figure 4.5: Phases weight percentages with error bar for all samples.	28
Figure 5.1: Quantum Design MPMSXL SQUID Magnetometer.	29
Figure 5.2: a) Low temperature measurement sample, b) High temperature measurement sample	30
Figure 5.3: Field dependence of magnetization for all samples at 10 K.	31
Figure 5.4: 10 times focused on origin field dependence of magnetization for all samples at 10 K.	31
Figure 5.5: Pyrolysis temperature dependences of coercive field and saturation magnetization.	33
Figure 5.6: Variation of magnetization in low and high temperature from a) F700-45 b) F750-45 c) F800-45.	34
Figure 5.7: Variation of magnetization in low and high temperature from a) F850-45 b) F900-45 c) F1000-45.	35
Figure 6.1: XRD characterization of low temperature and high-temperature magnetization measured F700-45 samples.	37
Figure 6.2: XRD characterization of low temperature and high-temperature magnetization measured F850-45 samples.	38
Figure 7.1: Curie Temperature calculation graphs.	39
Figure 8.1: Iron-Cementite magnetic moment calculation graphs.	41

LIST OF TABLES

	<u>Page</u>
Table 2.1: List of the samples' names with pyrolysis temperature and time	16
Table 4.1: Phases' literature structure information.	24
Table 4.2: Rietveld refinement analysis % weight.	27
Table 5.1: Masses of the samples used for low and high temperature magnetization measurements.	30
Table 5.2: Saturation magnetization, Remanence Ratio and Coercive Field list of the samples investigated.	32
Table 7.1: Calculated Curie Temperatures of Fe ₃ C.	40
Table 8.1: Magnetic moments of the Fe, Fe ₃ C and Fe/Fe ₃ C particles.	42
Table 8.2: Weight and weight percentages from magnetization calculations.	43
Table 8.3: Weight percentages from magnetization and XRD measurement calculations.	43

1. INTRODUCTION

Carbon-encapsulated iron-cementite magnetic nanoparticles have significant attention in the scientific community due to their wide range of applications and ease of production.

Their high surface area and electronic properties make them effective catalysts for various chemical reactions, including hydrogenation, carbon dioxide conversion, and organic synthesis [1]. The ability to synthesize iron-cementite nanoparticles with a carbon shell structure in a controlled manner provides an advantage in their use in chemical methods. Achieving controlled synthesis allows for the modification of properties such as surface area and electrical properties, facilitating the production of suitable materials.

Their magnetic properties make them suitable for applications as magnetic materials, such as magnetic data storage devices, sensors, and spintronics [2], [3]. Being coated with a carbon shell structure, iron/cementite showing ferromagnetic properties, reduce magnetic interactions, thus forming a more magnetically stable structure. This way, while achieving magnetization with external magnetic fields, magnetic and thermal stability is ensured in the nanocrystalline structure [4].

Also these electrical, magnetic and mechanical properties of carbon encapsulated iron/cementite magnetic nanoparticles give an opportunity to use in the realm of energy storage and conversion, offer potential in applications such as lithium-ion batteries, supercapacitors, and fuel cell catalysts [5]. One of its most important features is that, due to its carbon structure coating, it prevents the reaction of iron and cementite with oxygen, thus preventing oxidation [6]. This also particularly supports its use in industrial applications.

Additionally, they exhibit potential in biomedical applications. They can be utilized in drug delivery systems, as contrast agents for magnetic resonance imaging, and in hyperthermia-based cancer treatments. The magnetic properties of cementite nanoparticles enable targeted drug delivery, imaging, and therapeutic heating under alternating magnetic fields [7]. One of the most critical requirements for the use of magnetic nanoparticles in biomedical applications is their biocompatibility. They

should be biologically compatible to be chemically and biologically inert, avoiding any toxic effects. To achieve this biocompatibility, core/shell complex structures with coating layers are preferred [8]. Iron-cementite magnetic nanoparticles with a carbon shell structure are also suitable for use due to these properties. With all these usage areas, its popularity is increasing day by day.

In a general approach, carbon encapsulated Fe/Fe₃C magnetic nanoparticles consists of a core forming a complex structure of iron/cementite surrounded by graphite as shown in Figure 1.1.a. In reality, structure is more complex, as depicted in Figure 1.1.b, consisting of a core that is comprised of iron/cementite and it is surrounded by graphite which resembles a cloud-like structure. Systems composed of a magnetic core and a shell in this manner are referred to as magnetic core-shell structures.

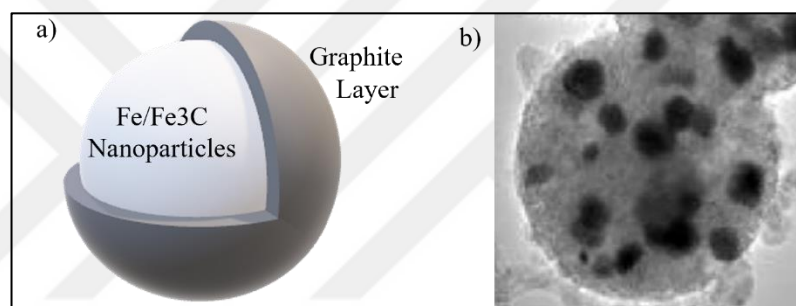


Figure 1.1: a) Schematic of carbon encapsulated Fe/Fe₃C magnetic nanoparticles
b) Carbon encapsulated Fe/Fe₃C magnetic nanoparticles [9].

The production of carbon encapsulated Fe/Fe₃C magnetic nanoparticles could be done by chemical vapor deposition (CVD) [10], detonation [11] and electric plasma discharge [12]. Different from these methods, studies have been started with the pyrolysis method [13] because it is simple, fast and reproducible [7], [9], [14].

With recent research, it has been observed that material production through solid-state pyrolysis can be controlled by altering parameters such as the precursor, pressure, temperature, and duration [15], [16]. However, due to its complex nature, occurring depending on multiple parameters, the exact mechanism is not yet fully understood.

The main motivation in this study was to produce the iron cementite magnetic nanoparticles by solid state pyrolysis method at different temperatures and observe changes that occur in the resulting samples magnetic behaviors, structures and bonding

due to ambient temperature variations and the amount of samples. The aim was to perform the structural and magnetic characterization of Fe/Fe₃C structures produced at different temperatures by solid state pyrolysis method. 6 different samples were produced by this method at 700-750-800-850-900 and 1000 °C in 45 minutes.

The effects of producing process temperature on samples were investigated with Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and Superconducting Quantum Interference Device Magnetometer (SQUID).

1.1. Magnetic Materials

Magnetic materials constitute an important field of study in the field of materials science and engineering. These materials have the distinctive feature of exhibiting magnetic properties in response to external magnetic fields. They play a fundamental role in numerous scientific disciplines and technological applications with profound implications for a variety of sectors, including electronics, electrical engineering and advanced materials research.

The basis of magnetic material studies lies in the complex behavior of atomic or molecular magnetic moments, each of which can assume different alignments. These arrangements lead to a variety of magnetic properties, and materials exhibiting these properties are classified as ferromagnetic, paramagnetic, diamagnetic, ferrimagnetic and antiferromagnetic. These categories cover the subtle magnetic behaviors that are used to engineer and optimize a wide variety of devices and systems.

Diamagnetism represents a property unique to all materials, resulting from the response of electrons to an externally applied magnetic field. In diamagnetic materials, the orbital movement of electrons at the atomic or molecular level causes tiny electrical currents to circulate. These induced currents cause magnetic moments to align in the opposite direction of the external magnetic field. Diamagnetic materials exhibit a weak, inherently negative magnetic susceptibility.

Paramagnetism is seen in materials containing unpaired electrons. When unpaired electrons are placed in an external magnetic field, they align their magnetic moments parallel to the direction of the field. This alignment creates a net magnetic moment, leading to positive magnetic susceptibility. Paramagnetic materials exhibit weak magnetization that is directly proportional to the strength of the applied magnetic field.

Unlike ferromagnetic materials, paramagnetic materials do not have spontaneous magnetization and their magnetization disappears when the external field is removed.

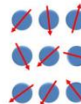
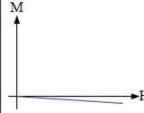
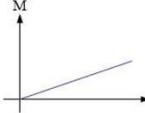
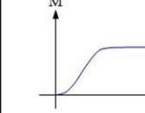
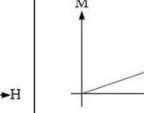
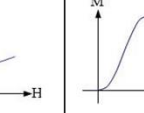
Magnetization	Diamagnetism	Paramagnetism	Ferrimagnetism	Antiferromagnetism	Ferromagnetism
Magnetic Behavior					
					

Figure 1.2: Moment alignment and behavior of the magnetic materials [17].

Ferrimagnetism is another magnetic property in which atomic magnetic moments align in both parallel and antiparallel directions. They have a weak but clear magnetization and occur when unequal magnetic moments align in opposite directions. It can maintain partial magnetization even in the absence of an external magnetic field.

For the antiferromagnetic materials, the magnetic moments are aligned in an antiparallel position with each other. With this alignment, the net magnetization is zero on a microscopic scale, making the material non-magnetic. Their magnetic configuration causes phase transition below the Néel temperature, and they exhibit long-range magnetic order.

The other and extremely popular type of magnetization is ferromagnetism, it is distinguished by the distinct and spontaneous alignment of atomic magnetic moments within a material; this causes their parallel orientation and the resulting emergence of macroscopic magnetization, even in the absence of an externally applied magnetic field. Ferromagnetic materials exhibit a characteristic phenomenon known as hysteresis; This refers to their ability to maintain magnetization when the external magnetic field recedes, making them capable of serving as permanent magnets. The most important parameter in ferromagnetism studies is the Curie Temperature, which represents the critical temperature at which ferromagnetic materials lose their ferromagnetic properties and undergo a phase transition. This magnetic behavior is

fundamentally governed by complex exchange interactions between neighboring magnetic moments.

1.2. Hysteresis Curve

The hysteresis loop is a graphical representation that gives insight into how ferromagnetic materials respond to changing magnetic fields. It provides information about the correlation between the applied magnetic field (H) and the magnetization (M) of the material and thus explains the magnetization behavior.

Observation of hysteresis loop can be understood as follows: The applied magnetic field intensity increases from its initial value of zero, the material demonstrates a nonlinear magnetization behavior. When the field strength reaches a certain threshold, the material initiates the process of magnetization, eventually reaching a state of saturation characterized by complete alignment of magnetic domains. Once saturation is achieved, the magnetic field can be decreased to zero, and the material retains its level of magnetization. However, to reset the magnetization to zero, it is necessary to reverse the direction of the magnetic field and increase its strength significantly till the reverse saturation value [18].

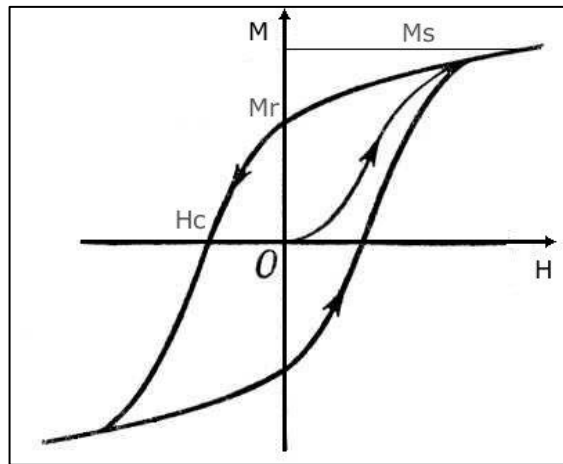


Figure 1.3: M-H hysteresis loops of a ferromagnetic [19].

The other important parameters in hysteresis loop are Remanence Magnetization (M_r), Coercive Field (H_c) and Saturation Magnetization (M_s) (Figure 1.3). Saturation magnetization is the maximum level of magnetization that can be achieved in a

material. It occurs when all the magnetic moments or domains are aligned with the direction of applied magnetic field. Remanence magnetization is the permanent magnetization that the material has when the applied magnetic field is removed after the material is saturated. Another parameter that is obtained by dividing remanence magnetization by saturation magnetization and plays a key role in determining the magnetic performance of the material is Remanence Ratio. A high remanence ratio indicates that the material has high remanence, that is, permanent magnetization ability, while a low remanence ratio indicates that the material is less magnetically stable and has less permanent magnetization. The external magnetic field needed to revert the magnetization of the material from saturation, back to a state of complete demagnetization is defined Coercive Field. Materials characterized by low remanence magnetization and coercivity field exhibit soft magnetic properties, while hard magnetic materials demonstrate opposite characteristics.

1.3. Cementite

Cementite, or iron carbide (Fe_3C), is a significant chemical compound that plays a crucial role in materials science and metallurgy. It is not a new material and well known especially from Fe/C phase diagram [20]. According to phase diagram, in general approach iron and carbon molecules changes their structures and bounds according to their concentration and the temperature (Figure 1.4).

Characterized by a consistent composition of three iron (Fe) atoms for each carbon (C) atom, cementite shows an orthorhombic crystal structure with a distinct atomic arrangement. Its remarkable attributes include exceptional ferromagnetism, alongside hardness and brittleness, a characteristic feature of iron-based materials. Cementite naturally occurs during the phase transition of carbon-containing iron alloys. Its microstructure substantially changes in terms of mechanical and magnetic properties, especially when subjected to processes like heat treatment and phase transformations. Due to this feature, it exists in a metastable phase that has also been known some time and has a significant advantage in material applications [21].

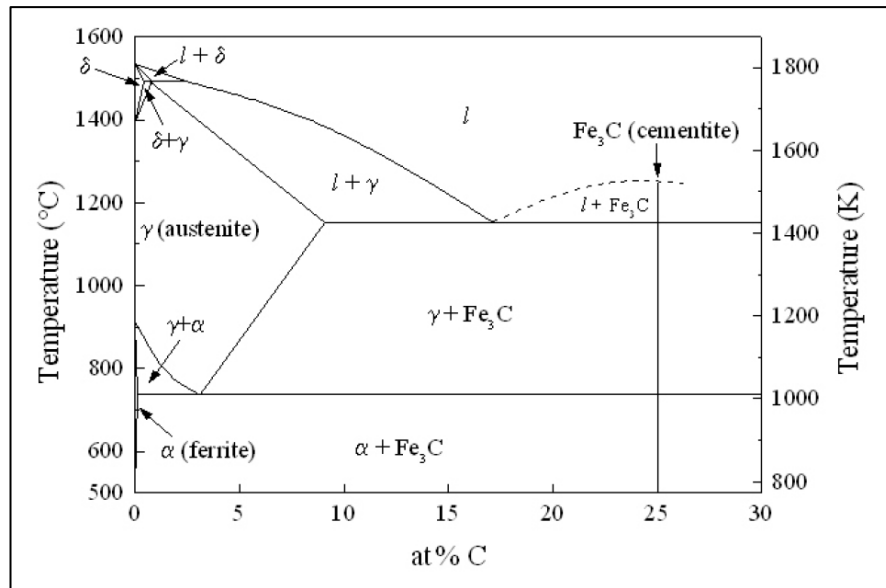


Figure 1.4: The metastable equilibrium of Fe + Fe₃C phase diagram [22].

Cementite in space group “Pnma” has an orthorhombic structure, and its lattice parameters are $\alpha=90.0$, $\beta=90.00$, $\gamma=90.00$, $a= 0.508475$ nm, $b=0.67367$ nm, $c=0.451394$ nm [23].

The structure of Fe₃C is given in Figure 1.5, orthorhombic structure. The carbon and iron atoms are depicted as black and white/grey spheres, respectively.

Fe₃C exhibits ferromagnetic properties at room temperature, undergoing a transition to the paramagnetic state when the temperature reaches the Curie Temperature (T_c) of approximately 483 K [24].

When compared to iron, iron carbides offer numerous advantages. When subjected subject to oxidation conditions [25], more stable structure of cementite makes it more resistant to oxidation and corrosion compared to iron [26]. In addition, its metastable phase gives more chemical stability to cementite compared to iron.

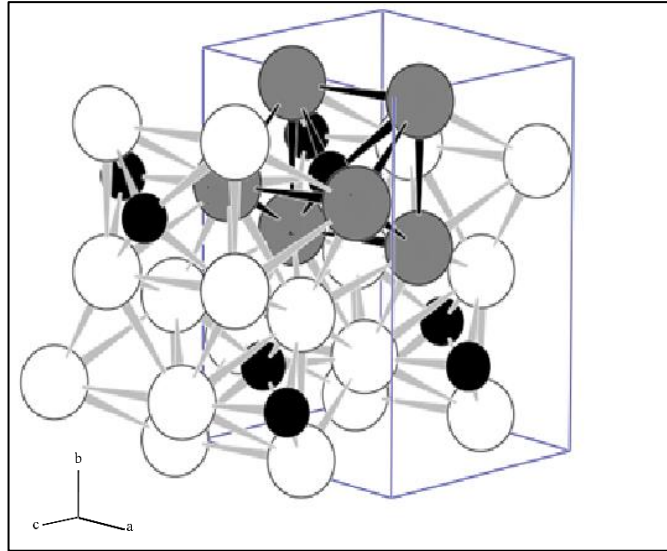


Figure 1.5: Structure of Fe_3C cell [27].

On the other hand, it is possible to produce $\text{Fe}/\text{Fe}_3\text{C}$ two-phase nanoparticles with Fe_3C fabrication. With these two phases, it is easier to control the magnetic behavior of the material because of the iron's higher saturation magnetization. The saturation magnetization value of the bulk cementite is approximately $140 \text{ A.m}^2/\text{kg}$ [9].

1.4. Solid State Pyrolysis Method

The mechanism of solid-state pyrolysis involves the thermal decomposition of organic compounds, which results in the release of volatile gases and the formation of a solid residue. The solid residue can be further processed to form the desired material. The reaction kinetics and the composition of the solid residue depend on several factors, including the nature of the precursor material, the temperature and duration of the pyrolysis process, and the presence of any additives.

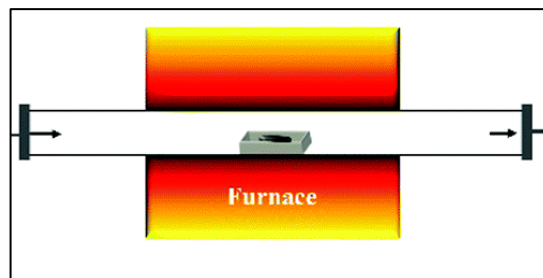


Figure 1.6: Schematic of Solid-State Pyrolysis Method's furnace.

In this production method, as in others, the most important criterion is the solid material selected depending on the material to be obtained. The material, called the precursor, reacts roughly by the solid-state pyrolysis method to form the desired material. In order for this reaction to occur as desired, parameters such as pressure, temperature and time are taken into consideration. To provide more controlled parameters, the precursor is enclosed in a quartz tube and this tube is heated in the tube furnace (Figure 1.6) for specified periods of time to increase the temperature. In this way, the completion of the reaction ensures the production of the desired material.

1.5. Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a powerful technique used to visualize the internal structure of materials with a resolution down to the atomic level. TEM imaging is based on the interaction of electrons with matter.

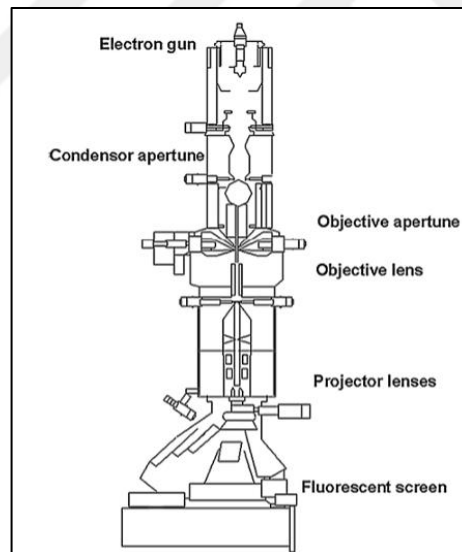


Figure 1.7: Schematic of Transmission Electron Microscope (TEM) [28].

In a typical TEM setup, a beam of electrons is generated by an electron gun, which accelerates electrons to high energies using an electric field. The electron beam is focused by a series of electromagnetic lenses and then passed through a thin sample mounted on a thin film grid. When the electrons pass through the sample, they interact with the atoms and electrons in the material. Some of the electrons are scattered by the atoms, while others pass through the sample without interacting. The transmitted

electrons are collected by a detector, which generates an image based on the intensity of the scattered electrons.

1.6. X-RAY Diffraction

An effective analytical method that is often used to examine the atomic and molecular structure and characteristics of materials is the X-ray diffraction. This technique relies on the scattering of X-rays in particular directions caused by the interaction of X-rays with electrons in a crystal lattice. It is possible to ascertain the crystal structure, content, and other physical characteristics of the substance being researched by examining the scattering pattern.

The X-ray diffraction principle is based on Bragg's law, which asserts that when X-rays are scattered by a crystal lattice, the scattering waves will only interfere constructively if their paths are integral multiples of the X-rays' wavelength. This condition is satisfied when the angle of incidence of the X-rays, the angle of scattering, and the spacing between the lattice planes in the crystal all meet specific criteria. The resulting pattern of constructive interference, called the diffraction pattern, is unique for each crystal structure and can be analyzed to determine the crystal structure.

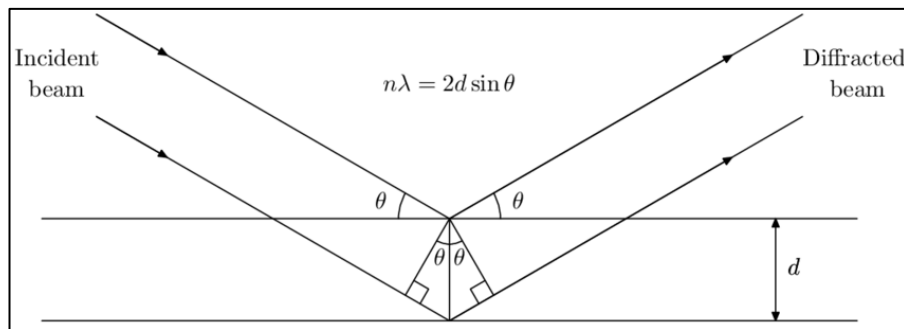


Figure 1.8: Bragg's Law's schematic illustration [29].

1.7. Rietveld Analysis

Rietveld analysis is a highly complex mathematical and computational method widely applied in the fields of X-ray and neutron diffraction. It serves as a tool for determining the crystal structure of various materials and provides information regarding the

arrangement of atoms and molecules within the material. It is widely used in materials science, chemistry and mineralogy, providing deep insights into the mechanical and thermal properties of crystalline materials.

The process typically begins with collecting diffraction data of the material. An initial model of the crystal structure is then designed, containing details of the types of atoms and their distribution within the crystal lattice. The next stage, known as Rietveld refinement, requires iterative tuning of the model's parameters. This involves fine-tuning the atomic positions and thermal vibrations to achieve the best possible fit between the observed diffraction data and the model's predictions. This iterative process continues until an optimal fit is achieved, resulting in a crystal structure that provides a comprehensive set of atomic arrangements within the crystal lattice [30].

These complex calculation processes, which offer many advantages such as determination of crystal structure, phase characterization, calculation of mass and volume ratios, can be easily performed today with various software programs such as Fullprof, GSAS, JANA, MAUD and TOPAS. In this study, the softwares JANA and MAUD were used.

1.8. Superconducting Quantum Interference Device Magnetometer

SQUID stands for Superconducting Quantum Interference Device. It serves as a remarkably sensitive and precise magnetometer employed for the measurement of exceedingly faint magnetic fields. Operating on the principles of superconductivity and quantum mechanics, these instruments possess the capability to discern magnetic fields at the quantum level. They play a crucial role in various scientific and medical areas, including the examination of material magnetism, biomagnetic assessments of physiological processes within the human body, and geophysical investigations. To maintain their superconducting attributes and achieve high sensitivity in detecting even the slightest magnetic field alterations, SQUIDs operate under extremely low temperatures.

SQUID magnetometers are highly sensitive devices used for measuring magnetic fields. SQUID can detect the magnetic field which are millions of times smaller/weaker than the Earth's magnetic field (25000-65000 nT/0.5 Gauss) [31]. They are based on the superconducting quantum interference device (SQUID)

principle, which involves measuring the change in the magnetic flux through a superconducting loop as a function of an applied magnetic field [32].

As detailed in Figure 1.9, it works under vacuum. The vacuum environment between two large superconducting magnets is provided by Helium gas. In the center, there is the sample chamber, where the sample moves up and down throughout the measurement, and around it, the copper jacket, where the temperature change is managed, and the thermometers, where the temperature is controlled. Between this and the magnets at the center, there are SQUID detection coils that provide magnetization measurement.

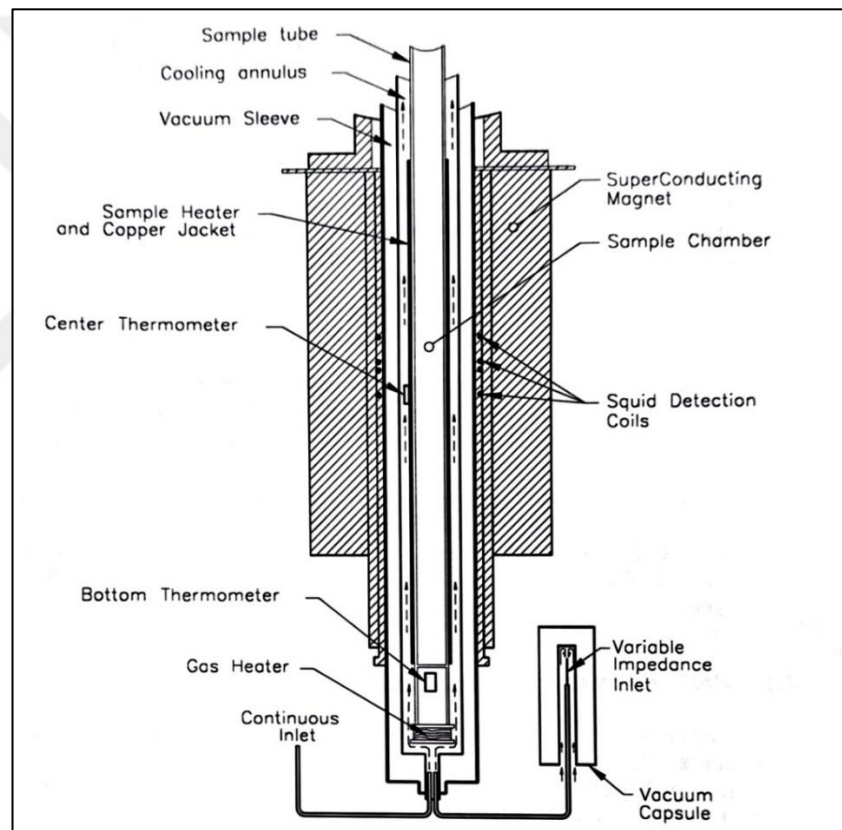


Figure 1.9: Schematic of the Superconducting Quantum Interference Device [32].

The working principle of the SQUID magnetometer is based on the principles of quantum mechanical effect: superconductivity, Josephson effect and magnetic flux quantization.

Superconductivity is a quantum mechanical phenomenon in which certain materials exhibit zero electrical resistance and perfectly repel magnetic fields from within them.

This occurs when materials are cooled below a certain critical temperature, and this temperature may vary depending on the type of material. With the transition to the superconducting state, the electrical resistance of the material suddenly drops, and electric current can flow freely within the material without loss of energy [33].

Magnetic flux quantization is also another special phenomenon of quantum mechanics that occurs in the case of superconductivity. It states that the magnetic flux passing through a superconducting circuit or ring cannot take any constant value but can only be in certain amounts (quantized values). This is a result of the macroscopic quantum field created by electrons in a superconducting ring [34].

Electron pairs (Cooper) in a superconductor are described by a wave function in correlation throughout the entire superconductor. In a superconducting ring, the phase of this wave function must be continuous throughout the ring. If we put this into a mathematical condition, we say that the phase change around the ring must be a multiple of exactly 2π . This phase condition also requires that the magnetic flux passing through the ring be quantized.

The Josephson effect is a fundamental phenomenon of quantum mechanics in superconductivity and occurs when a Josephson junction is formed by placing a very thin insulating layer between two superconducting materials [35]. Electrons in the form of Cooper pairs tunnel through this barrier, creating a supercurrent that carries current without the application of any voltage, this is the direct current (DC) Josephson effect. When a constant voltage is applied to the Josephson junction, an alternating current (AC) flows through the junction and the frequency of this current is directly proportional to the applied voltage.

In the working principle of the SQUID magnetometer, the sample is placed in the sample circle with a long rod and is aligned at the center of the magnets. The vacuum is first created, and then the measurement is started. Measurement is carried out by moving the sample through the detection coils as the sample passes through the coils. The sample's magnetic moment causes an electric current to flow through the detection coils due to the fact that the connecting wires, the detection coils, and the input coil of the SQUID are all enclosed superconducting loops. Any change in the magnetic flux of the detection coils results in a change in the persistent current of the detection circuit corresponding to the change of the magnetic flux. Because the SQUID is a linear

current-to-voltage converter, the variations of the current of the detection coils result in corresponding variations of the output voltage of the SQUID corresponding to the changes in the magnetic moment [32].



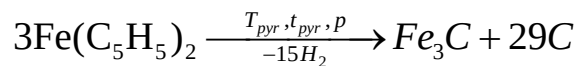
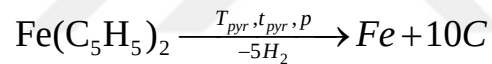
2. SYNTHESIS of Fe/Fe₃C MAGNETIC NANOPARTICLES

The synthesis of the Fe/Fe₃C NPs was performed by solid state pyrolysis method. Ferrocene powder precursor is put in the quartz tube which has 1 cm diameter and 55 cm length, inside the vacuum that has 0.01 Pa pressure.



Figure 2.1: Powder cementite.

Then, this prepared tube is placed in the tube furnace and the synthesis is started by increasing the temperature. Two different reaction, given below, can take place randomly depending on the amount of precursors and experimental conditions.



$$T_{\text{pyr}} = 700\text{-}1000\text{ }^\circ\text{C}$$

$$t_{\text{pyr}} = 45\text{ min}$$

$$P_i = 0.01\text{ Pa}$$

According to these reactions, Fe₃C, C, Fe particles and H₂ gas obtained. H₂ gas affects the pressure of the tube and along the process pressure also affects the reaction. This process proceeds in conjunction with each other. Thus, the production of Fe₃C, C and Fe nanoparticles in different ratios and structures depending on the reaction, pressure and temperature is achieved. Since the two reactions occur together without being fully controlled and there is a change in internal pressure, the only controlled parameter is temperature.

In this study all the samples were produced in 45 minutes but at different temperatures respectively of 700°C, 750°C, 800°C, 850°C, 900°C and 1000°C. The samples obtained were in powder form (Figure 2.1). For all the samples final pressure was estimated to be approximately 2-3 MPa that was related to reaction. In order to make the

measurements and experiments easier to follow, the samples produced were named according to their pyrolysis temperatures and are listed in Table 2.1.

Table 2.1: List of the samples' names with pyrolysis temperature and time.

Sample	Pyrolysis Temperature (°C)	Pyrolysis Time (min)
F700-45	700	45
F750-45	750	45
F800-45	800	45
F850-45	850	45
F900-45	900	45
F1000-45	1000	45

3. MORPHOLOGICAL ANALYSIS AND SIZE DISTRIBUTION

Morphological analyses of the samples were performed with FEI Tecnai F20 TEM/STEM/GIF Supertwin microscope (Figure 3.1). The field emission gun operating voltage was 200 kV and yielded a point resolution of 0.24 nm.

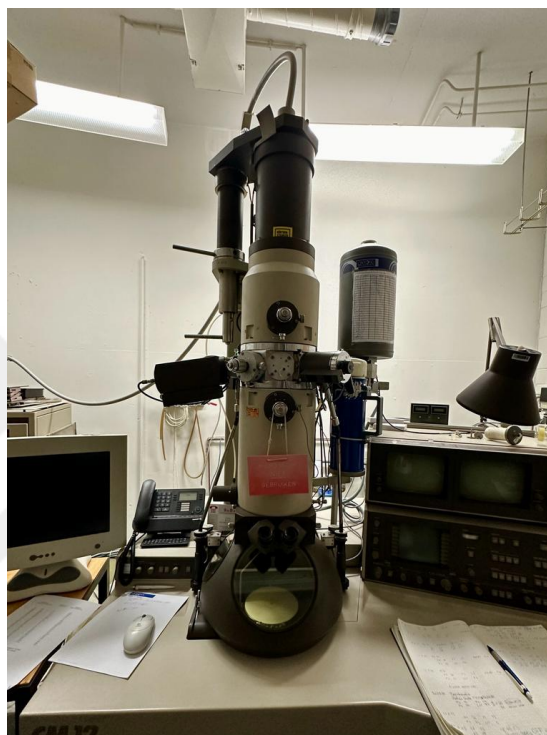


Figure 3.1: TEM device.

All TEM images were obtained by imaging the powdered sample at 31000 and 35000 times magnification and then with ImageJ software their scales were calibrated to 200 nm. Figure 3.2 shows TEM images for all samples from A to F respectively F700-45 to F1000-45, where the structures can be seen in detail. In those structures grey particles belong to carbon, the darker ones that look like black are Fe/Fe₃C nanoparticles.

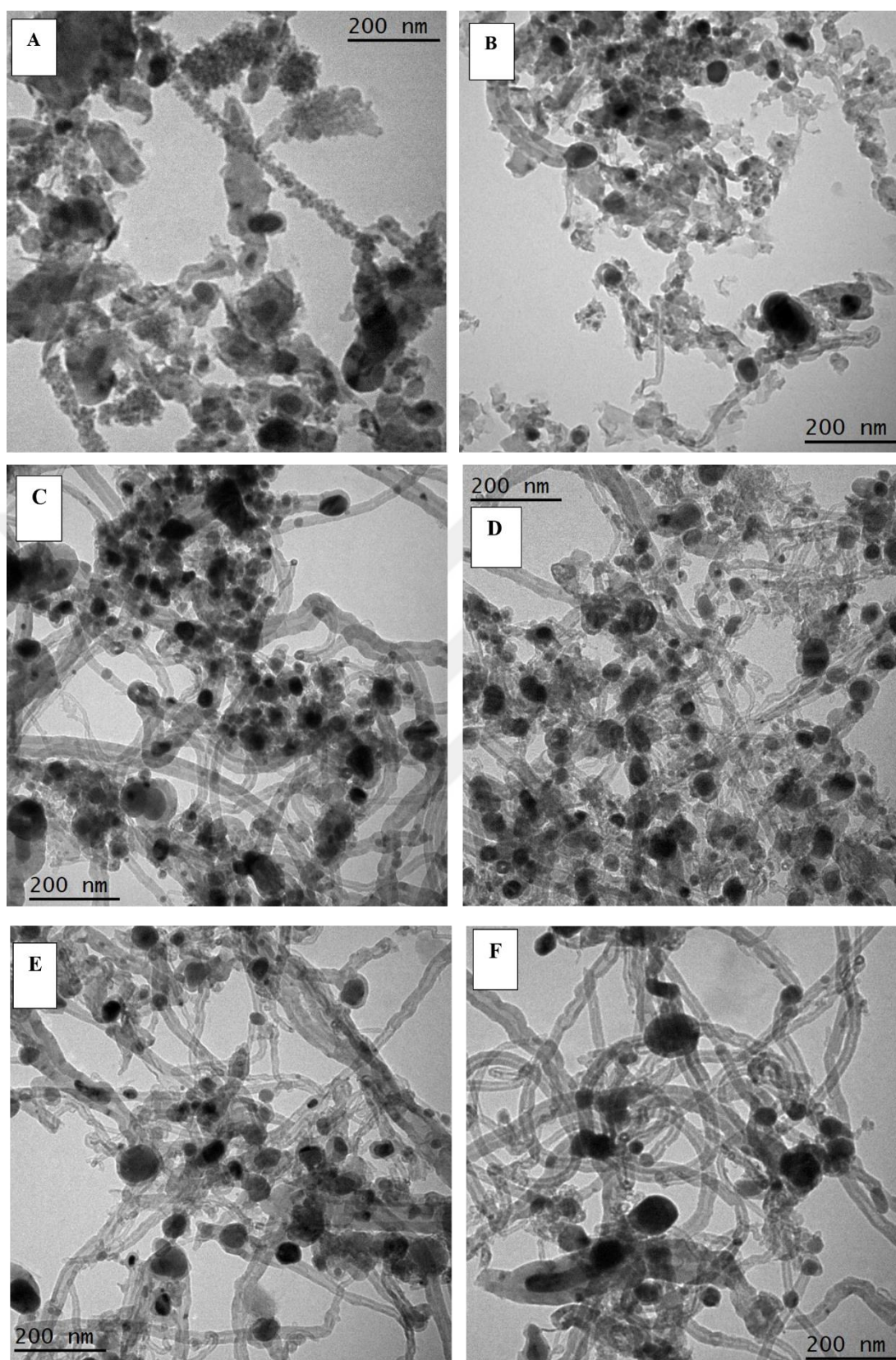


Figure 3.2: TEM images of A.F700-45, B.F750-45, C.F800-45, D.F850-45, E. F900-45, F. F1000-45.

As can be seen from TEM images, the samples prepared by the solid-state pyrolysis method at 700 °C and 750 °C have a bad crystallinity structure than others but when compared to each other, F750-45's structure is more regular.

When pyrolysis temperature is increased especially after 750 °C carbons are more like nanotubes structures. These structures are also visible in samples prepared at 700 and 750 °C but they are very rare. In addition, the Fe/Fe₃C nanoparticles have carbon shells for all samples. Furthermore, after 800 °C Fe/Fe₃C nanoparticles start to be placed inner and outer walls of the carbon nanotubes. As the production temperature rises, there is an observed increase in both the quantity and complexity of carbon nanotubes.

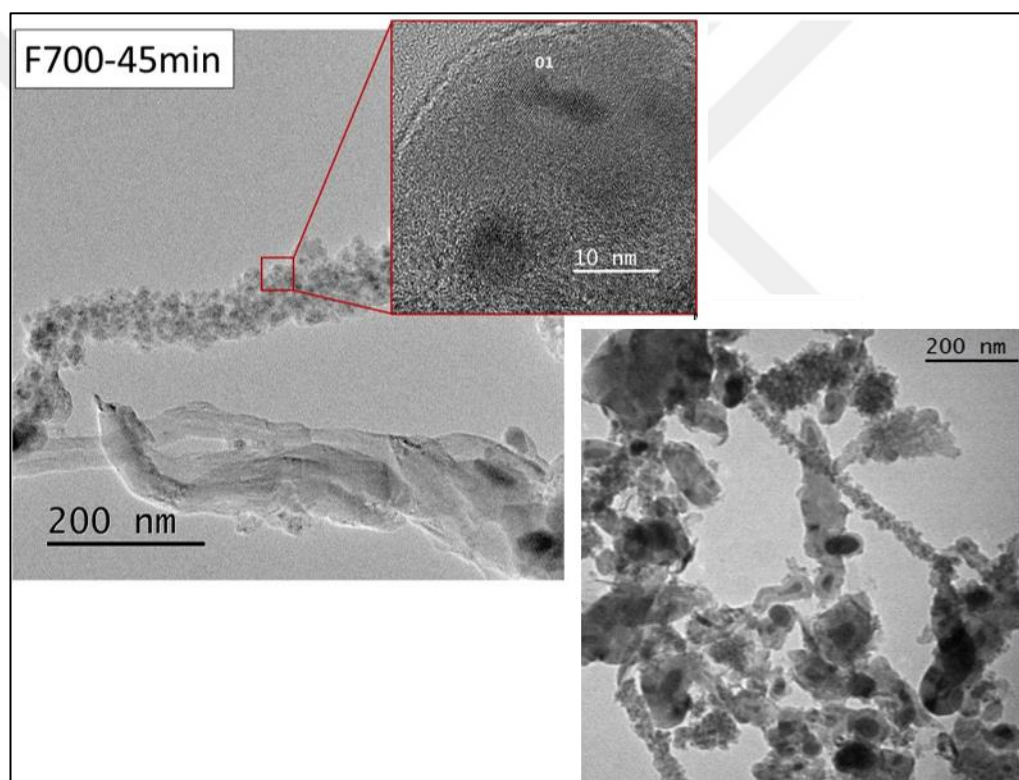


Figure 3.3: High- Resolution TEM images of F700-45.

Besides poor crystallization for F700-45 and F750-45 samples, other smaller structures were observed. As seen in Figure 3.2, these particles, which are very small compared to carbon and Fe/Fe₃C structures, are not seen in other samples. At first look it is not easy to see and define that particles from TEM images but from literature and high-resolution TEM images they can detect and define as Iron Oxide structures [36]. It was also confirmed in the XRD analysis in the following sections. The detailed structure

was shown in Figure 3.3, which contains the high-resolution TEM image taken for F700-45.

The diameter of particles is determined by analyzing approximately 50 images and measuring around 1500 particles using the ImageJ software. The diameter calculations depending on the number of particles were graphically drawn with the Origin software and fitted with the help of the lognormal function in line with the distribution pattern. Size distributions and fit plots are shown in Figure 3.4 in detail for all samples.

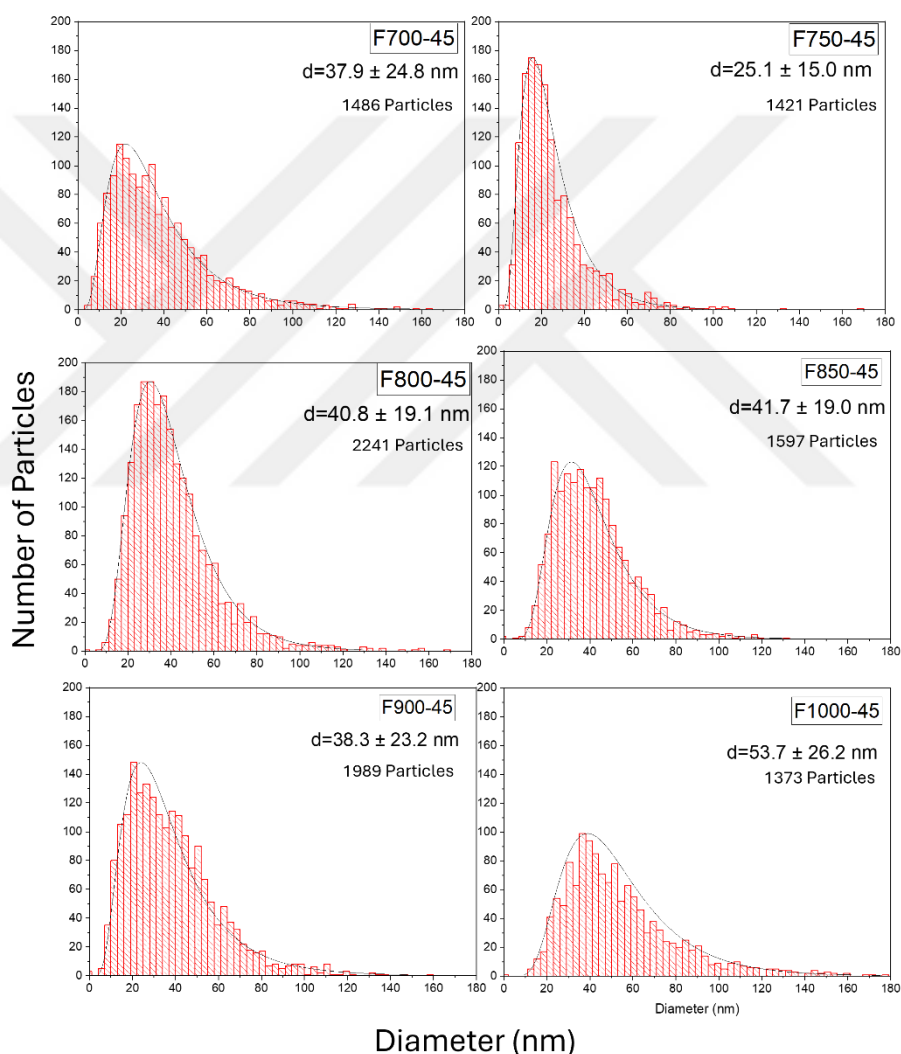


Figure 3.4: Size distribution of the samples measured with ImageJ software.

These diameter measurements and fit plots which can be seen in Figure 3.4 do not include iron oxide particles while they are very small, and it is not possible to calculate them accurately. Even so, when we look at the distribution of the number of particles

depending on their diameter, it is seen that very small and even large-sized particles are also included in the distribution graph. When the distribution is examined in general, it is known that it behaves similarly to the lognormal function distribution, and as a result of the lognormal fit, these large and small-sized particles are not important in the average size calculation but only affect the standard deviation [37].

The diameter of the samples and the number of the particles were calculated from lognormal fits (Figure 3.4) as: For F700-45 from 1486 particles 37.9 ± 24.8 nm, for F750-45 from 1421 particles 25.1 ± 15.0 nm, for F800-45 from 2241 particles 40.8 ± 19.1 nm, for F850-45 from 1597 particles 41.7 ± 19.0 nm, for F900-45 from 1989 particles 38.3 ± 23.2 nm and for F1000-45 from 1373 particles 53.7 ± 26.2 nm.

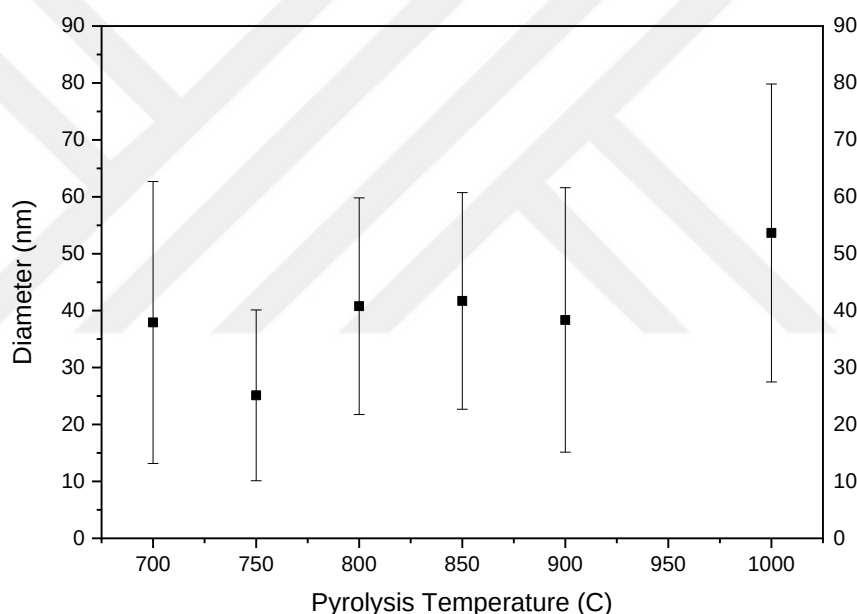


Figure 3.5: The size distribution of all samples with standard deviation according to solid state pyrolysis temperature.

For easier analysis, in Figure 3.5, the sizes and standard deviations of MNPs according to the pyrolysis temperature are compared. It is seen that the diameters of Fe/Fe₃C MNPs are in the range of 10-80 nm for all samples produced at different temperatures. Diameter dependence on temperature cannot be said to give big differences and changes. With some standard deviation, the diameter is appr. 35-40 nm.

4. STRUCTURAL ANALYSIS

X'Pert Panalytical Diffractometer which has Cu-K α radiation ($\lambda=0.15706$ nm) is used for $2\theta=10-120^\circ$ at room temperature XRD characterization.



Figure 4.1: X'Pert Panalytical Diffractometer.

The identification of crystalline phases was accomplished by utilizing the Crystallography Open Database. Phase contents and mass ratios were found by Rietveld refinement method using JANA and then MAUD software's (Figure 4.2).

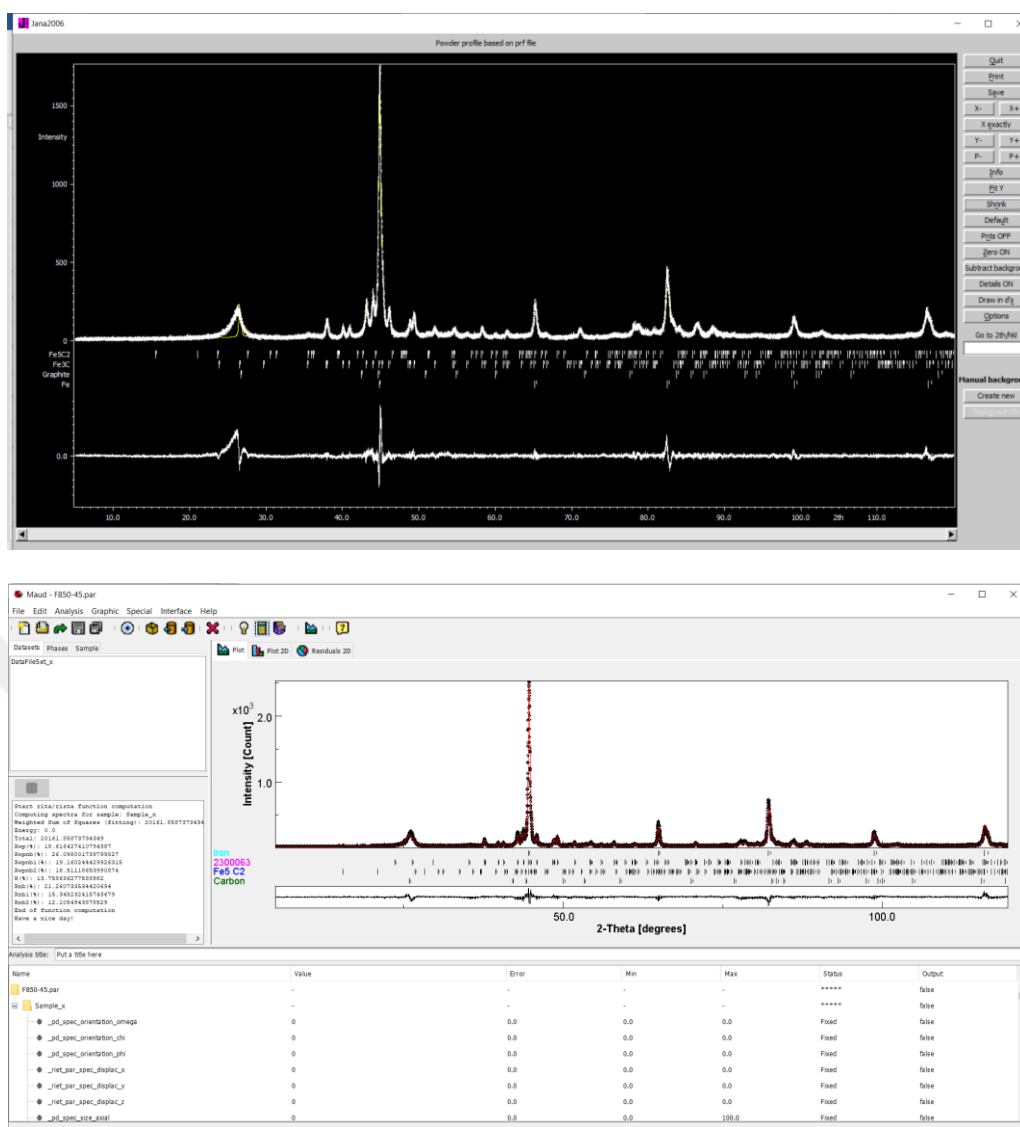


Figure 4.2: Jana and Maud software's' interface.

In order to separate the sample's XRD measurements into their phases, the lattice parameters of Fe, Fe₃C and C were used in the refinement. The initial refinement process was undertaken with the certainty that the resultant products derived via the solid-state pyrolysis method invariably contained the substances of interest, although their concentrations varied across the different samples. For the samples named F700-45 and F750-45, the refining of iron oxides was additionally tried with different iron oxides. The lattice parameters used in the refining process and taken from the Crystallography Open Database are as follows.

Table 4.1: Phases' literature structure information.

Phase	Space Group	Crystal	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	References
Fe	Im-3m	Cubic	2.8608	2.8608	2.8608	90	90	90	[38]
Fe ₃ C	Pnma	Orthorhombic	5.08475	6.7367	4.51394	90	90	90	[39]
C	P63mc	Hexagonal	2.47	2.47	6.79	90	90	120	[40]
γ Fe ₂ O ₃	Fd3m:2	Cubic with a tetragonal supercell	8.33	8.33	8.33	90	90	90	[41]
Fe ₃ O ₄	Pbcm	Hexoctahedral	2.7992	9.4097	9.4832	90	90	90	[42]

Elemental analysis were done with Rietveld method. When the structure information of phases is uploaded to software with the XRD data, it makes the refinement automatically and gives mass fraction of each phase separately. Thus, we can get more information from the sample (Appendix-A).

XRD patterns were redrawn with Origin Software to make calculations easier and analyze. The measured and calculated patterns for each sample is given separately in Figure 3.4. The observed experimental data is represented as solid black lines while the calculated data is given as red solid lines. The difference between the experimental and calculated data is given as gray lines under each pattern. The differences between observed and calculated data is a measure of the goodness of the fits and important to see realization of the chosen phases in the samples, and allows us to compare the results with literature.

Except for the 700 °C sample almost all the XRD peaks pretty good fitted. The reason for 700 °C which already discussed at TEM section, criticality is very bad. Peaks cannot be seen clearly. Additionally, F700-45 and F750-45 have Magnetite and Maghemite that are Iron Oxides peaks. The oxide peaks are broader compared the peaks belonging to the other phases which indicates that the particle sizes are exceedingly small.

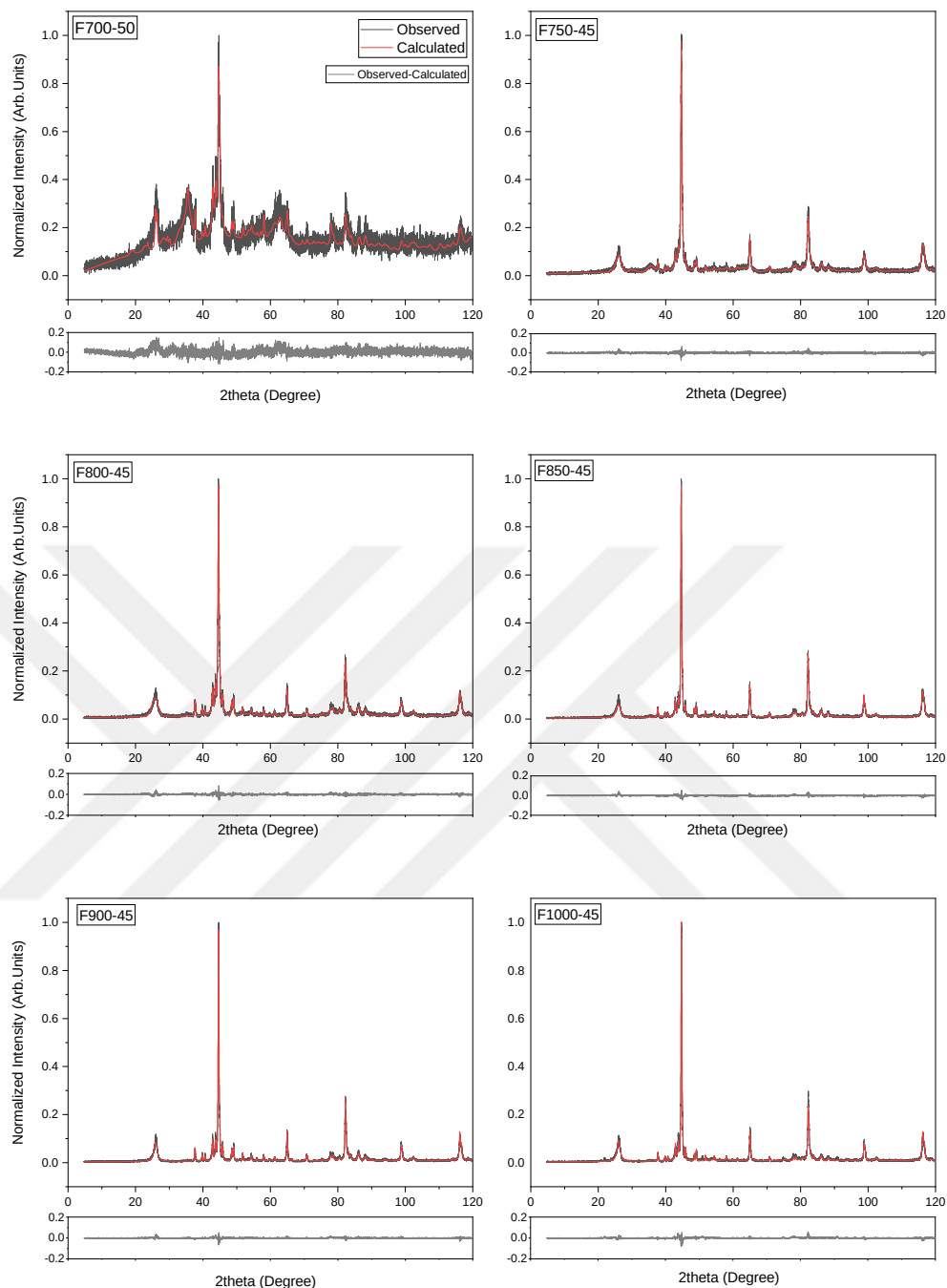


Figure 4.3: Observed and Calculated XRD patterns of the samples.

To compare all the samples calculated fits of the samples were merged in the same graph in Figure 4.4. The fits were placed according to solid state pyrolysis temperatures and from top to bottom in the order of F700-45, F750-45, F800-45, F850-45, F900-45, F1000-45. Peaks belonging to different phases are labeled with different symbols on the XRD pattern of F700-45 sample on the top of the figure, which is also valid for other samples. Peaks labeled as stars (*) are associated with Fe, those labeled

with arrows ($\rightarrow$) belong to Fe_3C , those marked with solid circles ($\bullet$) are related to C while the peaks associated with the oxides (Fe_3O_4 and $\gamma\text{Fe}_2\text{O}_3$) are labeled as open circles ($\circ$) in the figure.

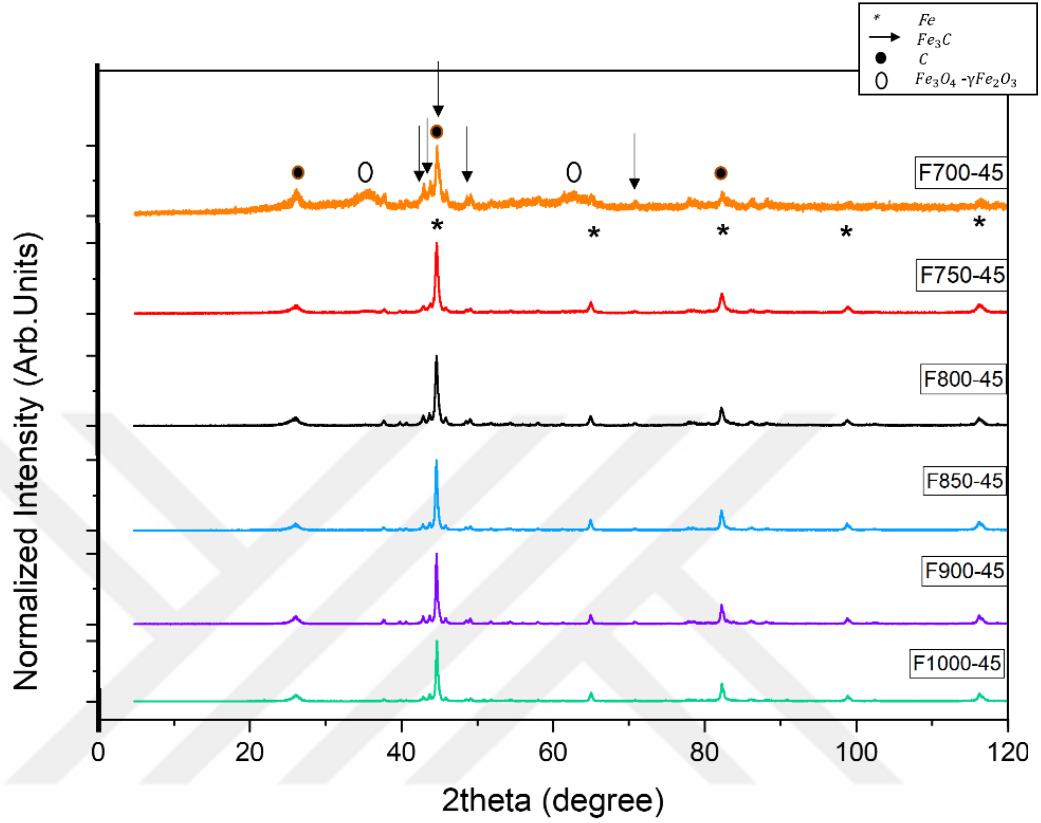


Figure 4.4: XRD Patterns of Cementite-Iron-Carbon nanocomposites.

The peaks belonging to the graphite (C) phase are observed at 2-theta angles of 26, 28 and 82, those belonging to iron (Fe) are observed at 44, 65, 82, 98 and 116, those belongig to cementite (Fe_3C) are seen at 43, 44, 45 and 70 while those associated with oxides (Fe_3O_4 & $\gamma\text{Fe}_2\text{O}_3$) are observed at 36 and 62. Oxide phases are only seen in F700-45 and F750-45 samples while peaks associated with the other phases are observed in all samples. The peak positions do not change among the samples, however there are clear changes in the peak intensities which is relates to the variations of the mass fractions of phases in different samples.

Table 4.2: Rietveld refinement analysis % weight.

Wt %	F700-45	F750-45	F800-45	F850-45	F900-45	F1000-45
Graphite (C)	14.7±2.0	43.1±1.5	65.8±3.9	44.2±1.6	40.5±0.9	60.0±1.9
Iron (Fe)	8.8±0.6	28.9±0.6	17.0±0.4	34.6±0.8	30.6±0.5	28.8±0.6
Cementite (Fe₃C)	30.2±2.1	19.1±1.6	17.3±0.4	21.2±1.8	29.0±0.5	11.1±0.2
Magnetite (Fe₃O₄)	42.1±4.2	0	0	0	0	0
Maghemite (γFe₂O₃)	4.3±0.3	8.9±0.6	0	0	0	0

The mass fractions of the samples listed in Table 4.2 were calculated with Reitveld Analysis by MAUD Software using lattice parameters. The maximum mass fraction belongs to Magnetite in F700-45 sample while the other oxide phase is Maghemite with a smaller concentration of approximately 4%. The 45% of the sample mass belongs to oxides which are indicated as “0” symbol in Figure 4.4. The oxide fraction in F-750-45 sample is about 9% which is much smaller than that in F700-45. However, peaks belonging to this phase can still be observed in Figure 4.4. When pyrolysis temperature increases from 700°C to 800°C carbon fraction in the sample increases, cementite fraction decreases. On the other hand, iron fraction increases first and then decreases. The reason for the observed behavior for iron is due to the presence of iron oxides. There is a 20% difference in the mass fraction of carbon in samples F750-45 and F800-45 samples, being higher in the latter. This is confirmed by the TEM images (Figure 3.2) which clearly indicate the increase in the amount of carbon nanotubes in the F800-45 sample. When F800-45 and F850-45 were compared with each other, large differences in mass fractions were observed compared to other samples. The mass fraction of carbon decreases while Fe₃C and Fe mass fractions increase accordingly. The reason is that Fe₃C has a metastable phase, and after almost 800°C in production temperature, Cementite decomposition reaction starts. The reactions work both ways; in addition to formation, decomposition also takes place. While F900-45 sample has the second highest Cementite mass fraction, the Fe₃C fraction decreases

again in F1000-45 sample and carbon mass fraction reaches the second highest concentration following the F800-45 sample. To better see the changes in the mass fractions of cementite-iron phases among the samples, the variations of the concentrations of different phases with pyrolysis temperature are given in Figure 4.5. As can be seen from this figure, we cannot say that there is linear relation between the mass fractions of cementite-iron phases and annealing temperatures.

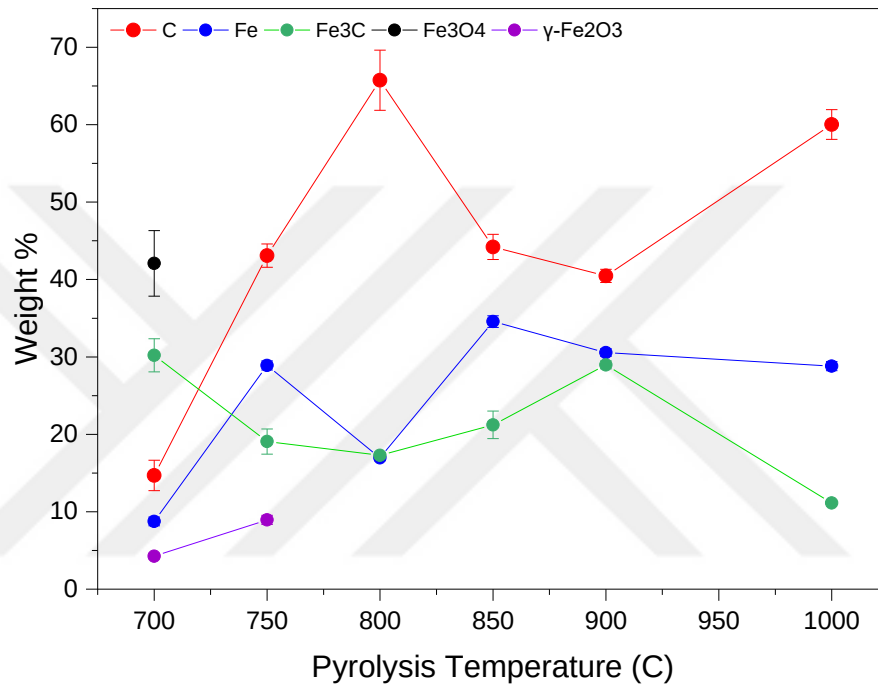


Figure 4.5: Phases weight percentages with error bar for all samples.

5. MAGNETIC PROPERTIES of Fe/Fe₃C NANOPARTICLES

Magnetic measurements were conducted on powder samples by Quantum Design MPMSXL SQUID Magnetometer (Figure 5.1).



Figure 5.1: Quantum Design MPMSXL SQUID Magnetometer.

In order to measure the magnetization of all samples produced at different temperatures, samples were prepared to be placed in sample tubes. Two different sample sets were prepared for each sample to be used in low and high temperature measurements in experiments carried out to measure saturation magnetization and observe magnetic behavior above Curie Temperatures. The mass of the samples was measured, and they were placed in the sample holders to be placed in the sample tube. The masses of the prepared samples were listed in Table 5.1 according to their names and uses in low and high temperature measurements.

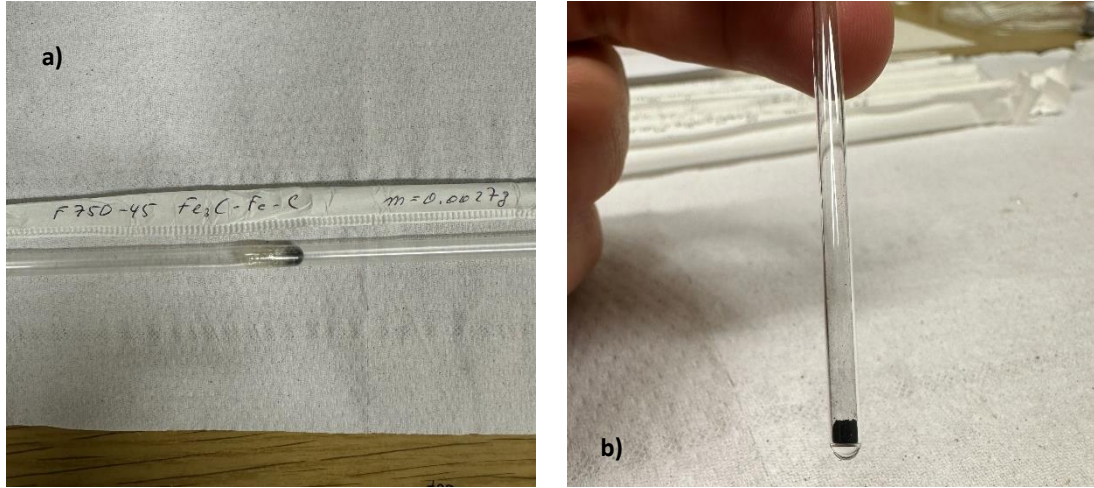


Figure 5.2: a) Low temperature measurement sample, b) High temperature measurement sample.

Table 5.1: Masses of the samples used for low and high temperature magnetization measurements.

Name of the Sample	Sample Mass (g)	
	Low Temperature Magnetization	High Temperature Magnetization
F700-45	0.0023	0.0031
F750-45	0.0027	0.0032
F800-45	0.0017	0.0017
F850-45	0.0020	0.0019
F900-45	0.0021	0.0018
F1000-45	0.0024	0.0019

First magnetization hysteresis loops were recorded to observe the saturation magnetizations at $T = 10$ K. All samples were going saturation circa 1-2 T (Figure 5.3). F850-45 has a maximum saturation magnetization value of $68.34 \text{ Am}^2/\text{kg}$. It is expected cause as known from the previous section Fe mass fraction is maximum in that sample. Minimum saturation magnetization is around $24.16 \text{ Am}^2/\text{kg}$ for F700-45, which has the minimum Fe mass fraction. For the other all samples M_s values are from high to low relatively; F850-45, F1000-45, F800-45, F900-45, F750-45, F700-45 (Table 5.2).

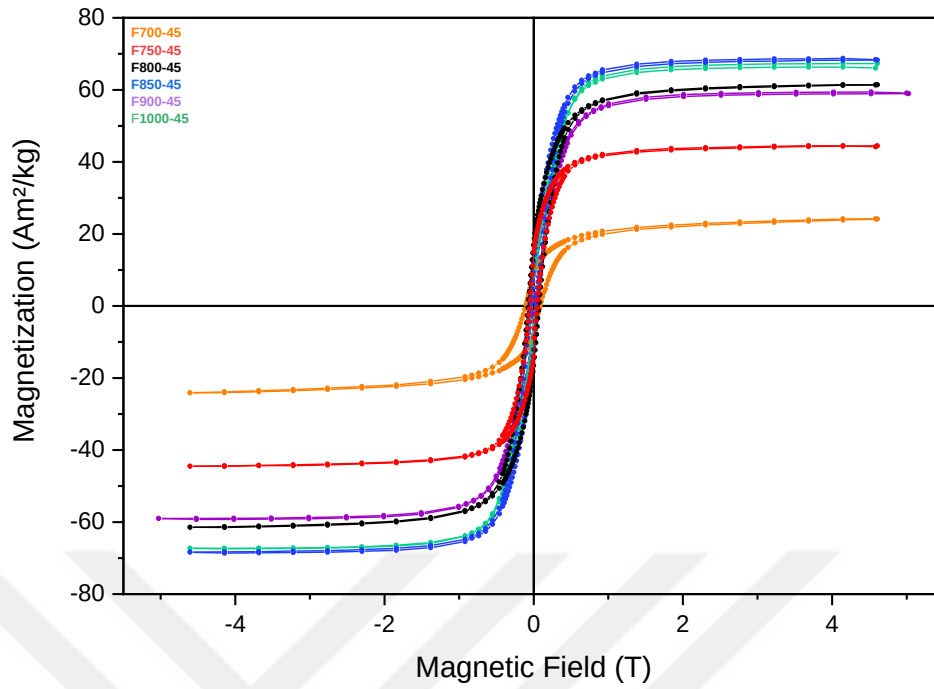


Figure 5.3: Field dependence of magnetization for all samples at 10 K.

To get more detailed information about the magnetic properties of the samples, the hysteresis curves were focused 10 times in the origin as in Figure 5.4.

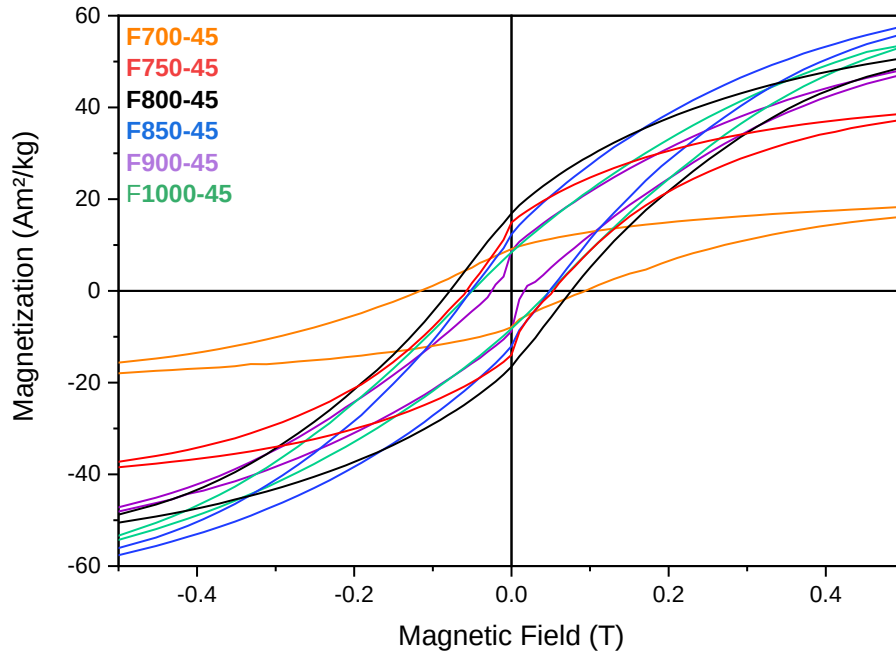


Figure 5.4: 10 times focused on origin field dependence of magnetization for all samples at 10 K.

Coercive field values of the samples except F700-45 are symmetric as expected like ferromagnetic behavior, but for F700-45, there is a left side shift on the coercive field value. The reason for that shift is that it has a very big amount of Iron Oxide. Since ferromagnetic Fe/Fe₃C nanoparticles and ferrimagnetic iron oxides have a multilayer structure, a pinning effect is observed at the interface between these two structures due to exchange bias. The ferrimagnetic layer pins the spins in the ferromagnetic layer, resulting in a shift towards the negative direction in the hysteresis curve. The coercive field values from high to low are listed as F700-45, F800-45, F750-45, F1000-45, F850-45, F900-45, also in Table 5.2. Remanence magnetization values have the highest value in sample F800-45, then F750-45, F850-45 and the lowest values are almost equal for F1000-45, F900-45 and F700-45. The ratio of remanence magnetization to saturation magnetization, M_{rem}/M_s , is calculated and the obtained values are given in Table 5.2. The maximum and minimum values of the M_{rem}/M_s ratio is obtained for the F700-45 sample (0.37) and F1000-45 (0.12), respectively.

Table 5.2: Saturation magnetization, Remanence Ratio and Coercive Field list of the samples investigated.

Sample	M_s (10K) [A.m ² /kg]	M_{rem}/M_s (10K)	H_c (10K) [kA/m]
F700-45	24.16	0.37	75.25
F750-45	44.46	0.33	42.45
F800-45	61.36	0.28	60.54
F850-45	68.34	0.18	38.56
F900-45	59.09	0.13	13.11
F1000-45	67.28	0.12	39.41

The solid-state pyrolysis temperature dependence of coercive field and saturation magnetization are shown in Figure 5.5. Red dots stand for saturation magnetization values of the samples while black squares are used for the coercive field values and lines are drawn as a guide to the eye to show the variations. The relation between mass fractions of the samples and saturation magnetization or coercive field is investigated in detail in next section.

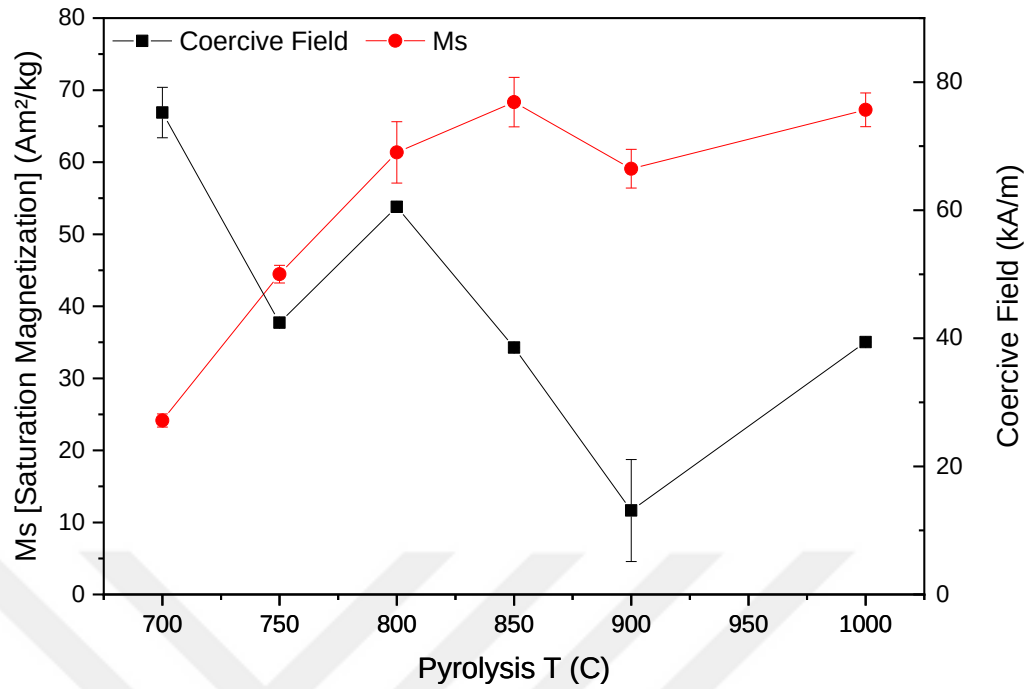


Figure 5.5: Pyrolysis temperature dependences of coercive field and saturation magnetization.

In addition, magnetizations were measured from 10 K to 650 K to see differences above Curie temperature of the Fe_3C , temperature dependence of magnetization and calculate Fe's and Fe_3C 's magnetic moments. The high temperature and low temperature measurements were performed separately with different samples that are listed in Table 5.1. An external oven was used in the SQUID system for the high temperature measurements, above 300 K. The measurements were conducted as follow: First samples were cooled at zero magnetic field, then the samples were heated to 300 K under the applied magnetic field of 2 T and finally the samples cooled down under the same magnetic field of 2T (Figure 5.6 and Figure 5.7). This process, named Zero Field Cool Field (ZFCF), was performed to observe whether the magnetization was reversible at low temperatures. For the high temperature measurement (Figure 5.6 and Figure 5.7) samples were heated till 650 K which is above the Curie Temperature of Fe_3C ($T_c(\text{Fe}_3\text{C})=485\text{ K}$ [43]) but below the Curie Temperature of Fe ($T_c(\text{Fe})=1042\text{ K}$ [43]). Then they were cooled again down to 300 K.

After the measurements, all the low temperature (LT) and high temperature (HT) magnetic moments of the samples were drawn with Origin and merged to analyze their

magnetic behaviors. The red circles represent LT measurements while blue circles represent HT measurements in Figure 5.6 and Figure 5.7. The arrows indicate the direction of the measurements.

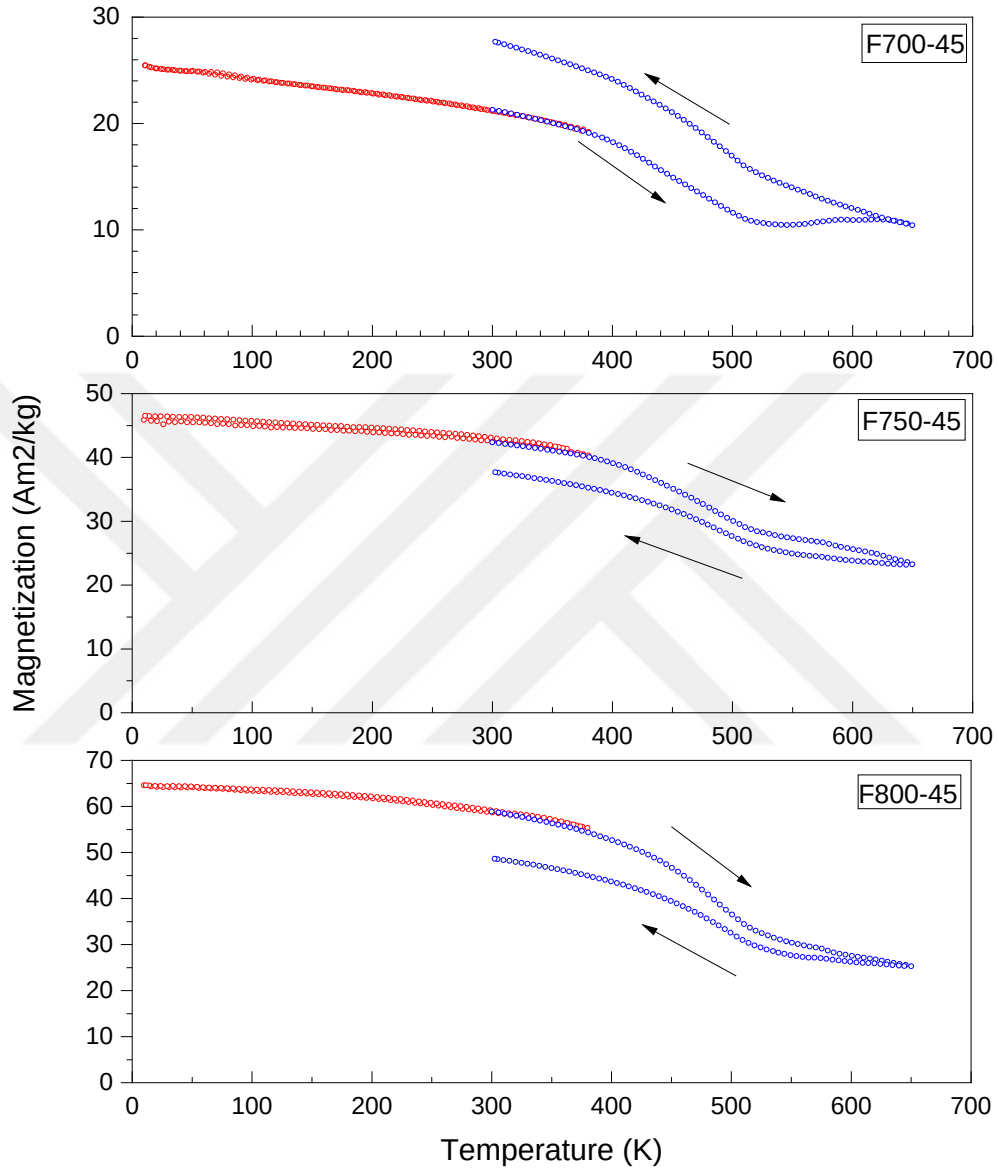


Figure 5.6: Variation of magnetization in low and high temperature from a) F700-45 b) F750-45 c) F800-45.

In LT measurement for all the samples especially between 5-300 K, there are almost no differences in magnetization values. In addition to that after ZFCF measurements the magnetizations are going back to same values and show reversible behavior. No differences at magnetization between initial temperature and final temperature as compatible with Fe/Fe₃C behavior.

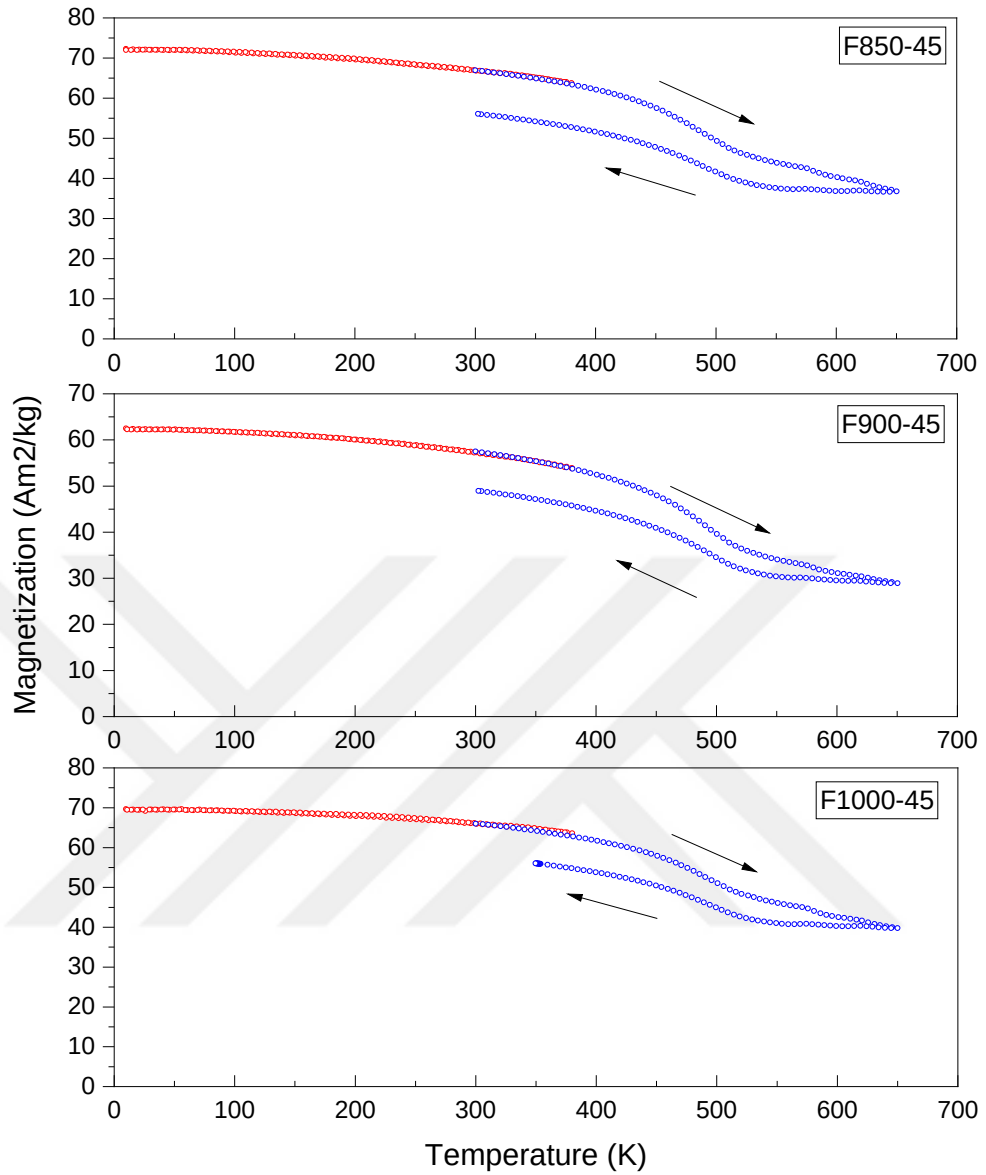


Figure 5.7: Variation of magnetization in low and high temperature from a) F850-45 b) F900-45 c) F1000-45.

In HT measurement differently from LT, magnetization of the all samples first start to decrease when the temperature reached approximately 450 K, then around 580-600 K it stays stable. This reduction comes from Fe₃C's paramagnetic behavior above the T_c. After this T value all the magnetization comes from only Fe. After the heating process was done at 650 K, at the cooling part magnetization is expected to increase below the T_c again due to Fe₃C's to be ferromagnetic again. In addition to that in case of some Fe₃C particles, which have metastable phase, decomposition to Fe and C, final magnetization value should be more than the initial one. Differently from all

expectation and interestingly except F700-45 all other samples' final magnetization values were less than the initial ones. For F700-45 has a large oxide content of around 50 % and iron oxide decomposes like cementite when the temperature increases. It explains this reduction. For the other samples as they do not have any oxidation and during the SQUID measurement, they have been inside Helium vacuum, external oxidation could not be taking into account. In this instance, the main reason is that temperature-induced structural modifications constitute the predominant factor.



6. STRUCTURAL DIFFERENTIATION CAUSED by MAGNETIZATION

In order to determine whether the different results obtained in magnetization measurement were due to structural change or not, XRD measurements were made again on the low temperature and high temperature magnetization measured samples of F700-45, which is the only sample showing an increase in magnetization, and F850-45, which showed the highest difference.

XRD characterizations were performed with the same X'Pert Panalytical Diffractometer in Cu-K α radiation ($\lambda=0.15706$ nm) at room temperature in the range $2\theta=0-100^\circ$ for 7 hours. XRD patterns of LT and HT samples are given in Figure 6.1 and 6.2, red curve belongs to the LT and black curve is from the HT sample.

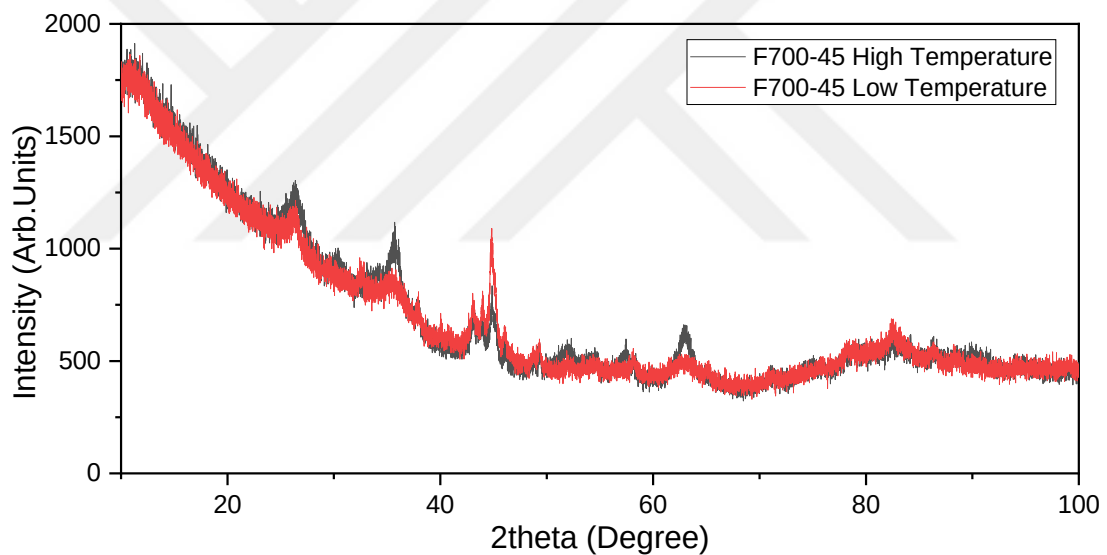


Figure 6.1: XRD characterization of low temperature and high-temperature magnetization measured F700-45 samples.

When comparing the high temperature and low temperature XRD patterns for F700-45, no peak formation other than the existing peaks was observed as in Figure 6.1. There is only a difference in the intensities of the XRD peaks. The intensity decreases at 46° , 49° , 54° and 57° are due to Fe_3C , since only Fe_3C has the peaks at these angles. Considering this situation, it has been observed that cementite, which is in a metastable state, decomposes into Fe and C due to the increase in temperature. Accordingly, increase in the intensity of C related can be seen clearly at 26° and 52° peaks as

expected. For the Fe peaks in addition to increase there are some decreases depending on the oxidation which can be seen at 30°, 35°, 62° and 90° peaks. Some of the decomposed Fe from Fe₃C causes an increase in the iron oxide structure that will combine with oxygen. For the XRD peak observed at 45°, which has the highest intensity and highest decrease, the situation is a little bit complicated, as it involves Fe, C and Fe₃C together.

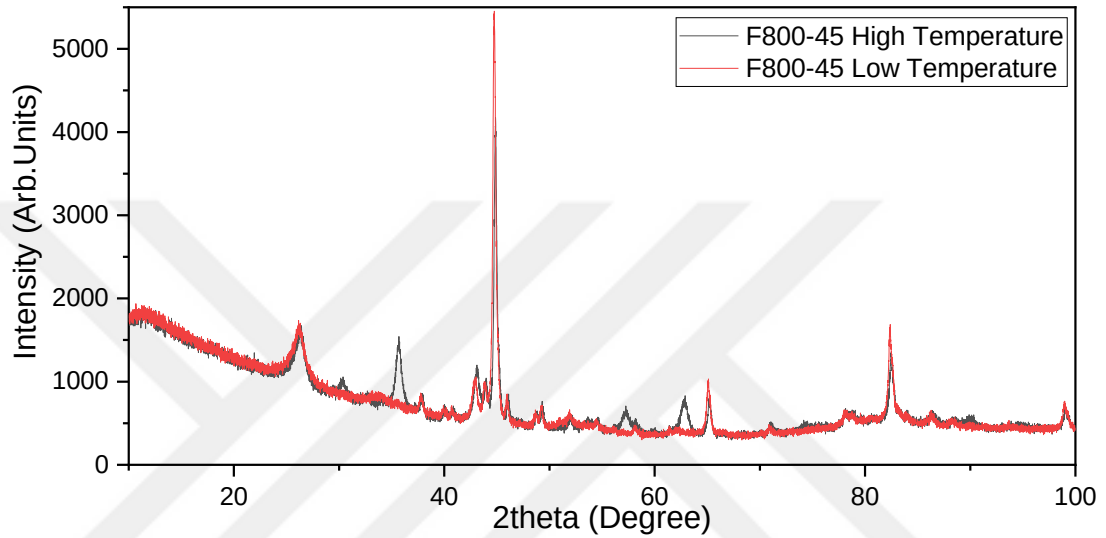


Figure 6.2: XRD characterization of low temperature and high-temperature magnetization measured F850-45 samples.

Upon comparison of the XRD patterns for F850-45 (as shown in Figure 6.2), it is seen that besides the variation in peak intensities similar to what is noticed in F700-45, other additional peaks are emerging. At first glance, it was observed that all patterns shifted slightly to the right. This shift may be due to expansion in the lattice parameters of the phases depending on temperature, or it may be due to the newly formed phase. The intensities of the C peaks at 26° and 82° degrees, as well as the Fe peaks at 65°, 82°, and 99°, diminished, whereas, in contrast, the Fe₃C peaks at 49° and 71° degrees experienced an increase in intensity. The intensity of the composite peak consisting of Fe, C, and Fe₃C at 45° was found to have also diminished. An additional significant distinction is the emergence of new XRD peaks observed at 30°, 35°, 57° and 63°. These XRD peaks, which are not compatible with the existing Fe, C and Fe₃C phases, indicate that a new phase has formed in the sample.

7. CURIE TEMPERATURE CALCULATION

It was shown in the earlier section that the magnetization value changes depending on the temperature, as the literature Curie temperature of cementite is exceeded in high temperature measurements. Since the Fe/Fe₃C magnetic nanoparticles produced by the solid-state pyrolysis method have a more complex structure than pure cementite, Curie temperature calculations were made to see whether the literature Curie temperature was compatible with the produced samples.

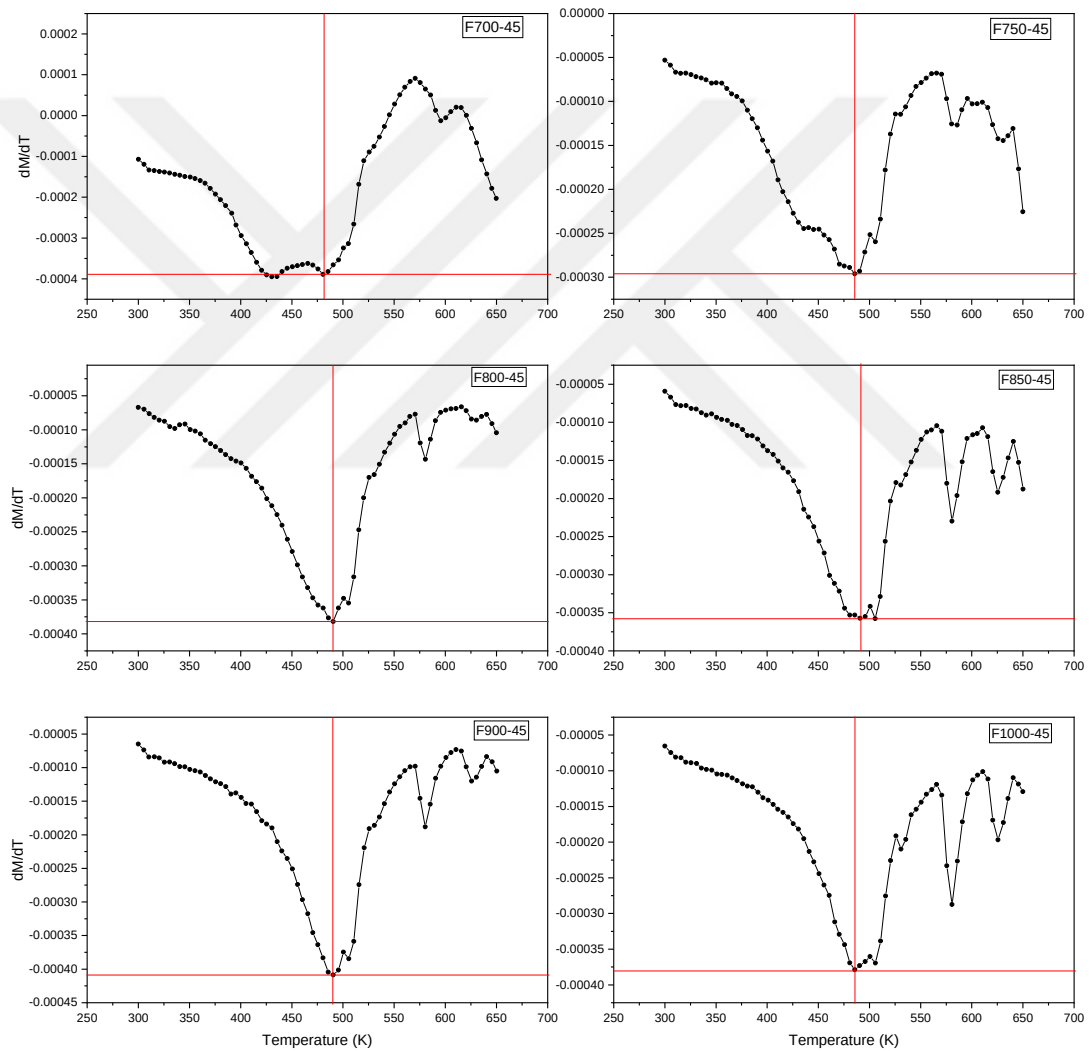


Figure 7.1: Curie temperature calculation graphs.

Since magnetization is a temperature-dependent function in the phase transitions here, the magnetization function can be minimized and the Curie temperature can be found from the temperature-dependent minimum points. According to Landau's theorem,

temperature at which the magnetization change is maximum correspond to Curie temperature. To make the calculation in line with Landau Theory, firstly the temperature increase part, which is the first stage of high temperature magnetization measurements of all samples, was considered. Then, the first derivative of magnetization according to temperature was calculated and its graph was plotted as a function of temperature (Figure 7.1). The minimum point of these graphs, which were pointed with red lines, shows the Curie Temperatures at which the largest magnetization change occurs. The list of the T_c 's is given in the Table 7.1, are related with the literature value [43]. In addition to these, there are some other minimums around 580 K and 620 K (Figure 7.1).

Table 7.1: Calculated Curie Temperatures of Fe_3C .

Sample	T _c	T _c	T _c	T _c
	Kelvin	Kelvin	Kelvin	Kelvin
F700-45	430±31	480±30	595±11	--
F750-45	--	485±33	585±6	630±11
F800-45	--	490±30	580±5	630±10
F850-45	--	491±27	581±5	625±4
F900-45	--	490±27	580±5	625±5
F1000-45	--	486±33	581±6	626±6

8. MAGNETIZATION ANALYSIS

The total value of the magnetization resulting from Fe and Fe₃C was obtained by measuring the temperature-dependent magnetization. To calculate how much of this magnetization comes from Fe and Fe₃C, it is necessary to calculate magnetization value above the Curie Temperature of Fe₃C. Since magnetization cannot occur from cementite, which has paramagnetic properties above T_c, above this value, it is assumed that all magnetization obtained is due to Fe.

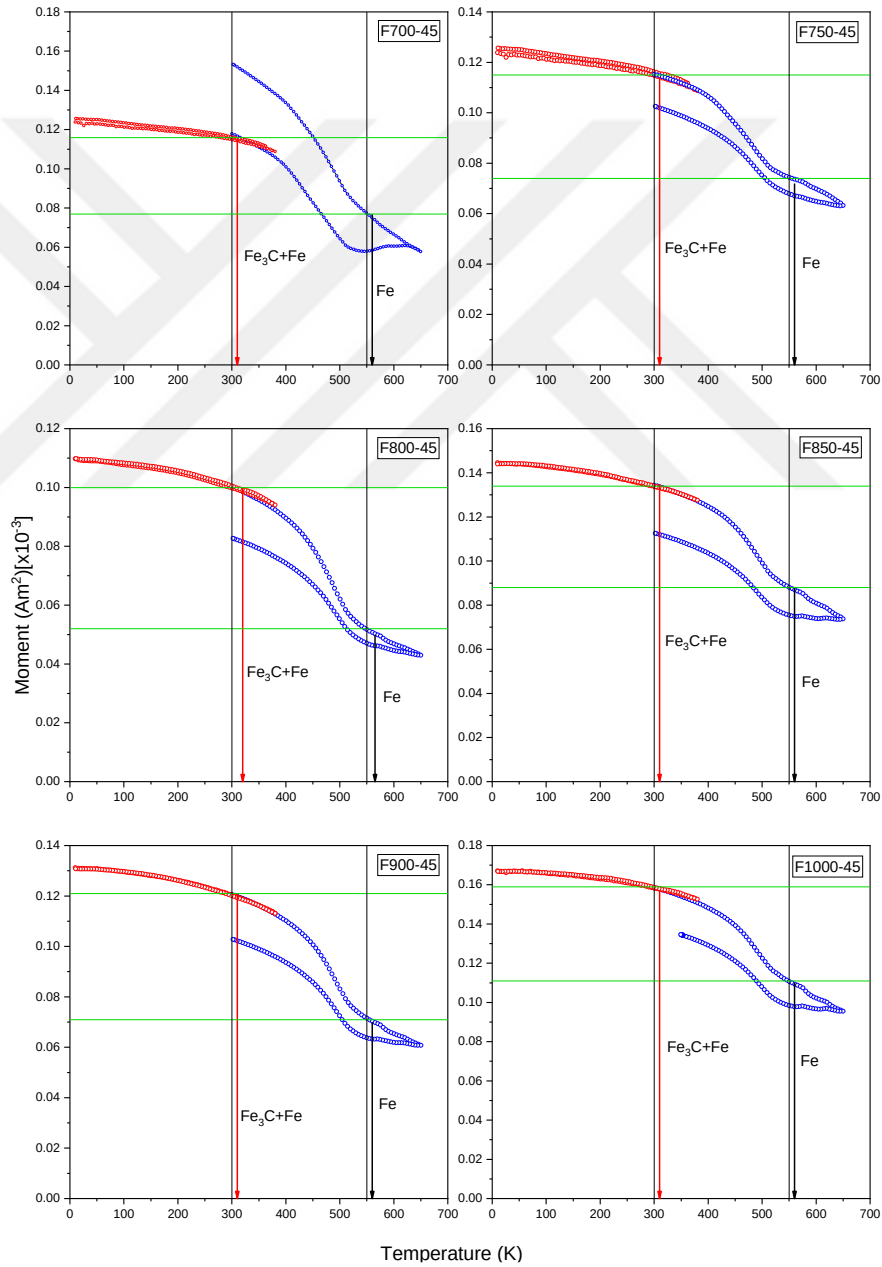


Figure 8.1: Iron-Cementite magnetic moment calculation graphs.

According to Curie temperature calculation the values are 480 K, 485 K, 490 K for the samples investigated in this thesis study, as listed in Table 6.1 Based on these data, a temperature of 550 K was chosen to make sure that the Curie temperature is reached for the calculation of magnetic moments of phases separately. Total magnetization values of the samples were taken from 300 K (Figure 8.1). Since the magnetizations of samples were obtained from Fe and Fe₃C and total values around room temperature includes both, also at the 550 K are based on only Fe because of the Fe₃C's Curie temperature, the differences between of them gives Fe₃C's magnetic moment (Table 8.1).

Table 8.1: Magnetic moments of the Fe, Fe₃C and Fe/Fe₃C particles.

Sample	Moment	Temperature	Moment	Temperature	Moment
	Fe		Fe+Fe ₃ C		Fe ₃ C
	Am ² [x10 ⁻³]	K	Am ² [x10 ⁻³]	K	Am ² [x10 ⁻³]
F700-45	0.077	550	0.116	300	0.039
F750-45	0.074	550	0.115	300	0.041
F800-45	0.052	550	0.100	300	0.048
F850-45	0.088	550	0.134	300	0.046
F900-45	0.071	550	0.121	300	0.050
F1000-45	0.111	550	0.159	300	0.048

To calculate the mass of the Fe and Fe₃C particles separately, the equation given below was used, where m represents mass (g), M (Am²) magnetic moment and Ms (Am²/kg) saturation magnetization:

$$m = \frac{M}{M_s} \quad (7.1)$$

Since saturation magnetization values needed to make this calculation, the Ms of Fe₃C was found at 300 K and the Ms of Fe was determined at 550 K for each sample. Fe₃C's Ms value at 300 K is 140 emu/g (0.140 Am²/g) as stated by L. Xiang et al [44]. For Fe, as this value is not at a specific temperature, it was determined as 176 emu/g (0.176

Am^2/g) from the value at 0 K multiplied by the proportionality coefficient previously calculated by Ma et al and Santos et al [45], [46]. (Appendix-B)

Table 8.2: Weight and weight percentages from magnetization calculations.

Sample	Fe weight (g) [10 ⁻³]	Fe ₃ C weight (g) [10 ⁻³]	Total weight (g) [10 ⁻³]	wt% Fe	wt% Fe ₃ C
F700-45	0.44	0.28	0.72	61.10	38.90
F750-45	0.42	0.29	0.71	58.94	41.06
F800-45	0.29	0.34	0.64	46.29	53.71
F850-45	0.50	0.33	0.83	60.34	39.66
F900-45	4,03	0.36	0.76	53.04	46.96
F1000-45	0.63	0.34	0.97	64.78	35.22

With magnetic moments of the particles and the literature M_s values using Equation 8.1 weight of the particles and weight percentages were calculated and the values obtained are listed in Table 8.2. To compare calculations with XRD analysis, weight percentages were also calculated from Rietveld Refinement as listed in Table 8.3.

Table 8.3: Weight percentages from magnetization and XRD measurement calculations.

Sample	Magnetization wt %		XRD wt %	
	Fe	Fe ₃ C	Fe	Fe ₃ C
F700-45	61.10	38.90	22.49	77.51
F750-45	58.94	41.06	60.24	39.76
F800-45	46.29	53.71	49.55	50.45
F850-45	60.34	39.66	61.96	38.04
F900-45	53.04	46.96	51.34	48.66
F1000-45	64.78	35.22	72.12	27.88

9. CONCLUSION

The production of Fe/Fe₃C nanoparticles could not be achieved properly at 700°C. Proper structuring occurred at higher pyrolysis temperatures, and carbon nanotubes decorated with Fe/Fe₃C particles by positioning on the inner and outer surfaces of the carbon nanotubes were formed. It has been observed that it occurs at different rates according to the pyrolysis temperatures but 700°C is not suitable for properly grow. In addition to that oxidation was seen due to the absence of carbon shells in the formation of Fe/Fe₃C magnetic nanoparticles at 700°C and 750°C.

Dimensional analysis of the formed Fe/Fe₃C magnetic nanoparticles were made from TEM pictures with ImageJ software. The size distribution of those particles does not include iron oxide particles since they are very small, and it is not easy to take account. The average diameter of the Fe/Fe₃C magnetic nanoparticles were calculated to be around 40 nm and it is consistent with each other, and also with the literature.

Phase analyzes were made with XRD measurement and Rietveld analyses with 2 different calculation softwares JANA and MAUD. Beside the Fe, C and Fe₃C, iron oxide structures were occurred in F700-45 and F750-45 which were determined as Magnetite and Maghemite by attempting the refining of these and all other iron oxide phases. It is shown by the mas fraction calculations for each sample that different strucutres and phases form in different proportions in samples depending on the pyrolysis temperatures. When the solid state pyrolysis temperature is reaches 800 °C and beyond, the decomposition of cementite phase in the strucutre starts and the mechanism takes more complex situation. The reason for the decreasing of the cementite's mass fraction could be this decomposition. It has been determined that the most suitable construction occurs at 850°C compared to other pyrolysis temperatures according to the TEM images and phase analyses from mass fraction.

Magnetization measurements were first performed at 10 K with magnetic field dependent magnetization measurement, and hysteresis loops compatible with ferromagnetic nanoparticles were recorded. Saturation occurred for all samples and saturation magnetizations were measured around 1 T. The highest saturation magnetization value belongs to F850-45 and lowest was observed for F700-45 which are related to the mass fractions of the Fe and Fe₃C. From the hysteresis curve coercive

field, remanent magnetization values were taken and then remanent ratio is calculated with saturation magnetization and remanent magnetization.

For F700-45 sample there is a shift on coercive field due to its content of Magnetite and Maghemite and their ferrimagnetic nature. The coercive field values varied among the samples: F700-45, F800-45, F1000-45, F850-45 and F900-45 list the samples with coercive field values from high to low.

The temperature dependent magnetization measurements were made for all samples at both low and high temperatures in the range of 0-650 K. In the low temperature magnetization measurement made in the range of 0-300 K, the temperature was first decreased from room temperature to lower temperature and then increased back to room temperature. As a result of the measurement, it was observed that the magnetization value increased as the temperature decreased to a lower temperature, and when it returned to the initial temperature of 300 K, it returned also to the initial magnetization value, that is, it followed a reversible process. In the high temperature measurement, which was made in the range of 300-650 K and included the Curie temperature of Fe_3C , magnetization decreased as the temperature increased, especially when the Curie temperature of cementite was reached, a serious decrease in magnetization was seen. This decrease, which is due to the paramagnetic behavior of ferromagnetic cementite above the Curie temperature, occurred around 485 K, as expected. Although there was an increase around this temperature when returning from 650 K to room temperature, a reversible process did not occur unlike the low temperature case.

Moreover, magnetization value increased from initial to final value in F700-45, it was expected due to the decomposition of cementite into Fe and C when measured back from high temperature to low temperature. Differently from that for all other samples final magnetization value is less than the initial one in HT measurement. It is an interesting result during that process. Differences in structuring at high temperatures have been taken into consideration as a reason for the decrease in magnetization.

To investigate the reason for the changes in magnetization, XRD analyses of low and high temperature magnetization measurement samples of F700-45 and F850-45 were performed and low and high temperature analyses were compared for each sample. Although no new phase formation was seen in F700-45, it was observed that Fe_3C in

the metastable phase decomposed, resulting in a decrease in Fe_3C intensity, and an increase in C, Fe, and oxidation-related iron oxides intensities. While a decrease in magnetization is expected due to the increase in oxidation and decrease in cementite, an increase is also expected due to decomposite Fe. Since iron is magnetically harder than cementite, the observation that magnetization increases with temperature increase was found to be consistent with magnetization and XRD analysis. For F850-45, the decrease in the intensities of Fe and C, the increase in Fe_3C and the appearance of new peaks indicate that a new temperature-dependent phase has formed in the sample. The rightward shift in XRD patterns also supports this. Since the sample had only Fe, C and Fe_3C phases before the magnetization measurement and the magnetization measurement took place in vacuum in SQUID, it is thought that the newly formed phase is another phase containing Fe and C. Since the sample had only Fe, C and Fe_3C phases before the magnetization measurement and the magnetization measurement took place in vacuum in SQUID, it is thought that the newly formed phase is another phase containing Fe and C. However, despite the low possibilities' oxidation can be observed in SQUID measurements under the vacuum. Although possible similar phases such as Fe_2C , Fe_5C_2 , Fe_7C_3 and iron oxides were tried in the Rietveld refinements, it was seen that they were not compatible with the new phase formed. In addition, it is seen that the newly formed peaks are in a position compatible with the oxide peaks at F700-45. It is observed that oxidation may occur during or after the SQUID measurement due to unstable phases that occur due to temperature. As a result of these and considering the decrease in magnetization, it appears to be due to the temperature-dependent decomposition of Fe_3C into Fe and C or the oxidation of a newly formed unstable iron carbide phase.

It was evaluated by temperature-dependent magnetization measurement that the Curie temperature of Fe_3C was exceeded at high temperatures and therefore there was a decrease in magnetization. To test the decrease in magnetization with temperature and calculate the Curie temperature of Fe_3C for all the samples, Landau Theorem was used. The Curie temperatures were found as; 480 K for F700-45, 485 K for F750-45 and F1000-45, and 490 K for F800-45, F850-45 and F900-45. These values are consistent with the values reported in literature. Since the curie temperature of Fe is much higher, the values obtained are the curie temperature values of Fe_3C . In addition, other minimum values were seen around 580 K and 620 K. These minima are due to the

complex structures of the samples and the increase in lattice parameters at high temperature values [26].

To determine to what extent the obtained magnetization was caused by Fe and Fe₃C, magnetization value was determined at around 550 K which is above the T_c of Fe₃C, for Fe's value. Since the magnetization value at 300 K is the total magnetization of Fe and Fe₃C, the difference between total and Fe's was found and the magnetization of each was calculated. Again, saturation magnetizations were calculated at these temperature values, and the weights of Fe and Fe₃C in the samples were calculated from the magnetization measurements, and the weight ratios were calculated from these weight values. When weight ratios calculation from magnetization analysis and XRD measurement were compared except the F700-45 for all other sample the values are pretty close to each other. The the considerable amount of oxide presence in F700-45 sample is the reason for that, as a result of magnetite and maghemite being antiferromagnetic. The fact that the other values are close and consistent with each other shows that the XRD and magnetization measurements support each other, and the content of the material is analyzed correctly.

As a result, Fe/Fe₃C nanoparticles produced at 45 minutes at different pyrolysis temperatures of 700°C, 750°C, 800°C, 850°C, 900°C and 1000°C show different structural and magnetic properties in line with their complex structure. Structurally, it has been observed that Fe/Fe₃C nanostructures cannot crystallize properly at 700°C and 750°C, and at other temperature values, C nanotubes settle on the inner and outer walls and form more suitable crystal structures. It has been seen that the mass ratios of the formed Fe/Fe₃C nanoparticles change depending on the temperature, and due to the metastable feature of Fe₃C, the coalescence and dissociation processes can occur simultaneously. In the magnetization measurements, it was seen that they reached magnetic saturation around 1 T at 10 K. While temperature-dependent magnetization changes were reversible for low temperatures, they tended to decrease, especially at high temperatures, due to the metastable state of Fe₃C. The consistency of mass ratios calculated from structural and magnetic measurements validate the obtained results.

REFERENCES

- [1] S. Li, J. Yang, C. Song, Q. Zhu, D. Xiao and D. Ma, "Iron carbides: Control synthesis and catalytic applications in CO_x hydrogenation and electrochemical HER," *Advanced Materials*, 2019, 31.
- [2] J. Borysiuk, A. Grabias, J. Szczytko, A. M. Bystrzejewski, Twardowski and H. Lange, "Structure and magnetic properties of carbon encapsulated Fe nanoparticles obtained by arc plasma and combustion synthesis," *Carbon*, 2008, 46, 13, 1693-1701.
- [3] G. Pilatos, E. C. Vermisoglou, A. Perdikaki, E. Devlin, G. S. Pappas, G. E. Romanos, N. Boukos, T. Giannakopoulou, C. Trapalis, N. K. Kanellopoulos and G. N. Karanikolos, "One-step, in situ growth of unmodified graphene – magnetic nanostructured composites," *Carbon*, 2014, 66, 0008-6223, 467-475.
- [4] A. Wu, D. Liu, Tong, Y. L. L. and H. Yang, "Magnetic properties of nanocrystalline Fe/Fe₃C composites," *CrystEngComm*, 2011, 13, 876-882.
- [5] J. F. Shultz, W. K. Hall, T. A. Dubs and R. B. Anderson, "Studies of the Fischer-Tropsch synthesis. XV. Cementite as catalysts.," *Journal of the American Chemical Society*, 1956, 78, 282–285.
- [6] R. P. Alagar, K. Yohannes, S. Bjorn and V. Hilmar, "Core/Shell structure nano-iron/iron carbide electrodes for rechargeable alkaline iron batteries," *J. Electrochem. Soc.*, 2017, 7, A1665-A1672.
- [7] H. Gyulasaryan, L. Avakyan, A. Emelyanov, N. Sisakyan, S. Kubrin, V. Srabionyan, A. Ovcharov, C. Dannangoda, L. Bugaev, E. Sharoyan, M. Angelakeris, M. Farle, M. Spasova, K. Martirosyan and A. & Manukyan, "Iron-cementite nanoparticles in carbon matrix: Synthesis; structure and magnetic properties.," *Journal of Magnetism and Magnetic Materials*, 2022, 559.
- [8] D. Valery, R. Alexandra, K. Igor, I. Alieva, Z. Oksana, S. Olga, V. Dianova, T. D. Samani, K. Mireles, Y. L. Hocine, R. Uzbekov, A. Viatcheslav and K. Valery, "Solid state synthesis of carbon-encapsulated iron carbide nanoparticles and their interaction with living cells," *Journal of Materials Chemistry B*, 2014, 2, 27, 4250-4261.
- [9] E. Papadopoulou, N. Tetos, H. Gyulasaryan, G. Chilingaryan, A. Ginoyan, A. Manukyan, M. Angelakeris, M. Farle and M. Spasova, "Structural and magnetic properties of carbon-encapsulated Fe/Fe₃C nanoparticles," *Nano-Structures & Nano-Objects*, 2023, 2352-507.

- [10] H. Zhanbing, M. Jean-Luc, G. Aurélien, L. Chang Seok, P. Didier and C. Costel Sorin, "Iron catalysts for the growth of carbon nanofibers: Fe, Fe₃C or both?," *Chemistry of Materials*, 2011, 23, 5379-5387.
- [11] Z. Tiejun, Y. Honghao, Y. Jianwei, W. Jianqi, Z. Jianwei and W. Zifa, "Electromagnetic wave absorption mechanism of Fe@C nanoparticles prepared by gaseous detonation," *Materials Chemistry and Physics*, 2021, 259.
- [12] R. Sergiienko, E. Shibata, Z. Akase, H. Suwa, T. Nakamura and D. Shindo, "Carbon encapsulated iron carbide nanoparticles synthesized in ethanol by an electric plasma discharge in an ultrasonic cavitation field.," *Materials Chemistry and Physics*, 2006, 98, 34-38.
- [13] A. Leon, M. Aram, B. Alena, G. Harutyun, C. Jose, P. Ekaterina, S. Galina, S. Vasiliy, S. Eduard and B. Lusegen, "Synthesis and structural characterization of iron-cementite nanoparticles encapsulated in carbon matrix," *Journal of Nanoparticle Research*, 2020, 30.
- [14] R. Kumar and B. Sahoo, "Investigation of disorder in carbon encapsulated core-shell Fe/Fe₃C nanoparticles synthesized by one-step pyrolysis," *Diamond and Related Materials*, 2018, 90, 62-71.
- [15] L. Qingfeng, C. Zhi-Gang, L. Bilu, R. Wencai, L. Feng, C. Hongtao and C. Hui-Ming, "Synthesis of different magnetic carbon nanostructures by the pyrolysis of ferrocene at different sublimation temperatures," *CARBON*, 2008, 46, 1892–1902.
- [16] S. Sangaraju and G. Aharon, "Generation of hydrophilic, bamboo-shaped multiwalled carbon nanotubes by solid-state pyrolysis and its electrochemical studies," *The Journal of Physical Chemistry B*, 2006, 110, 5, 2037-2044.
- [17] "Classification of Magnetic Materials," [Online]. Available: <http://www.birmingham.ac.uk/Documents/college-eps/metallurgy/research/Magnetic-Materials-Background/Magnetic-Materials-Background-4-Classification-of-Magnetic-Materials.pdf>. [Accessed 22 11 2023].
- [18] T. Scepka, (2016), Noninvasive control of magnetic state in ferromagnetic nanodots by Hall probe magnetometry, Bratislava: Slovak University of Technology.
- [19] V. Koval, G. Viola and Y. Tan, (2015), "Biasing effects in ferroic materials", "Ferroelectric Materials - Synthesis and Characterization", InTech Open.
- [20] H. Okamoto, "The C-Fe (carbon-iron) system", *JPE*, 1992, 13, 543–565.

- [21] L. S. Darken and R. W. Gurry, "Free energy of formation of cementite and the solubility of cementite in austenite," *JOM* 3, 1951, 3, 11, 1015-1018.
- [22] W. Pepperhoff and M. Acet, (2001), "Interstitial alloys and compounds", "Constitution and Magnetism of Iron and its Alloys", Springer, 145.
- [23] I. Wood, L. Vočadlo, K. Knight, D. Dobson, W. Marshall, G. Price and J. Brodholt, "Thermal expansion and crystal structure of cementite, Fe_3C , between 4 and 600 K determined by time-of-flight neutron powder diffraction," *Journal of Applied Crystallography*, 2004, 37, 0021-8898, 82-90.
- [24] A. Tsuzuki, S. Sago, S. Hirano and e. al., "High temperature and pressure preparation and properties of iron carbides Fe_7C_3 and Fe_3C ," *Journal of Materials Science*, 1984, 13, 2513–2518.
- [25] A. Galwey, D. Jamieson, B. Wheeler and R. R., "The oxidation of cementite," *Corros Sci*, 1974, 14, 527–532.
- [26] H. K. D. Bhadeshia, "Cementite," *International Materials Reviews*, 2020, 65, 1, 1-27.
- [27] W. Pepperhoff and M. Acet, (2001), "Interstitial alloys and compound", "Constitution and Magnetism of Iron and its Alloys", Springer, 163.
- [28] C.Y. Tang, Z. Yang, (2017), "Transmission electron microscopy (TEM)", In: N. Hilal, A. F. Ismail, T. Matsuura, D. Oatley-Radcliffe, Editors, "Membrane Characterization", Elsevier.
- [29] T. Sochi, "High throughput software for powder diffraction and its application to heterogeneous catalysis", *Data Analysis, Statistics and Probability*, 2010.
- [30] H. M. Rietveld, "A profile refinement method for nuclear and magnetic structures," *Journal of Applied Crystallography*, 1969, 2, 65-71.
- [31] D. Robbes, "Highly sensitive magnetometers," *Sensors and Actuators A: Physical*, 2006, 129, 1-2, 86-93.
- [32] M. Mcelfresh, (1994), SQUID manuel quantum design fundamentals of magnetism and magnetic measurements, Indiana USA: Quantum Design.
- [33] O. H. Kamerlingh, "Further experiments with liquid helium," *Royal Netherlands Academy of Arts and Sciences*, 1911, 1093-1113.
- [34] R. Doll and M. Näbauer, "Experimental proof of magnetic flux quantization in a superconducting ring," *Phys. Rev. Lett*, 1961, 7, 2, 51-52.

- [35] B. Josephson, "Possible new effects in superconductive tunnelling," *Physics Letters*, 1962, 1, 7, 251-253.
- [36] R. Cornell and U. Schwertmann, "Characterization", *The iron oxides: Structure, properties, reactions, occurrences and uses, 2nd completely revised and extended edition*, 2006, 167-168.
- [37] E. Crow and K. Shimizu, Lognormal distributions: theory and application, Dekker, 1987.
- [38] E. A. Owen and G. I. Williams, "A low-temperature X-ray camera," *Journal of Scientific Instruments*, 1954, 31, 49-54.
- [39] I. G. Wood, L. Vočadlo, K. S. Knight, D. P. Dobson, W. G. Marshall, G. D. Price and J. Brodholt, "Thermal expansion and crystal structure of cementite, Fe_3C , between 4 and 600 K determined by time-of-flight neutron powder diffraction", *Journal of Applied Crystallography*, 2004, 37, 82-90.
- [40] O. Hassel, "Ueber die kristallstruktur des graphits", *Zeitschrift fuer Physik*, 1924, 25, 317-337.
- [41] C. Pecharroman, T. Gonzalez-Carreno and J. E. Iglesias, "The infrared dielectric properties of maghemite, $\gamma\text{-Fe}_2\text{O}_3$, from reflectance measurement on pressed powders Sample: a) idealized", *Physics and Chemistry of Minerals*, 1995, 22, 21-29.
- [42] Y. Fei, D. J. Frost, H. K. Mao, C. T. Prewitt and D. Hausermann, "In situ structure determination of the high-pressure phase of Fe_3O_4 Sample data recorded at $P = 23.96 \text{ GPa}$, $T = 823 \text{ K}$ ", *American Mineralogist*, 1999, 84, 203-206.
- [43] E. Duman, M. Acet, T. Hülser, E. F. Wassermann, B. Rellinghaus, J. P. Itié and P. Munsch, "Large spontaneous magnetostrictive softening below the Curie temperature of Fe_3C Invar particles", *Journal of Applied Physics*, 2004, 96, 5668-5672.
- [44] L. Xiang, W. Wei, Y. Zhantong, Z. Nan and Y. Hua, "High saturation magnetization of Fe_3C nanoparticles synthesized by a simple route", *Dyes and Pigments*, 2016, 139.
- [45] G. D. Santos, R. Aparicio, D. Linares, E. Miranda, J. Tranchida, G. Pastor and E. Bringa, "Size- and temperature-dependent magnetization of iron nanoclusters", *Physical Review B*, 2020.
- [46] P. Ma, C. H. Woo and S. L. Dudarev, "Large-scale simulation of the spin-lattice dynamics in ferromagnetic iron", *Physical review B*, 2008, 78.

- [47] K. Lipert, J. Kaźmierczak, I. Pelech, U. Narkiewicz, A. Slawska-Waniewska and H. Lachowicz, "Magnetic properties of cementite (Fe_3C) nanoparticle agglomerates in a carbon matrix", *Materials Science-Poland*, 2007.
- [48] W. C. Chiou and E. A. Carter, "Structure and stability of Fe_3C -cementite surfaces from first principles", *Surface Science*, 2003, 530(1-2), 88-100.
- [49] T. I. Yang and S. H. Chang, "Controlled synthesis of metallic iron nanoparticles and their magnetic hyperthermia performance in polyaniline composite nanofibers", *Nanotechnology*, 2017, 28(5).
- [50] G. Dos Santos, R. Aparicio, D. Linares, E. N. Miranda, J. Tranchida, G. M. Pastor and E. M. Bringa, "Size- and temperature -dependent magnetization of iron nanoclusters", *Phys. Rev. B*, 2020, 102, 18.
- [51] X. Lei, Z. Ye and E. al., "High saturation magnetization of Fe_3C nanoparticles synthesized by a simple route", *Dyes and Pigments*, 2016, 139.

BIBLIOGRAPHY

Aydan AKYILDIZ MERT, after completing Istanbul Technical University Physics Engineering Department in 2019, started her master's degree at Gebze Technical University, Physics Graduate School in 2020. In 2021, she joined Farle Research Group at University of Duisburg Essen Germany, through Erasmus program to study about magnetization. She is still a part of this group.



PRESENTATIONS FROM THE THESIS

Akyildiz, A., Papadopoulou, E., Spasova, M., Acet, M., Farle, M., Karabulut, M., (2023), “Magnetic and Structural Properties of Fe/Cementit Nanoparticles Produced by Solid State Pyrolysis”, Gebze Technical University 7th Graduate Research Symposium, Kocaeli, Turkiye, 31 May-1 June.



APPENDICES

APPENDIX-A: RIETVELD REFINEMENT

The detailed refinement with all phases separately is given below. MAUD uses terms such as sig., Rwp%, Rb% and Rexp% to indicate the accuracy and appropriateness of the analyses.

The “sig.” value shows the difference between the value predicted by the model used in the analysis and the actual measured value of each data point. A smaller sig value indicates that the model fits the data better and the analysis is more reliable.

Rwp% (Rietveld Weighted Profile Residual) is a statistical measure used to evaluate the quality of results obtained during a Rietveld refining analysis. Rwp% refers to the fit of the analysis to the actual X-ray diffraction data of the model. A lower Rwp% value indicates that the model fits the data better and the analysis is more reliable. The Rwp% value is often used to determine the degree of confidence in the results of the analysis.

Rb% (Rietveld Refining Factor) is another measurement used for score evaluation of results obtained during a Rietveld refining analysis. Rb% expresses how well the analysis model fits the actual X-ray diffraction. A lower Rb% value indicates a better fit of the model and a more reliable analysis.

Rexp% (Rietveld Expected Profile Residual) is another statistical measure used to evaluate the quality of results obtained during a Rietveld refining analysis. Rexp% represents a measure of the difference between measured and calculated data. A lower Rexp% value indicates that the model fits the data better and the analysis is more reliable.

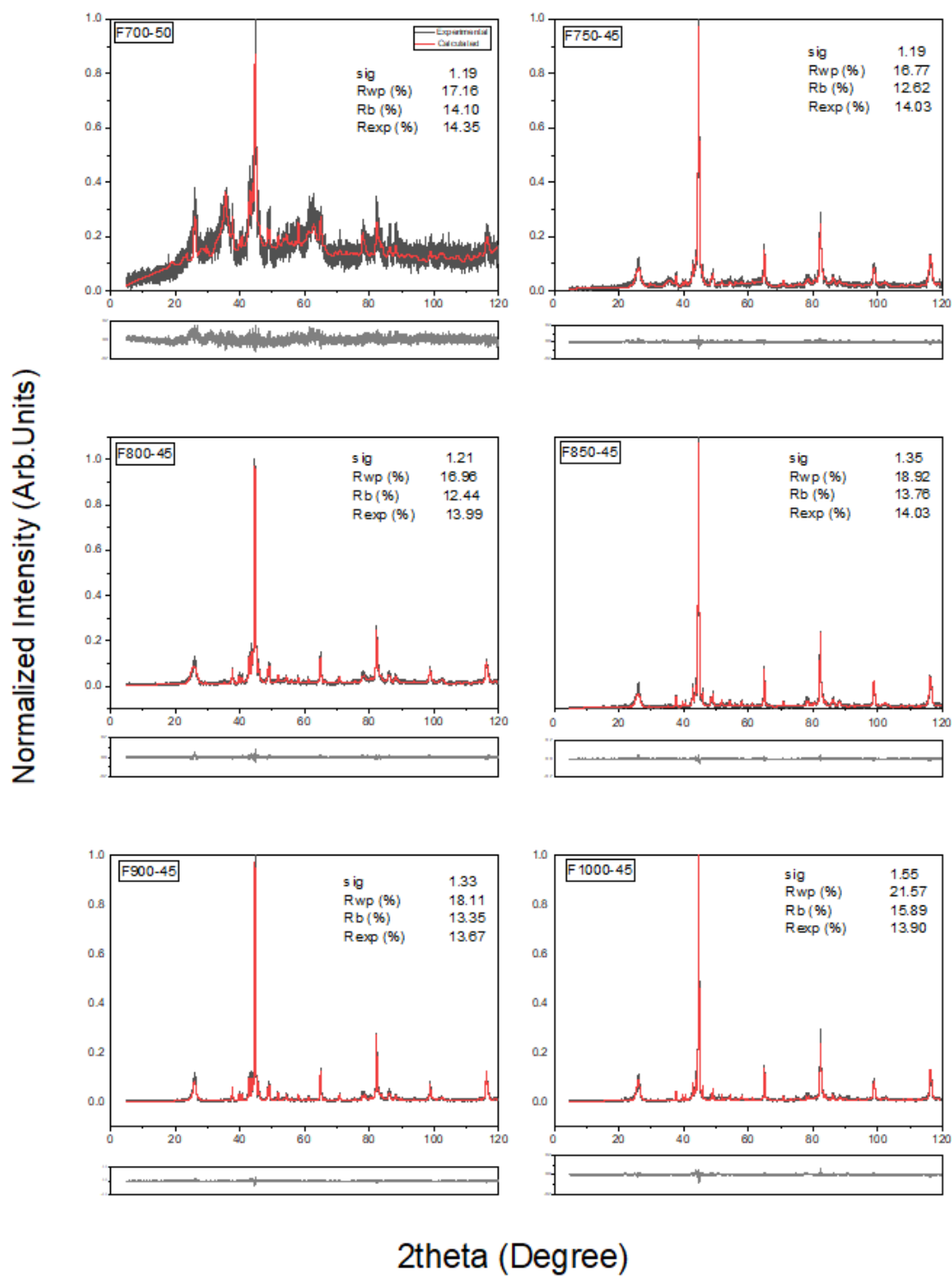


Figure A.1: Rietveld refinements with accuracy parameters.

APPENDIX-B: Fe SATURATION MAGNETIZATION CALCULATION

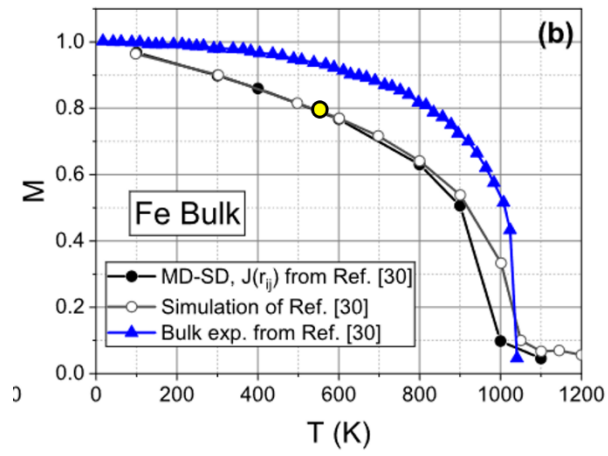


Figure B.1: Reference value of Fe's Saturation Magnetization at 0K [45] [46].