

İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

MAGNETIC AND STRUCTURAL PROPERTIES OF Fe-Ni-Al ALLOYS

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Fe-Ni-Al ALAŞIMLARININ MANYETİK VE YAPISAL ÖZELLİKLERİ

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ABBREVIATIONS

BCC	: Body Centered Cubic
CCD	: Charge-coupled Device
EDX	: Energy-dispersive X-ray Spectroscopy
FCC	: Face Centered Cubic
FEG	: Field Emission Gun
FIB	: Focused Ion Beam
LaB6	: Lanthanum Hexaboride
TEM	: Transmission Electron Microscopy
XRD	: X-ray Diffraction
VSM	: Vibrating Sample Magnetometer

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MAGNETIC AND STRUCTURAL PROPERTIES OF Fe-Ni-Al ALLOYS

SUMMARY

Fe-Ni alloys with low Ni concentration are known to go through Martensitic transformation under heat treatment. Martensitic transformation is interesting for us since it leads to a special property called shape memory effect. Therefore we focused our attention on a binary $\text{Fe}_{75}\text{Ni}_{25}$ alloy. We kept Fe:Ni ratio constant and added different percentages of Al to $\text{Fe}_{75}\text{Ni}_{25}$ in order to see how its magnetic and structural properties are affected. $\text{Fe}_{75}\text{Ni}_{25}$, $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ samples were produced in an arc-melting furnace with tungsten as electrode. This was done in an argon atmosphere and all samples were re-melted three times. In addition $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$, $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ and $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ samples were produced from powders under argon atmosphere in a glove box system. Fe concentration was kept constant for these 3 alloys. After being pressed in the glove box, arc-melting and induction melting were applied to the bulks. All the bulk samples were homogenized at 1050°C for 12 hours. Magnetic susceptibility and VSM measurements were done in order to characterize the magnetic properties of the materials. TEM and XRD examinations were carried out in order to characterize the structural properties of the samples. Magnetic susceptibility, VSM and XRD were measured for all samples. TEM study was applied only for the $\text{Fe}_{75}\text{Ni}_{25}$, $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ samples. Susceptibility-temperature curves were obtained in order to determine the magnetic phase transformations in the range of $24\text{--}700^{\circ}\text{C}$. The Curie temperature of $\text{Fe}_{75}\text{Ni}_{25}$ was measured as 580°C . $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ sample made a magnetic phase transformation from ferromagnetic phase to paramagnetic phase around 700°C . The large hysteresis obtained from the χ -T curves of $\text{Fe}_{75}\text{Ni}_{25}$ and $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ samples indicate structural transformations in the temperature range where magnetic transformations take place. This structural transformation is reported as Martensitic transformation which may lead to shape memory effect. The Curie temperatures of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys were above 700°C . For the alloys where Fe:Ni ratio was constant, as Al concentration increased (as Fe and Ni concentrations decreased) the Curie temperatures of the materials increased. $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$ sample made magnetic transition at 80°C . The reverse transition also happened at 80°C , as a result no hysteresis was observed. $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ and $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ samples made magnetic transition above 700°C . Magnetization - magnetic field curves were obtained in order to determine the magnetic behaviours of the materials by VSM. Magnetic measurements showed that all the samples are soft magnets with very low coercivity and remanence values. The TEM measurements were carried out at room temperature. The TEM study focused on diffraction patterns and structures of the samples were investigated. The structures were determined together with the XRD results. XRD was applied to bulk plates at room temperature. TEM results suggest that FCC structure exists for the binary $\text{Fe}_{75}\text{Ni}_{25}$ alloy. BCC and B2 structures exist

for the ternary alloys. For $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ alloy only BCC structure was found. For the $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys BCC and B2 structures were found. Literature data suggest that these B2 structures are either FeAl or NiAl phases. The calculated lattice parameters of the studied materials match the lattice parameters of FeAl and NiAl phases. XRD results also support the phases found by TEM. In addition, EDX examination was carried out to confirm the atomic percentages of the elements in the samples. The structural properties of $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$, $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ and $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ samples were determined only by XRD.

Fe-Ni-Al ALAŞIMLARININ MANYETİK VE YAPISAL ÖZELLİKLERİ

ÖZET

Düşük Ni konsantrasyonuna sahip Fe-Ni alaşımlarının ısıtılma işlemi altında martensitik değişime uğradığı bilinir. Martensitik geçiş, kendi şeklini hatırlama etkisiyle ilişkili olduğu için ilgi çekicidir. Bu yüzden ikili $\text{Fe}_{75}\text{Ni}_{25}$ alaşımına yoğunlaştık. Bu alaşıma farklı oranlarda Al ekledik ve manyetik ve yapısal özelliklerin nasıl etkilendiğini inceledik. Fe:Ni oranını 3:1 olarak sabit tutup bu alaşıma farklı oranlarda Al ekledik ve manyetik ve yapısal özelliklerin nasıl etkilendiğini inceledik. $\text{Fe}_{75}\text{Ni}_{25}$, $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ ve $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ örnekleri tungsten elektrotlu ark ergitme yoluyla üretildi. Bu işlem argon atmosferinde yapıldı ve tüm örnekler üçer kez ergitildi. $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$, $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ ve $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ örnekleri glove box sisteminde argon atmosferi altında üretildi. Glove box içinde preslendikten sonra örnekler sırasıyla ark ergitme ve indüksiyon ergitme uygulandı. Tüm örnekler 1050°C 'de 12 saat boyunca homojenize edildi. Malzemelerin manyetik özelliklerini belirlemek için manyetik duygunluk - sıcaklık ve manyetizasyon - manyetik alan ölçümleri uygulandı. Malzemelerin yapısal özelliklerini belirlemek için TEM ve XRD çalışmaları yapıldı. Manyetik duygunluk, VSM ve XRD tüm örnekler üzerine uygulandı. Sadece $\text{Fe}_{75}\text{Ni}_{25}$, $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ ve $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ örnekleri TEM ile incelendi. Manyetik faz geçişlerini belirlemek için $24-700^{\circ}\text{C}$ arasında manyetik duygunluk - sıcaklık eğrileri elde edildi. $\text{Fe}_{75}\text{Ni}_{25}$ alaşımının Curie sıcaklığı 580°C olarak bulundu. $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ alaşımı 700°C civarında ferromanyetik fazdan paramanyetik faza geçiş yaptı. $\text{Fe}_{75}\text{Ni}_{25}$ ve $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ örneklerinin χ -T eğrilerinden elde edilen geniş histerezis, manyetik geçişin gerçekleştiği sıcaklık aralığında yapısal bir geçişin olduğuna işaret ediyor. Bu yapısal geçiş martensitik geçiş olarak biliniyor ki martensitik tip yapısal geçişlerin bizi kendi şeklini hatırlama etkisine götürebildiğini biliyoruz. $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ ve $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ örneklerinin Curie sıcaklıkları 700°C 'nin üzerindedir. Fe:Ni oranı sabit kaldıkça, artan Al oranıyla (azalan Fe ve Ni oranı ile) malzemelerin Curie sıcaklıklarında artış tespit edildi. $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$ örneği 80°C 'de manyetik faz geçişi yaptı. Ters geçiş yine aynı sıcaklıkta gerçekleşti ve dolayısıyla histerezis gözlenmedi. $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ ve $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ örneklerinin manyetik faz geçişleri 700°C 'nin üzerinde gerçekleşti. Örneklerin manyetik davranışlarını belirlemek için M-H eğrileri oda sıcaklığında VSM ile ölçüldü. Sonuçlar, tüm örneklerin düşük koersivite ve kalıcı mıknatıslanma değerlerine sahip geçici manyetler olduğunu gösterdi. TEM çalışması oda sıcaklığında gerçekleştirildi. TEM çalışması kırınım desenleri üzerine yoğunlaştı ve örneklerin yapısal özellikleri araştırıldı. Yapısal özellikler XRD sonuçları ile birlikte kararlaştırıldı. XRD ölçümü oda sıcaklığında gerçekleştirildi. TEM sonuçları gösteriyor ki $\text{Fe}_{75}\text{Ni}_{25}$ alaşımı FCC yapıdadır. Üçlü alaşımlarda BCC ve B2 yapıları görülmüştür. $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ alaşımında sadece BCC yapısı gözlenmiştir. $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ ve $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alaşımlarında BCC ve B2 yapıları birlikte gözlenmiştir. Literatürden elde edilen bilgiler, Fe-Ni-Al sisteminde bulunan B2

yapıların FeAl veya NiAl fazlarına karşılık geldiğini göstermektedir. Üzerinde çalışılan örneklerin hesaplanan örgü sabitleri literatürden bulunan FeAl ve NiAl fazlarının örgü sabitleriyle eşleşiyor. XRD sonuçları da TEM ile bulunan fazları destekliyor. Buna ilaveten, elementlerin örneklerdeki atomik yüzdelerini desteklemek için EDX çalışması yapıldı. $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$, $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ ve $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ örneklerinin yapısal özellikleri sadece XRD ile tespit edildi.

1. INTRODUCTION

1.1 Iron-Nickel and Iron-Nickel-Aluminum Alloys

1.1.1 Iron-Nickel Alloys

Binary alloys of Fe with transition metals (such as Ni, Cu, Zr, Pt, Ag...) are stable, disordered solid solutions and they are known to go through structural transformations on heat treatment [1]. From the mentioned alloys, Fe-Ni system shows some interesting properties (such as low cost, availability in high temperatures...) which make them attract great attention [1]. Due to their interesting properties and the lack of knowledge of the system, several studies were focused on Fe-Ni alloys.

One of the most important properties of the system is that the Fe-Ni alloys with low Ni content are known to go through fcc $\rightarrow$ bcc martensitic transformation (MT) [2]. The transition temperature depends on the composition and the preparation of the sample.

Martensitic transformation (austenite $\rightarrow$ martensite) is a sub group of diffusionless transformation. As understood from the name no long-range diffusions take place in this kind of transformation. Martensite is obtained by rapid cooling of austenite phase so that no time for diffusion is allowed. On cooling, when a critical temperature is reached, austenite begins to form martensite. This is named as martensite start temperature (M_s). The temperature at which the transformation ends is named as martensite finish temperature (M_f). When M_f is reached all austenite is transformed to martensite. Accordingly, on heating A_s and A_f are the temperatures at which the transformation from martensite to austenite starts and finishes. [3].

The transition temperatures can be seen on Figure 1.1.

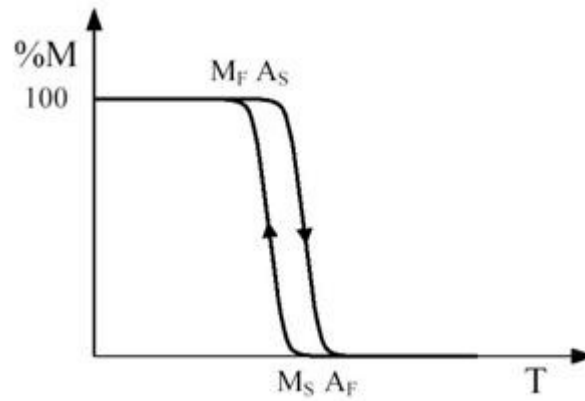


Figure 1.1: Martensitic transformation [url-1]

Martensitic transformation leads to a special property called shape memory effect, which attracts a great attention [3]. A shape memory alloy is an alloy that remembers its original shape on heating or cooling. Martensite has a lower density than austenite, so martensitic transformation will end up in change of volume. When austenite transforms to martensite, the volume of the atom increases. Therefore, on cooling when M_f is reached the volume of the atom will be larger than before. Shape memory alloys will reach their original volume after heating back to A_f temperature which ends up in the property of remembering its shape.

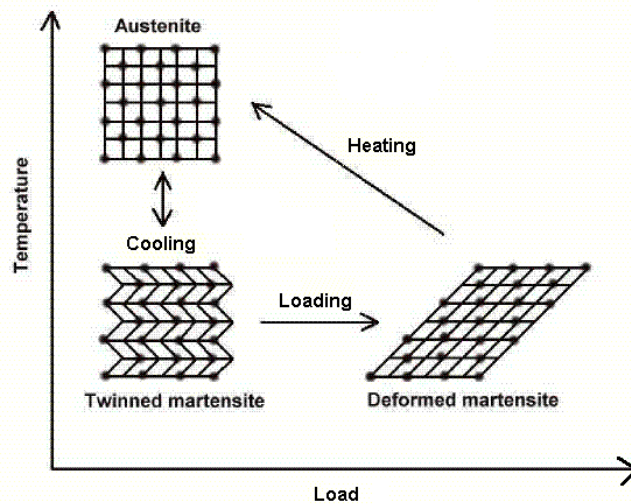


Figure 1.2: The demonstration of shape memory effect [url-2]

When austenite is cooled down, as it reaches the M_s temperature, martensite will be formed. When stress is applied, deformed martensites will be obtained. When this phase is heated, as it reaches the A_s temperature we will end up in undeformed austenite.

There are two parameters that effect the transition, temperature and stress. The transition does not depend on time.

When a material is in martensite phase, it can be deformed (it can be bended or stretched) and it will stay in that shape. If the material is heated upon its A_s temperature, it will have its original shape and if it stays in that state even when it is cooled again it is said to have one way shape memory effect. If the material shows shape memory effect on both cooling and heating it has two way shape memory effect [3].

In ferromagnetic materials, the magnetic field is known to play the role of stress. When a magnetic material goes to martensite phase, the alignment of the magnetic moments of the atoms change. When a magnetic field is applied, it forces these magnetic moments to realign in the direction of the field.

Figure 1.3 can explain the effect of magnetic field on martensite of ferromagnetic materials.

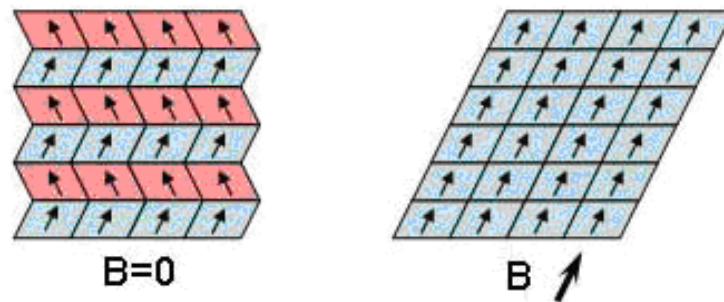


Figure 1.3: Ferromagnetic shape memory efekct [url-3]

As the shape memory effect is theoretically and technologically very important, we will be investigating if our produced materials show this property too since Fe-Ni alloys with low Ni content are known to make martensitic transformation.

To investigate the Fe-Ni system, we will start with the study of the phase diagram. Ni-rich part of the diagram had been studied more detailed so there is a wider range of information on different percentages of Ni content on the Ni-rich part of the diagram. After completing this part of the diagram, more studies were focused on the Fe-rich part. Figure 1.4 shows the binary phase diagram of Fe-Ni.

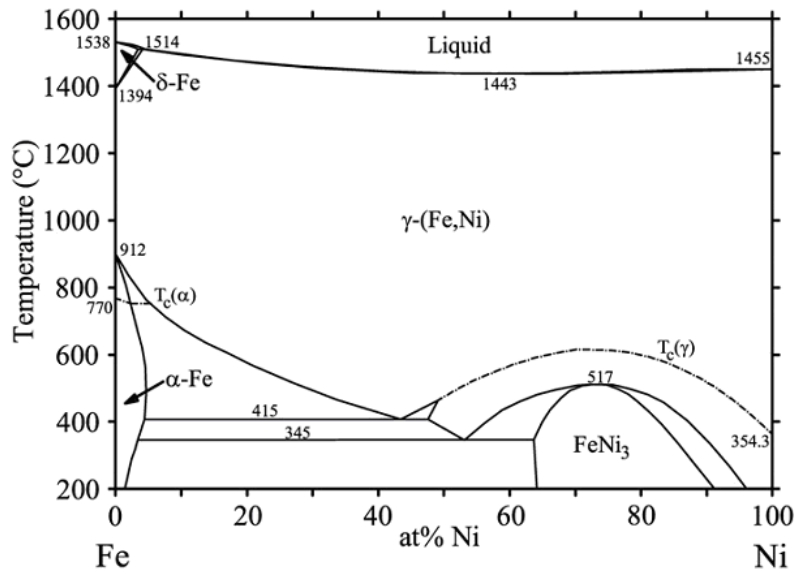


Figure 1.4: Fe-Ni phase diagram [4]

The main phases of the diagram are γ -(Fe,Ni), δ -Fe, α -Fe and FeNi₃ [5].

γ -(Fe,Ni) solid solution is in disordered fcc (A1) structure and as we can see from the diagram this phase can be formed in the complete composition range at high temperatures. Below 250°C γ -(Fe,Ni) forms ordered Fe₃Ni phase [6].

High temperature δ -Fe and low temperature α -Fe solid solutions are in disordered bcc (A2) structure and are formed in a narrow composition range.

The FeNi₃ solid solution is in ordered fcc (L1₂) structure. It is formed from A1 γ -(Fe,Ni) above 500°C and shows a good solubility.

Both of the γ -(Fe,Ni) and α -Fe phases go through para to ferromagnetic transitions with decreasing temperature.

Below 400°C it is difficult to reach equilibrium because of very slow interdiffusion between Fe and Ni [5].

Alloys that contain about 30% to 100% nickel form γ (disordered fcc) phase when cooled from high temperatures. In alloys with low nickel γ phase undergoes a martensitic transformation to α (disordered bcc) phase when cooled down from high temperatures.

From the phase diagram which was adopted from Goldstein (1973) it is seen that for Fe₇₅Ni₂₅ alloy the T_c is 400°C. Bozorth (1951) reported that the T_c of Fe₇₅Ni₂₅ was 650°C and according to the study of Acet et al [7] it is around -113°C.

Bozorth (1951) suggested that in the Fe-rich part, as the nickel content increases the Curie temperature decreases. For the Ni-rich parts, the Curie temperature increases with increasing iron, reaches a maximum (612°C at 68%Ni) and then starts to decrease [8].

According to Hopkins, Fe-Ni alloys with 5-30 at% Ni go through structural change between room temperature and Curie temperature [6].

The structural change of the Fe-Ni system was also investigated by Hansen (1958) and he reported that the phase transformation from α (bcc) $\rightarrow \gamma$ (fcc) starts at 500°C for Fe₇₅Ni₂₅ and end at around 530°C [6]. The diagram of the phase transformation is given in Figure 1.5. From the figure, it can also be seen that the reverse transformation happens at lower temperatures and this results a hysteresis in the phase transformation diagram.

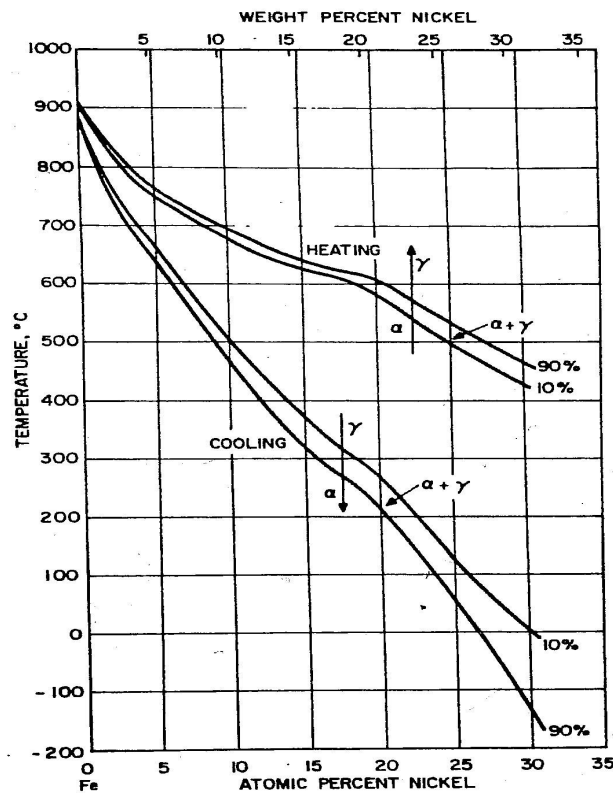
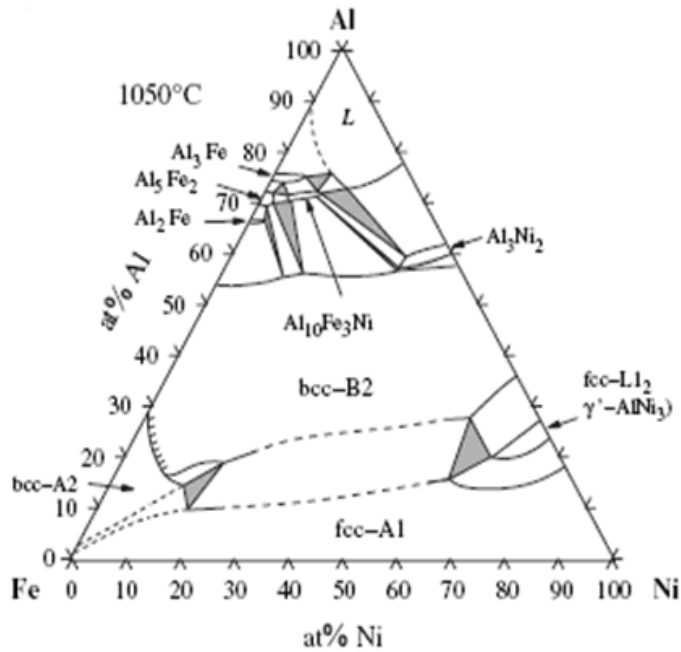


Figure 1.5: Phase transformations of Fe-Ni system with low Ni contents [8]

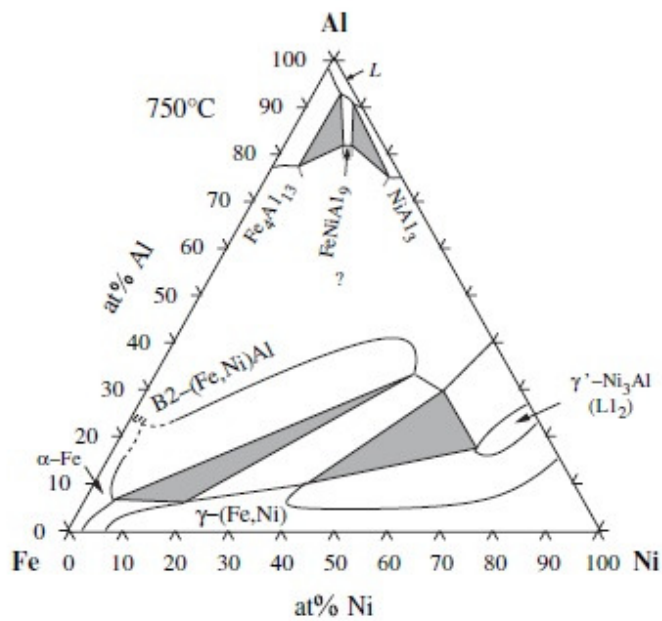
1.1.2 Iron-Nickel-Aluminum Alloys

Fe-based intermetallic alloys have high melting points which make them available in high temperature applications. Due to their resistance to high temperatures and their interesting structural and magnetic properties, many works were focused on these alloys. The iron-nickel-aluminum system is one of them for their promising magnetic

properties. In Figure 1.6 (a) the ternary phase diagram for Fe-Ni-Al system is given at 1050°C which is the homogenization temperature of our samples and in Figure 1.6 (b) the phase diagram is given for 750°C which is the lowest temperature studied so far.



(a)



(b)

Figure 1.6: Ternary phase diagram of Fe-Ni-Al at (a) 1050°C (b) 750°C [4]

It is important to investigate the binary phases of the system. Binary Fe-Ni system was investigated in the previous part. Now information on Fe-Al and Ni-Al systems will be given.

1.1.2.1 Fe-Al

The binary Fe-Al phase diagram is given in Figure 1.7.

It is reported that Fe-Al alloys with 30, 40 and 50 at% Al have bcc structures and alloys with above 50 at% to 90 at% Al were amorphous. Without any heat treatment, the Fe-Al system with up to 23 at% Al is ferromagnetic and in bcc structure. With heat treatment and quenching, this limit can be expanded to 50 at% Al. The alloys that contain 50 at% Al form ordered structures after heat treatment. This ordered system can be either FeAl or Fe₂Al₅. Alloys that contain less than 50 at% Al do not go through a change in phase composition. [9]

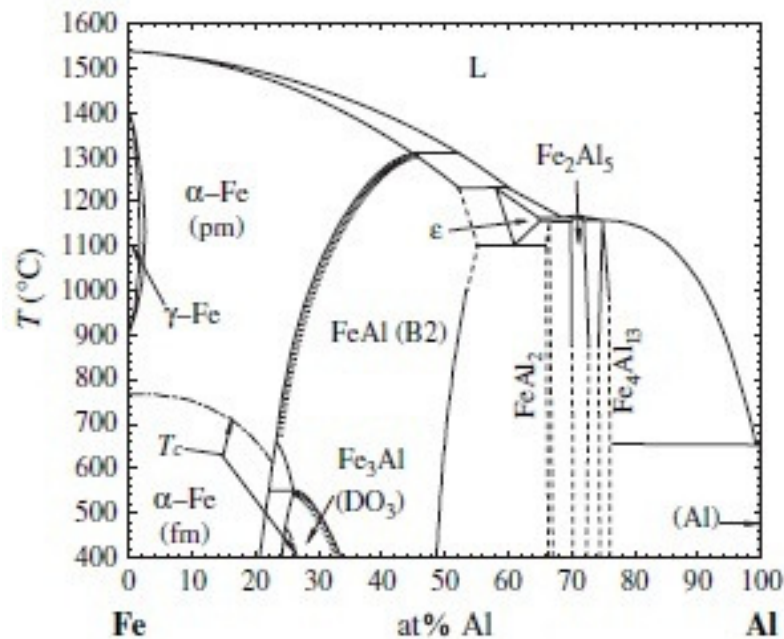


Figure 1.7: Phase diagram of Fe-Al [4]

1.1.2.2 Ni-Al

Ni and Al forms AlNi phase in B2 structure in a wide temperature range and as seen from the diagram this phase is paramagnetic. The phase is known to have high melting temperature, good oxidation resistance, high thermal conductivity, and low density. [10].

Figure 1.8 shows the binary Ni-Al phase diagram.

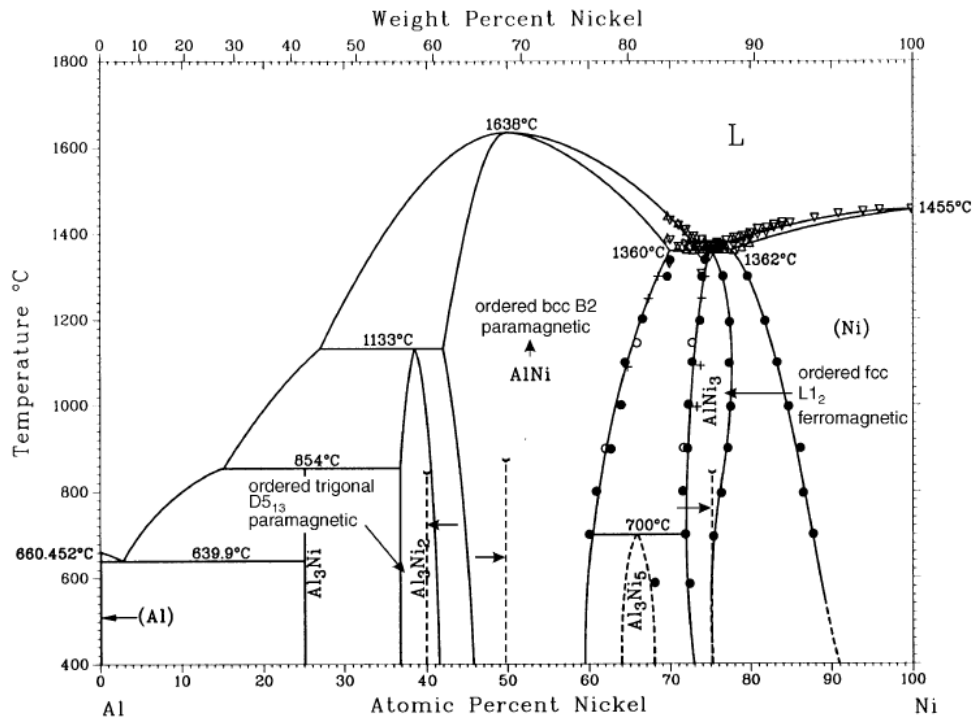


Figure 1.8: Phase diagram of Al-Ni [11]

1.2 Magnetic Susceptibility

In order to characterize the magnetic properties of materials, one can determine the magnetization (M) of the material but also how it varies with the applied field (H). The ratio between M and H is called susceptibility (χ) and it is the degree of magnetization in an applied magnetic field. [16].

$$M = \chi H \quad (1.1)$$

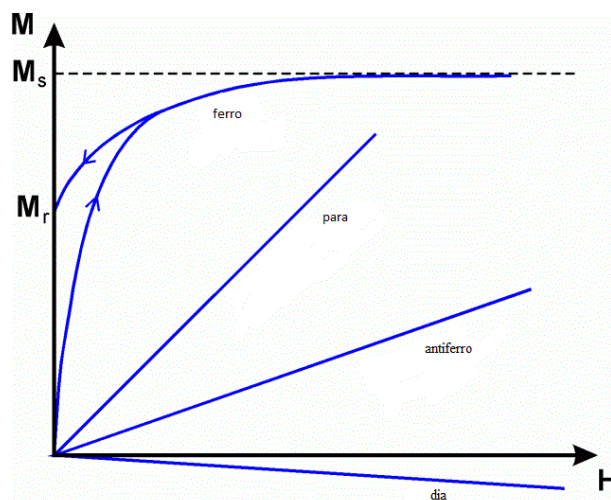


Figure 1.9: Typical magnetization curves of diamagnetic, paramagnetic, antiferromagnetic and ferromagnetic materials [url-4]

Figure 1.9 shows typical magnetization curves (M-H graphics) for materials with different magnetic properties. The M-H curves are linear for diamagnetic, paramagnetic and antiferromagnetic materials and when the applied field is removed they show no magnetic properties. The behaviour of the curve referring to ferro- or ferrimagnetic materials is nonlinear. It can be seen that at a certain value of H, the magnetization M becomes constant and the value that M starts being constant is called the saturation magnetization (M_s). After saturation, when H is decreased to zero, M decreases, but does not drop to zero, making a hysteresis as shown in the figure. The meaning of this is that the ferromagnetic or ferrimagnetic materials show magnetic properties even after the applied magnetic field is removed.

When a magnetic field is applied, a material can response through its susceptibility but also through its permeability. The degree of total flux density (B) produced by an applied magnetic field (H) is permeability [16].

$$B = \mu H \quad (1.2)$$

$$\text{Since } B = H + 4\pi M \text{ (cgs)} \quad (1.3)$$

$$H + 4\pi M = \mu H$$

$$H(\mu - 1) = 4\pi M$$

Merging this with the equation (1.1) we get;

$$H(\mu - 1) = 4\pi\chi H$$

$$\mu = 1 + 4\pi\chi \quad (1.4)$$

Metals with negative χ such as copper, silver, gold and bismuth are diamagnetic materials. Metals with positive χ values are either paramagnetic or ferromagnetic. Those with small χ are paramagnetic and those with very large χ are ferromagnetic materials. Iron, nickel and cobalt are ferromagnetic materials at room temperature. Their χ is very large and has a value around 1000. [17]

Magnetic materials are mainly grouped in two, magnetically soft (temporary magnets) and magnetically hard (permanent magnets) materials [17]. Soft magnets have large permeabilities and very small coercivities, while hard magnets have large saturation magnetizations and large coercivities. When the applied field H is removed, a certain magnetism remains in the material. In order to remove this

magnetism, in other say to demagnetize the specimen, a field in the opposite direction must be applied. This field shown as H_c is called the coercive force, or simply coercivity [6]. A soft magnet is easy to magnetize and demagnetize. To magnetize a soft magnet a smaller H value will be enough when we compare it to the field needed to magnetize a hard magnet. Accordingly, a small coercivity will be enough to demagnetize sample. A large field is needed to magnetize a permanent magnet and high coercivity is needed to demagnetize it.

1.2.1 Classification of magnetic materials

The magnetic moment of an atom is the vector sum of its spin moment and orbital moment. In a diamagnetic material all the electron spins are coupled. The magnetic moments are induced from the the orbital motion of electrons in an applied field. Since all atoms have electrons orbiting the nucleus, diamagnetism is a property that all materials have in common. If an atom has unpaired electrons, the coupling of their moments in an applied field leads to magnetization. Such materials are simply called magnetic materials. Magnetic materials can be para-, ferro-, antiferro- or ferrimagnetic [16].

1.2.1.1 Diamagnetism

Diamagnetism is the common property of all materials. In a diamagnetic material the spins of the electrons are coupled. As a result there will be no net spin magnetic moment. The magnetism will appear only due to the orbital motion of the electrons.

When the magnetic field is applied, electrons orbiting around the nucleus will be under the effect of Lorentz's force. The magnetic field will reduce the effective current of the orbit, thus magnetic moments that oppose the field will be produced. This is in good accordance with Lenz' law which suggests that "An induced current is always in such a direction as to oppose the motion or change causing it" [18].

As a result when a magnetic field is applied, diamagnetic materials create a magnetic moment in the opposite direction to the applied field, causing a repulsive effect.

Their relative magnetic permeability is less than 1, so their magnetic susceptibility is negative (Eq 1.4).

When we consider the Equation (1.4) when μ is negative χ is also negative which leads to the condition that $B < H$. As a result diamagnetic materials are repelled by magnetic fields.

Diamagnetism occurs only in an applied magnetic field and the magnetization of a diamagnetic material is very weak when we compare it to paramagnetism and especially ferromagnetism.

1.2.1.2 Paramagnetism

Paramagnetic materials have unpaired electrons. When there is no applied field, the atomic moments cancel each other, so there is no net magnetization if there is no applied field. When a field is applied, the atomic moments will orient in the direction of the field, causing a very large magnetization in the specimen. But due to the thermal agitation of the atoms the atomic moments will orient in random directions. As a result only a small magnetization in the field direction will remain. This will also end up with a small positive susceptibility value. As the temperature is increased, the effect of thermal agitation which results in random moments will increase. So the susceptibility of the specimen will decrease [19].

Paramagnets differ from diamagnetic materials with their positive relative magnetic permeability and magnetic susceptibility.

When the positive μ (where positive χ is required) is put in the Equation (1.4) it can be seen that $B > H$. In the absence of magnetic field they show no magnetism. The magnetization that occurs in an applied field is weak and linear and given by the Curie law as; [16]

$$M = \chi_m H = \frac{C}{T} H \quad (1.5)$$

Which also implies that;

$$\chi_m = \frac{C}{T} \quad (1.6)$$

From the Curie's law;

$$M = \frac{n\mu a}{3} = \frac{n\mu^2 H}{3kT} \quad (1.7)$$

$$\chi_v = \frac{M}{H} = \frac{n\mu^2}{3kT} \quad (1.8)$$

and

$$\chi_m = \frac{\chi_v}{\rho} = \frac{n\mu^2}{3\rho kT} \quad (1.9)$$

where ρ is the density, χ_v is the volume susceptibility and χ_m is the mass susceptibility [16].

The number of atoms per unit volume is equal to;

$n = \frac{N\rho}{A}$ where N is the Avogadro's number (atoms/mol), ρ is density and A is atomic weight.

This leads to the expressions;

$$\chi_v = \frac{N\mu^2}{3AkT} = \frac{C}{T} \frac{emu}{cm^3 Oe} \text{ (cgs) or } \frac{Am^2}{m^3 Am^{-1}} [\text{dimensionless}] \text{ (SI)} \quad (1.10)$$

and

$$\chi_m = \frac{N\mu^2}{\rho 3AkT} = \frac{C}{\rho T} \frac{emu}{g Oe} \text{ (cgs) or } \frac{Am^2}{kg Am^{-1}} = \frac{m^3}{kg} \text{ (SI)} \quad (1.11)$$

So the Curie constant can be written as;

$$C = \frac{N\mu^2}{3Ak} \quad (1.12)$$

In summary, the magnetic behaviours of diamagnetic and paramagnetic materials can be shown as in Figure 1.10;

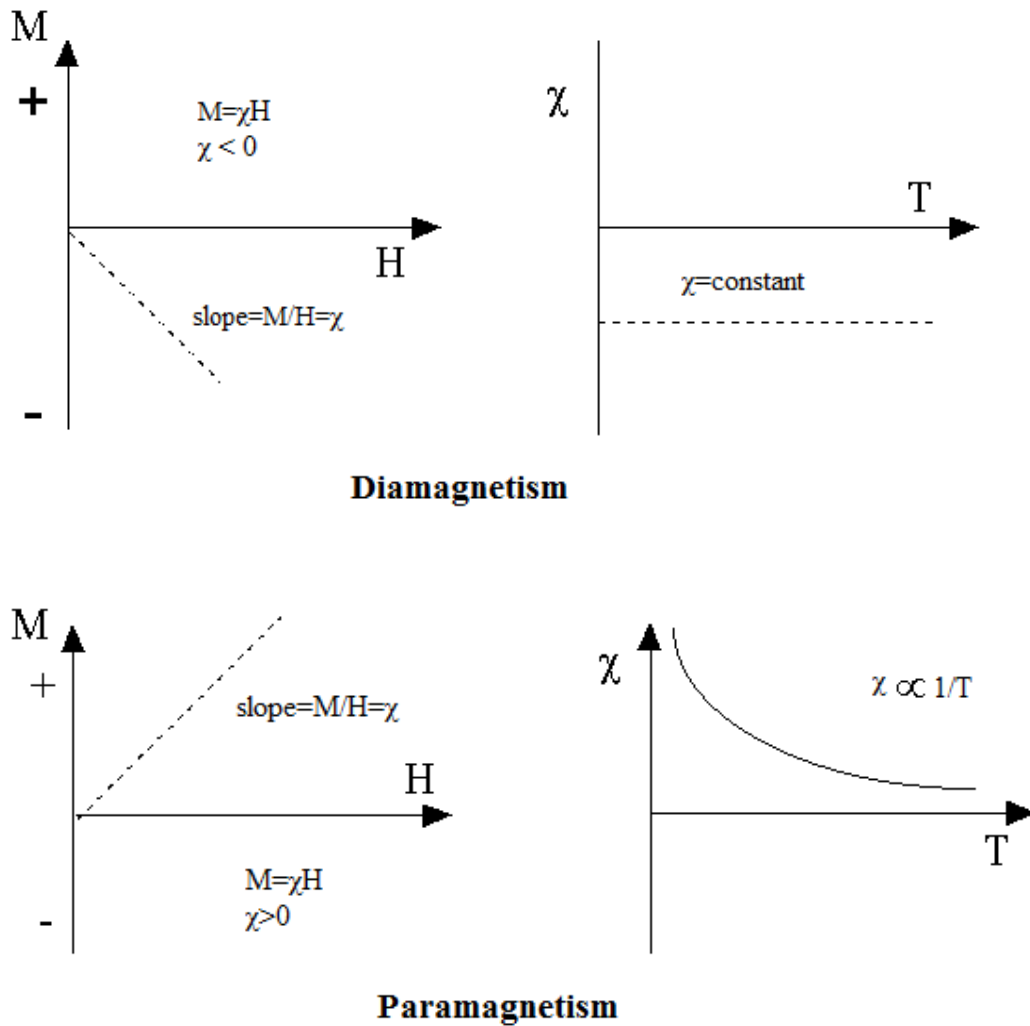


Figure 1.10: Magnetic behaviours of diamagnetic and paramagnetic materials [url-5]

1.2.1.3 Ferromagnetism

Due to its complex behaviour ferromagnetism is not very easy to understand. There are 3 approaches to explain ferromagnetism, namely the Weiss molecular field theory, exchange forces and band theory.

The theory of the Curie law was presented by Langevin for paramagnets and in his theory Langevin suggested that the atoms or molecules (which are the carriers of magnetic moments) do not interact with each other and they are only under the effect of the applied field and thermal agitation. In ferromagnetic materials, the interactions have to be taken into account. Even many paramagnets do not obey the simplified Curie law in real. So a more general law was derived with the addition of Weiss to the Curie's law where the interaction of elementary moments was taken in consideration [16].

$$M = \chi_m H = \frac{C}{T - \Theta} H \quad (1.13)$$

And

$$\chi_m = \frac{C}{T - \Theta} \quad (1.14)$$

where Θ is a constant with the dimensions of temperature.

Weiss suggested atoms/molecules which are the carrier of magnetic moments interact with each other and that this interaction could be explained by an additional “molecular field” H_m to the applied field [16]. According to his assumption the intensity of the molecular field was proportional to the magnetization in such a way that;

$$H_m = \gamma M \quad (1.15)$$

Where γ is the molecular field constant. Thus, the total field that acts on a material is given as;

$$H_t = H + H_m \quad (1.16)$$

When this equation is put in Curie’s law:

$$\chi_m = \frac{M}{\rho H} = \frac{C}{T} \quad (1.17)$$

where H changes place with H_t we get;

$$\frac{M}{\rho(H + \gamma M)} = \frac{C}{T} \quad (1.18)$$

If we rearrange the equation according to M we find;

$$M = \frac{\rho C H}{T - \rho C \gamma} \quad (1.19)$$

If we put this in the Currie’s law again we result in;

$$\chi_m = \frac{M}{\rho H} = \frac{C}{T - \rho C \gamma} = \frac{C}{T - \Theta} \quad (1.20)$$

Where $\Theta = \rho C \gamma$ is the measure of the strength of interaction. For materials that obey the Curie's law; $\Theta = \gamma = 0$.

From the equations 1.15 and 1.19 where $\Theta = \rho \gamma C$ it is seen that θ is directly related to the molecular field H_m . If θ is positive, γ is also positive and it results that H_m and M are in the same direction.

When a critical temperature called the Curie temperature T_c is reached, a ferromagnetic material becomes paramagnetic and its susceptibility is given by the Curie-Weiss law where θ takes the value T_c [16]. The Curie temperature of Fe is 770°C and the Curie temperature of Ni is around 358°C.

In ferromagnetic materials magnetic moments of atoms are parallel to each other in a region called a domain. The magnetic field is intense in a domain because the moments align in the same direction. In each domain, the direction of the alignment is different. The domains are separated from each other by domain walls. When we go from one domain to another (when we cross a domain wall) the direction of the magnetization changes. In a bulk material, all the domains that are aligned in random directions will cancel each other and it will result in zero magnetization. But when even a small magnetic field is applied to ferromagnetic materials the field will cause the magnetic domains to line up with each other, resulting in magnetization, and this effect will stay even when the applied field is removed [19].

In general it is put out that the Weiss theory contains random magnetization and division into domains. [16].

We have mentioned that the effect of magnetization will stay in a ferromagnetic material even when the applied field is removed. The most common way to investigate the magnetic properties of materials is to plot the M-H or B-H curves [20]. Let's say we apply a magnetic field of H and it causes a magnetization M in the material. When the magnetization reaches a maximum, let's say the H is removed. In this situation a ferromagnetic material will have some magnetization left in the material and the M value will not drop to zero although the H field is removed. This property leads to the term; hysteresis, which means "to lag behind" and it was first introduced by Ewing [21]. The Figure 1.11 can show the hysteresis better.

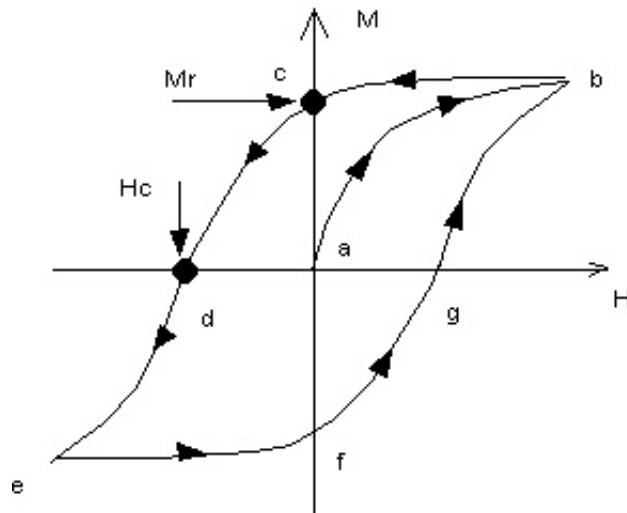


Figure 1.11: A typical hysteresis loop [url-6]

As in the figure, when a field is applied the material follows the path a, but when the field is removed, the magnetization of the material does not drop to zero but it lags behind, following path c. This is what we mean by hysteresis.

From Figure 1.11, we see that when a field is applied the magnetization of the sample increases and then it reaches a maximum in ferromagnetic materials. This maximum magnetization is the saturation magnetization (M_s). At that point, when the applied field is removed, the magnetization does not drop to zero but it decreases to a value. This value is the remanence or the remanent magnetization (M_r). After this point, in order to reduce the magnetization to zero, a field in the opposite direction should be applied. This field is coercivity or coercive field (H_c).

The hysteresis loops vary from material to material. Materials with a large hysteresis loop are desired for permanent magnets and magnetic recording devices. Materials with a narrow hysteresis are desired for transformers and motor cores. [22]

2. EXPERIMENTAL METHODS

2.1 Preparation of Samples

The bulk samples of Fe-Ni-Al were produced at University of Leuven in an arc-melting furnace with tungsten as electrode. It was done in an argon atmosphere and all samples were re-melted three times.

The different elements were separately weighted on a microbalance before the melting. Five samples were produced in total. The weights and atomic percentages of the elements are given in Table 2.1.

Table 2.1: The weights and atomic percentages of the elements

Sample (10g)	x	Fe		Ni		Al	
		(g)	Atomic %	(g)	Atomic %	(g)	Atomic %
$\text{Fe}_{0,75}\text{Ni}_{0,25}$	-	7.5335	75.00	2.5155	25.00	-	-
$(\text{Fe}_{0,75}\text{Ni}_{0,25})_{1-x}\text{Al}_x$	0,10	7.2240	67.50	2.5310	22.50	5.2445	10.00
$(\text{Fe}_{0,75}\text{Ni}_{0,25})_{1-x}\text{Al}_x$	0,15	7.0330	63.75	2.3930	21.25	0.7765	15.00
$(\text{Fe}_{0,75}\text{Ni}_{0,25})_{1-x}\text{Al}_x$	0.20	6.6165	60.00	2.3179	20.00	1.0660	20.00
$(\text{Fe}_{0,75}\text{Ni}_{0,25})_{1-x}\text{Al}_x$	0,25	6.3895	56.25	2.2385	18.75	1.3720	25.00

In addition 3 more samples were produced at Istanbul Technical University with constant Fe contents. Fe and Ni powders and Al particles were mixed and then pressed to obtain a bulk sample. This was done under argon atmosphere in a glove box system as shown in Figure 2.1. The pressed samples were melted by arc-melting and then induction melting. The samples were then homogenized at 1050°C for 12 hours. The weight and atomic percentages of these specimen are given in Table 2.2.

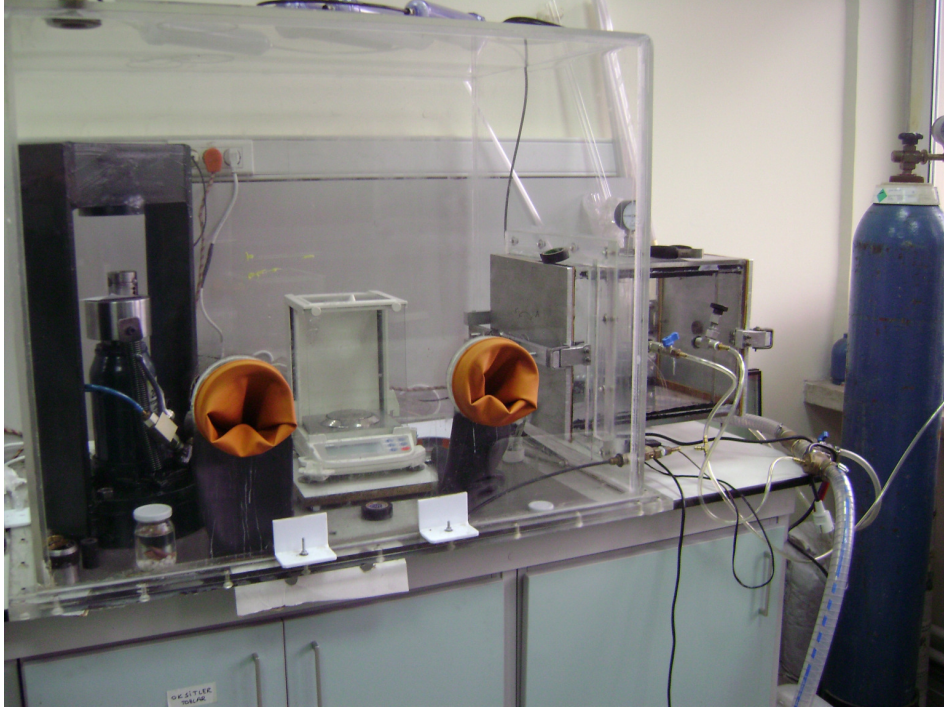


Figure 2.1: Glove Box

Table 2.2: The weights and atomic percentages in the new samples

Sample (3g)	Fe	Ni	Al
	(g)	(g)	(g)
$\text{Fe}_{0,50}\text{Ni}_{0,35}\text{Al}_{0,15}$	1.5952	1.1736	0.2312
$\text{Fe}_{0,50}\text{Ni}_{0,30}\text{Al}_{0,20}$	1.6448	1.0373	0.3178
$\text{Fe}_{0,50}\text{Ni}_{0,25}\text{Al}_{0,25}$	1.6977	0.8922	0.4107

After preparation, the samples were cut and polished properly for the susceptibility-temperature, M-H, TEM-EDX and XRD measurements. Table 2.3 shows which analyses were applied to the samples.

Because the structural and magnetic properties of the materials will be investigated, it is useful to give some related data found in literature.

Lechermann *et al* [12] reported the lattice parameters ($\text{\AA}$) and $M (\mu_B)$ values of the possible phases in the Fe-Ni-Al system. Considering our compositions and the given phase diagrams, values for the related phases are given in Table 2.4.

Table 2.3: Analyses of the samples

Sample	Susceptibility	VSM	TEM	XRD
Temperature range	24-700°C	at room temperature	at room temperature	at room temperature
Fe ₇₅ Ni ₂₅	X	X	X	X
Fe _{67.5} Ni _{22.5} Al ₁₀	X	X	X	X
Fe _{63.75} Ni _{21.25} Al ₁₅	X	X	X	X
Fe ₆₀ Ni ₂₀ Al ₂₀	X	X		X
Fe _{56.25} Ni _{18.75} Al ₂₅	X	X	X	X
Fe ₅₀ Ni ₃₅ Al ₁₅	X	X		X
Fe ₅₀ Ni ₃₀ Al ₂₀	X	X		X
Fe ₅₀ Ni ₂₅ Al ₂₅	X	X		X

Table 2.4: Lattice parameters and magnetizations of related Fe-Ni-Al phases [12]

Structure	a (Å)	M (μ_B)
BCC-Fe	2.782	2.27
BCC-Ni	2.812	0.56
B2-NiAl	2.898	0
B2-FeAl	2.872	0.73
Fe ₂ NiAl	2.834	4.88
L1 ₂ -Fe ₃ Ni	3.630	8.56

In another study, Eleno *et al* [4] summarized the given data on Fe-Ni-Al system and gave lattice parameters of the related phases as in Table 2.5.

Table 2.5: Compositions and their lattice parameters of related Fe-Ni-Al phases [4]

Phase	Composition range	a (Å)
B2-NiAl	30.8-58 at% Al	2.877 [13]
B2-FeAl	23.3 to ~ 55 at% Al	2.907 [14]
γ -(Fe,Ni)	0-100 at% Ni	3.587 [15]

2.2 Susceptibility Measurement

Susceptibility-temperature curves are plotted in order to determine the magnetic phase transitions. When a ferromagnetic material is heated upon a critical temperature, a transition to paramagnetic phase occurs. This critical temperature is the Curie temperature (T_c) and the transition to paramagnetic state is complete when the susceptibility value drops to zero. The sample is placed in a quartz tube and heated to 700°C. After that the sample is cooled to room temperature and any transition that occurs between 24-700°C and 700°C-24°C is plotted. Figure 2.2 shows the measurement system. The sample is placed at the bottom of this device and the device is put in the theormo cup. An AC magnetic field is applied and it induces a current in the probe. This current creates another field which is sensed by the receiver coils of the sytem which is connected to a computer system.

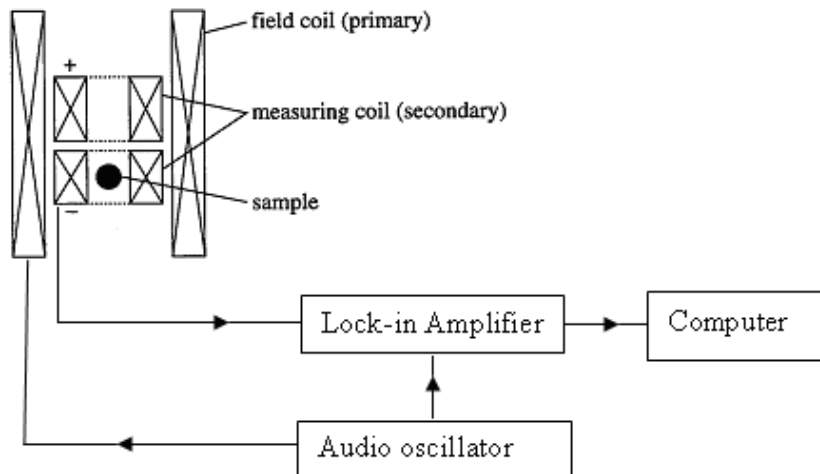


Figure 2.2: The susceptibility measurement system [27]

Figure 2.3 shows the temperature-specific magnetization curve of a system with two ferromagnetic phases (α and β). This is related to the magnetic phase transition of a system with two ferromagnetic phases, so the magnetic transition of such a system can be understood from Figure 2.3 better.

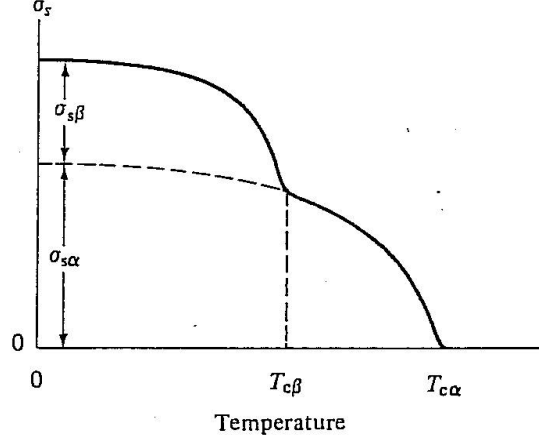


Figure 2.3: Temperature-specific magnetization curve of an alloy with two ferromagnetic phases [16]

2.3. M-H Measurement

The M-H plots of the samples were obtained by a home made model VSM in a magnetic field of maximum 8 kOe with a sensitivity of $10^{-5} emu$.

VSM (Vibrating Sample Magnetometer) is one of the most common methods to determine the magnetic properties of materials. It was invented in 1955 by Simon Foner at MIT [16].

The material is placed in a holder and it is put between the electromagnets. A magnetic field is created between these two electromagnets. This induces a dipole moment in the sample and due to this dipole moment a magnetic field will be created around the sample. During the measurement, when the sample is moved up and down, the magnetic field will change with time and it will be sensed by pick-up coils of the system. The time-dependent magnetic field creates an alternating electromotor force in the pick-up coils [16] and this will be amplified by a lock-in amplifier. An emf in coils will be induced and it will be proportional to the magnetization of the material.

A schematic VSM device is given in Figure 2.4.

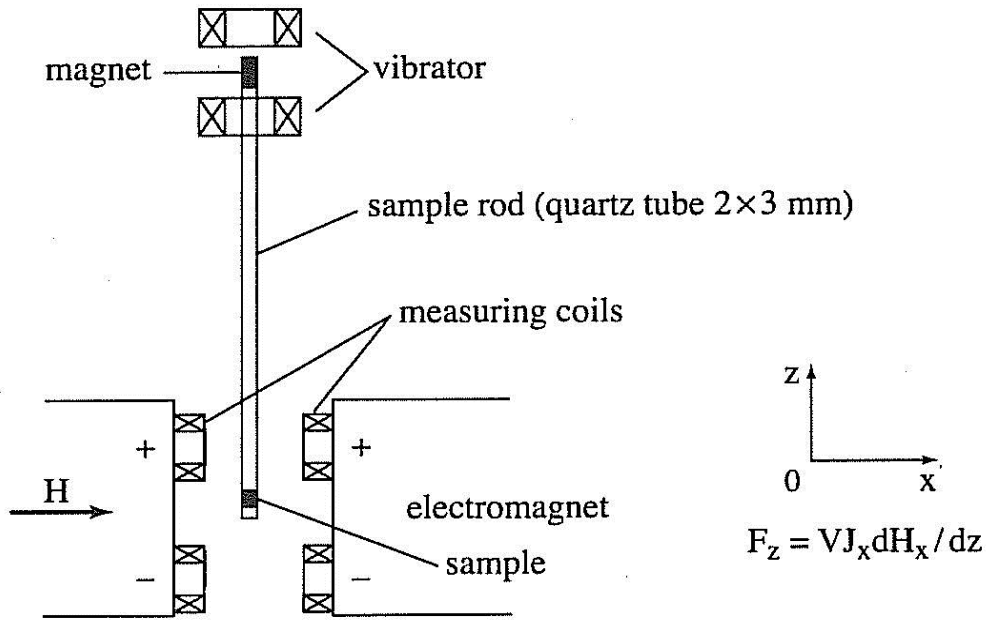


Figure 2.4: VSM (schematic) [27]

As a first step, calibration of the VSM is done by measuring the signal of a pure Ni standard. Then the samples ($2\text{mm} - 3\text{mm}$ in our case) are fixed to a small sample holder located at the end of a sample rod one by one for each measurement. The sample will oscillate along the z axis perpendicular to the magnetizing field. With the rest of the components of the device that are connected to a computer, the system can give information of the magnetization of the sample and how its magnetization depends on the applied magnetic field.

The specimen is inserted in the system in a way that the magnetic field is applied along its long axis, because it is easier to magnetize and demagnetize a material in the long axis. The reason to this can be understood from the demagnetizing field in the sample. When a magnetic field is produced by magnetic poles, the H lines start from north pole and end up in south pole both in and out of the material. The magnetization of the material will be from south to north pole [16]. Thus, the H lines within the sample will tend to demagnetize the sample. The demagnetizing field H_d is proportional to the magnetization M in such a way that;

$$H_d = -N_d M \quad (2.1)$$

Where N_d is the demagnetizing factor which depends mainly on the shape of the body [16]. The demagnetization effect can be seen from Figure 2.5 and we see that the equation 2.3 which is;

$B = H + 4\pi M$ now becomes

$$B = -H_d + 4\pi M \text{ (cgs)} \quad (2.2)$$

As a result the flux density in the material will be smaller than its magnetization, but they are still in the same direction.

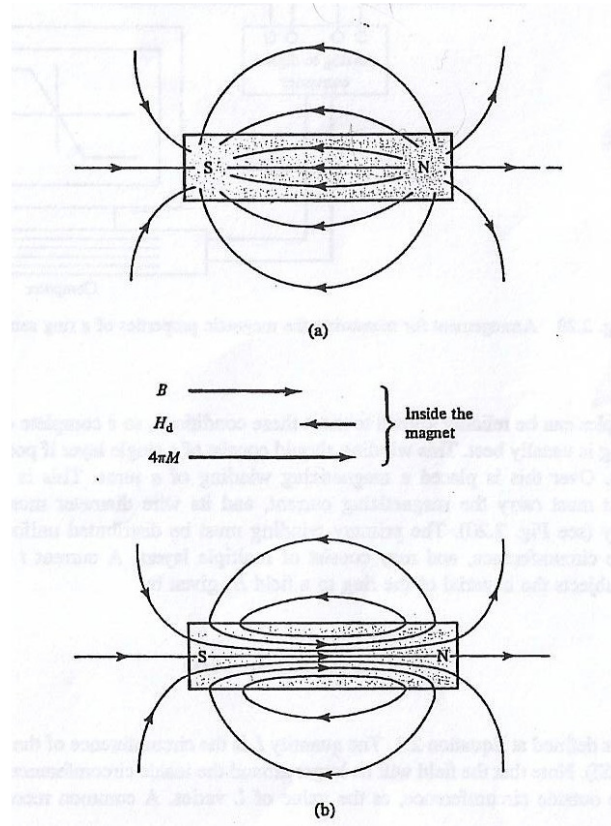


Figure 2.5: Fields of a bar magnet in zero applied field (a) H field (b) B field [16]
The values in the center indicate the directions.

Demagnetizing field will be larger between smaller plates and smaller between larger plates, which means the demagnetizing field is larger along a short axis. As a result, stronger field should be applied along a short axis in order to produce the same field inside a specimen. This effect is also known as shape anisotropy. For this reason, the specimens were inserted in the VSM in the way that the field is applied along their long axis (the axis that is 3mm long).

Figure 2.6 shows the VSM we use.

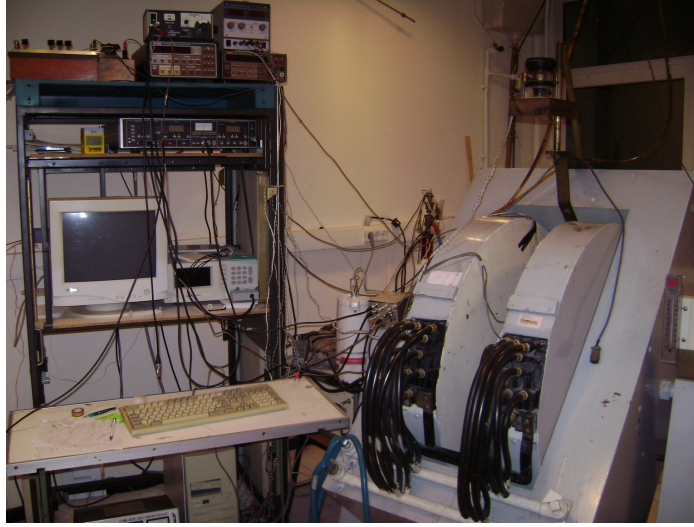


Figure 2.6: The VSM

If we look back in the previous chapter to Figure 2.5, the details of an M-H curve were given. In this chapter we will be interested in these M_s , H_c and M_r values of the samples.

2.3.1 Calculating the magnetization and M-H curves for studied samples

The magnetization of Ni found from the maximum possible signal is 54,78 emu/g . The standard Ni that was used for calibration is 0,676 g, so the standard Ni is expected to have a magnetization of 0,676 times of 54,78 emu/g for its maximum signal. Ni used in calibration gave a maximum signal of 8077,945. So this is the maximum signal that corresponds to the magnetization of $0,676 \times 54,78$ emu/g. Now for each measured sample, the magnetizations can be calculated.

If we get $0,676 \times 54,78$ emu/g magnetization corresponds to the signal of 8077,945 we can find how much magnetization we get for each signal value of the measured samples simple as follows;

$$M_{sample} = \frac{0,676 \times 54,78 \times Signal_{sample}}{Signal_{Ni_{max}} \times m_{sample}} \quad (2.3)$$

2.4 TEM

TEM is a sophisticated electron microscopy technique with a much better resolution than a usual light microscope. A beam of electrons is transmitted through an ultra thin sample and the electrons interact with the sample, gathering information. This information is turned into an image or a diffraction pattern which are magnified by lenses inside the device and focused on a fluorescent screen or detected by a sensor such as a CCD camera [23].

In order to better understand the mechanism of imaging, it is essential to have a further look into the entire instrument.

The configuration of a typical TEM is shown in the Figure 2.7 below. Figure 2.7 (a) shows the source of the electrons, where the specimen is inserted and where the observer is while in Figure 2.7 (b) some more technical details of the device are shown.

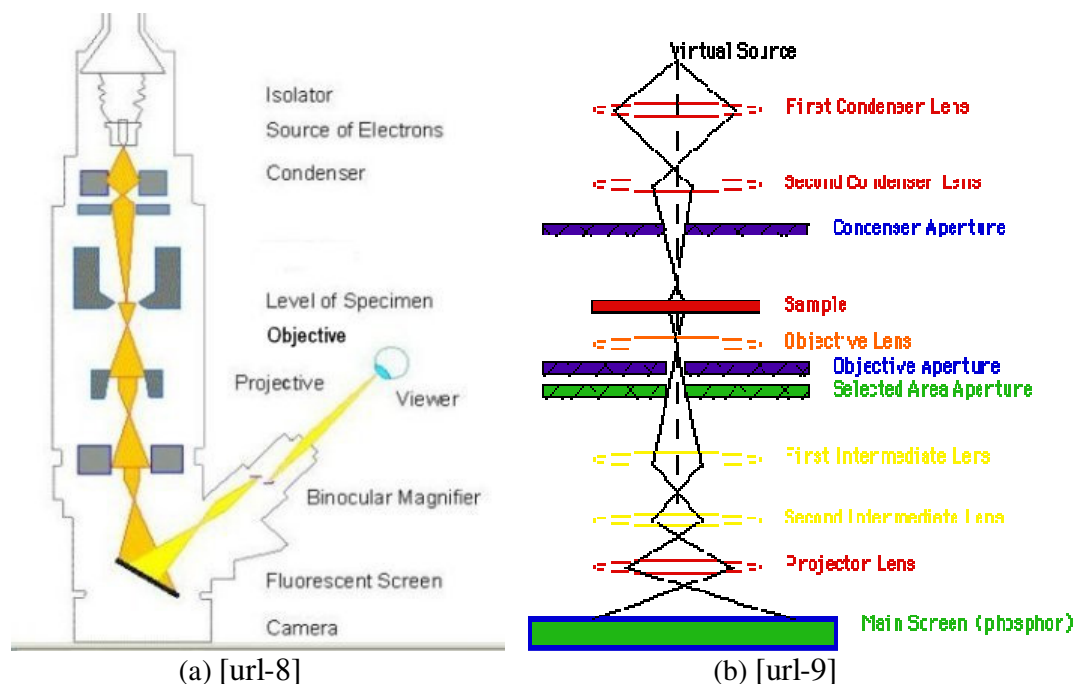


Figure 2.7: A typical TEM device

The most important parts of TEM are the electron gun, the double condenser (illumination) system and the objective lens [24].

The electron gun is the source of electrons. LaB6 or FEG guns are the most commonly used guns in which the electrons can be accelerated with a potential in the range of 80-300 keV.

The double condenser or illumination system consists of two or more lenses and a set of apertures. Its function is to control the spot size and beam convergence.

The specimen is inserted into the device below the condensor system. It is very important to use an ultra thin electron transparent specimen and put it in exactly the right position. It is also important that the specimen does not move as it is tilted which is easily done by rotating the holder.

The function of the objective lens is to form an initial inverted image or a diffraction pattern which is magnified by the intermediate and projector lenses and displayed on the viewing screen.

When electrons interact with the specimen, they may be reflected, scattered or absorbed. Possible outcomes are shown in the Figure 2.8 below. For different outcomes, different imaging or analyzing techniques can be used. In the present work we will be primarily interested in scattered electrons.

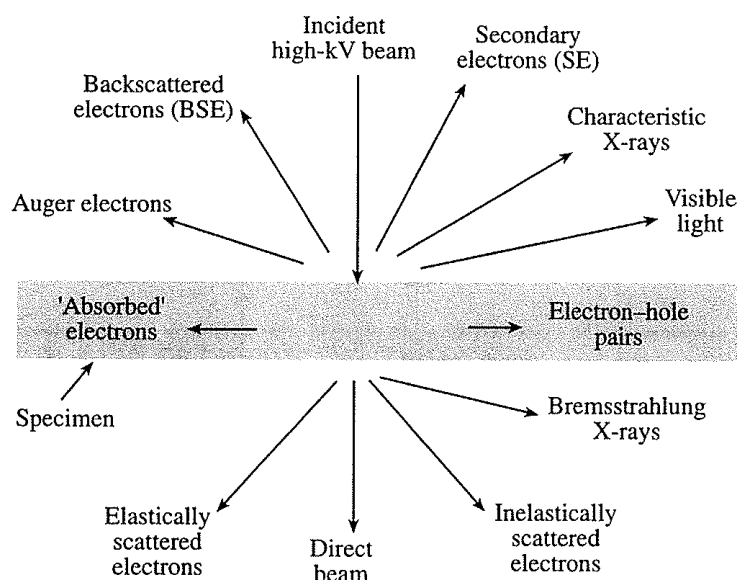


Figure 2.8: Possible outcomes of an electron interacting with a specimen [23]

The diffraction pattern is formed in the back focal plane of the objective lens and the image is formed in the image plane of the objective lens. The first projector lens can be switched between these two modes. The diffraction pattern can be magnified by

the projector lenses and its calibration is described in terms of the camera length [25].

2.4.1 Preparation Techniques

There is a wide range of sample preparation techniques. The method depends on what material is used and what kind of information is needed. The TEM specimen will be very small, but still it should represent the whole sample. It should be transparent for the electron beam but should also be stable under the beam. As the materials studied in this work are electrically conductive alloys, electrochemical polishing was used to prepare the samples for TEM. Depending on the material, this method can take a few minutes or about 15 minutes, but in general it is a relatively fast method. The foil produced is not mechanically damaged. Basic steps of sample preparation can be summarized as;

- Cutting of the bulk into 3 mm discs
- Mechanical polishing of discs till ± 150 micron thickness
- Electrochemical polishing

The bulk sample first has to be cut in slices around $300\mu m$ thick. Then the slices are drilled by spark erosion method to obtain $3mm$ diameter rounded pieces.

These pieces are mechanically polished until a thickness of around $150\mu m$. At this point they are ready to be electrochemically polished until perforation to be used in the TEM.

There are certain parameters that affect the electropolishing process. These parameters can be listed as;

- Electrolyte type
- Flow rate of electrolyte
- Polishing time (photosensitivity detector)
- Potential (voltage)
- Current
- Temperature

The choice of the values of the parameters highly depends on the material itself, the electrolyte used and the geometrical shape of the specimen.

Figure 2.9 is taken from Dr Wim Tirry from EMAT/University of Antwerp and shows the voltage dependance of electrochemical polishing. When too low voltage is applied we will obtain an etched surface with many small holes covering the entire sample. If the applied voltage is too high, then we will end up with a bean like hole at an edge. To obtain a good hole around in the middle of the specimen, optimum voltage should be applied.

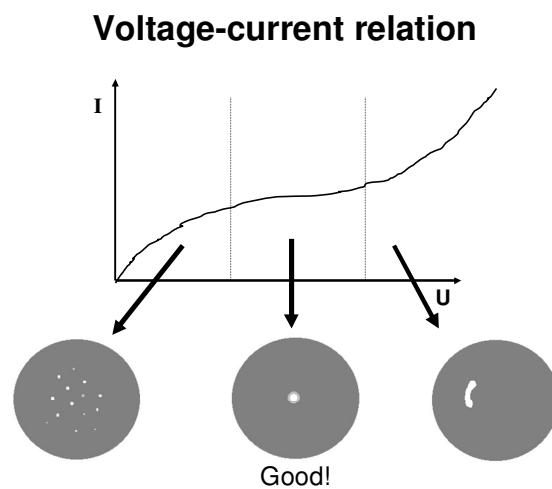


Figure 2.9: Voltage-current relation in electropolishing

The samples were annealed for homogenization at 1050°C for 5 hours and water quenched. Electropolishing was applied with the conditions of 25% nitric acid in methanol at -30°C with $V=20V$ for the Fe-Ni alloy. For the samples that had some Al content, the same electrolyte and temperature conditions were applied but now at 5V.

2.4.2 Calibrating the camera length of the TEM

The magnification of the diffraction pattern is described by the camera length (L). If the magnification of the lenses between the specimen and the viewing screen is increased, the effective distance (L) between the specimen and the screen is increased [25].

As in the Figure 2.10, when electrons are scattered through an angle of 2θ from the specimen, the relation between r and L is given as;

$$r = L \tan 2\theta \quad (2.4)$$

For very small angles we can make the approximation $\tan 2\theta \approx 2\theta$. So we have the equation;

$$r = 2L\theta \quad (2.5)$$

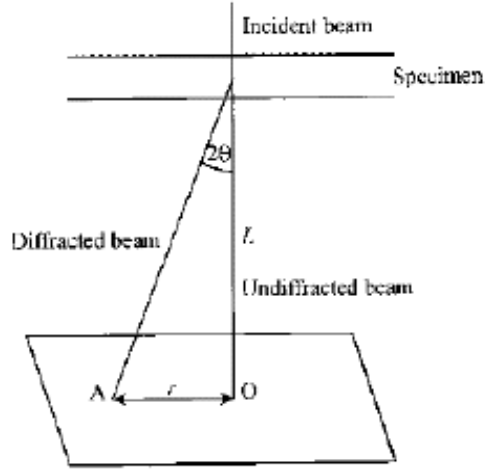


Figure 2.10: Scattering of electrons [25]

The diffraction Bragg conditions imply that;

$$2d \sin \theta = \lambda \quad (2.6)$$

Again, if we make the approximation $\sin \theta \approx \theta$ for small angles, we have;

$$2d\theta = \lambda \quad (2.7)$$

Combining (4.2) and (4.4) we have;

$$r = \frac{L\lambda}{d} \quad (2.8)$$

where L is the camera length and $L\lambda = C$ is the camera constant. Taking L in mm and λ in $\text{\AA}$, the camera constant C is given in $[\text{\AA} \text{ mm}]$ dimension.

The camera length can be calibrated by finding a diffraction pattern in a zone axis from a well-known sample where the d-spacings are listed, measuring r and finding $L\lambda$ from the equation (2.8). For our case Si was used.

Si has the diamond structure and the specimen is oriented along the $[001]$ zone axis. In addition to the main reflections, weaker spots which can arise from double diffraction can sometimes be seen in the diffraction pattern of the diamond structure (Figure 2.11).

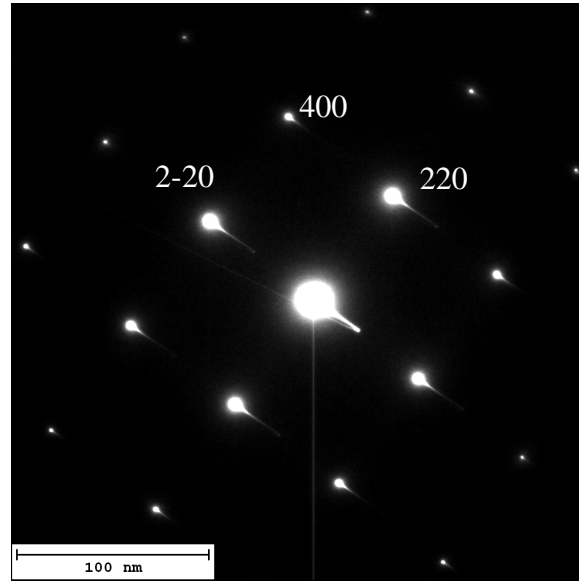


Figure 2.11: Diffraction pattern of Si

What has to be done is measuring the r distances between the origin and nearest spots. If the directions of the spots are shown as in Figure 2.12, it is better to measure distances between the spots that are located at the $-y$ and y positions, $-x$ and x positions and $-z$ and z positions and then dividing the length by 2, in order to have a more precise result.

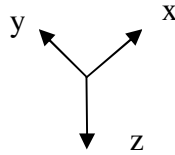


Figure 2.12: Directions of the spots

In the pattern above (Figure 2.10), the distances are measured as;

$$r_{220} = \frac{78 \pm 1}{2} = 39 \pm 0.5 \text{ mm} = r_B \quad (2.9)$$

$$r_{022} = \frac{78 \pm 1}{2} = 39 \pm 0.5 \text{ mm} = r_B \quad (2.10)$$

$$r_{400} = \frac{111 \pm 1}{2} = 55.5 \pm 0.5 \text{ mm} = r_A \quad (2.11)$$

For the given h , k and l , d -spacings are given from the crystal structure data. For silicon it is given in Table 2.6 as;

Table 2.6: d-spacings of Si for given Miller indices

d-spacing (Å)	h	k	l
1.9198	2	2	0
1.3575	4	0	0

Now, since the r distances and d-spacings are known, the camera constant C can easily be calculated from the equation (2.8). Table 2.7 shows the calculation of C.

Table 2.7: Calculation of camera constant

$C_1 = r_{220} d_{220}$	$r_{220} = 39 \pm 0.5 \text{ mm}$ $d_{220} = 1.9198 \pm 0.0001$	$C_1 = 75.3521 \pm 0.5 \text{ Åmm}$
$C_2 = r_{400} d_{400}$	$r_{400} = 55.5 \pm 0.5 \text{ mm}$ $d_{400} = 1.3575 \pm 0.0001$	$C_2 = 75.3413 \pm 0.5 \text{ Åmm}$
$C = \frac{C_1 + C_2}{2}$		$C = 75.3467 \pm 0.35 \text{ Åmm}$

2.5 XRD

The X-ray diffraction (XRD) was applied to bulk plates with an X ray source of Cu K_α in the range of $2\theta=10-120^\circ$ with a scan speed of $1^\circ/\text{min}$ and step increment of 0.02 at room temperature. All the alloys except $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ were examined by a GBC-MMA model XRD while $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloy was examined by a Bruker axs-D8 advance model XRD. The GBC-MMA model equipment is shown in Figure 2.13.

The main purpose of the analysis was to support the phases that were detected by TEM and find the phases for the samples where no TEM study was done.



Figure 2.13: XRD Equipment

3. RESULTS AND DISCUSSION

3.1 Magnetic Susceptibility

The magnetic susceptibility was measured in the temperature range of 24-700°C in order to determine the magnetic phase transitions and Curie temperatures of the materials. χ diverges at the critical temperature at which the material goes from ferromagnetic phase to paramagnetic phase and T_c values of the materials are found from the χ -T curves. The measured susceptibility-temperature curves for the studied materials are given below.

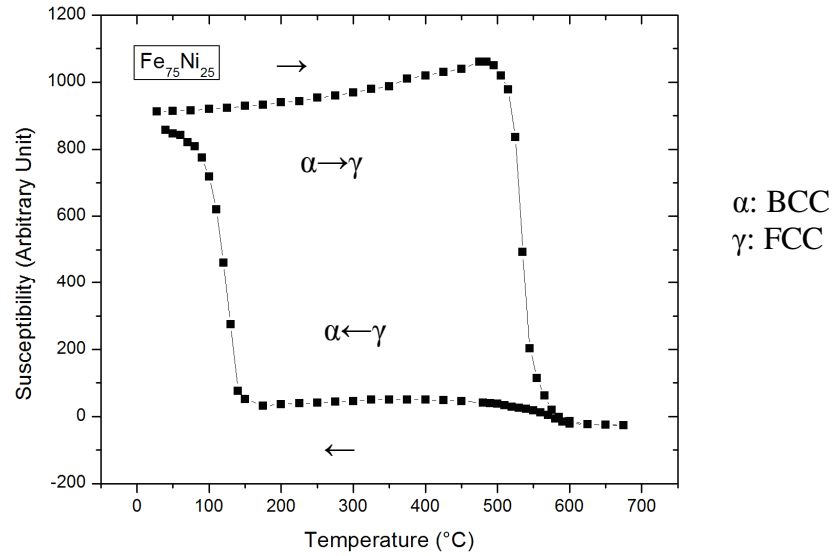


Figure 3.1: $\chi - T$ curve of Fe₇₅Ni₂₅

The $\chi - T$ curve of Fe₇₅Ni₂₅ makes a large hysteresis. On heating, magnetic phase transition happens between 450-650°C from ferromagnetic to paramagnetic phase. One reason to this can be a structural transformation in the material, such as from ferromagnetic BCC-Fe-Ni phase to paramagnetic FCC Fe-Ni phase. As seen from the graphic the reverse transition is not completed until the specimen is cooled below 150°C where the magnetic properties are recovered [11]. Martinez-Blanco *et al* show in their work that on heating the magnetization of Fe₈₀Ni₂₀ alloy drops to zero between 427-667°C and the MA transformation happens between 367-647°C [12].

These temperature values are very close to what is found in our measurement. They also report that the reverse transformation does not happen until they cool the sample below 127°C, so they result in a large hysteresis as we do. As a result this structural change can explain what happens.

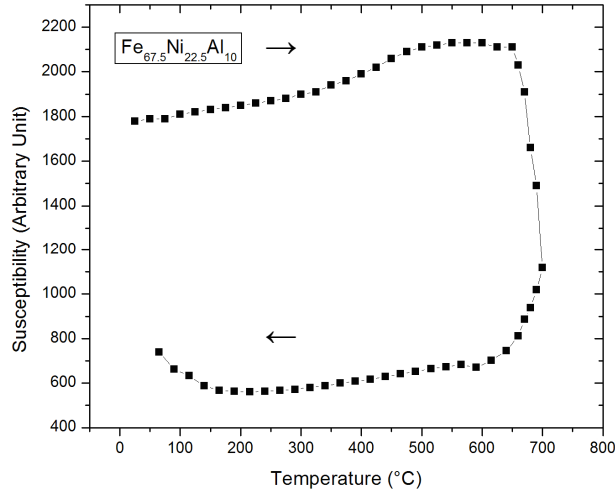


Figure 3.2: $\chi - T$ curve of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$

The magnetic phase transition happens at around 700°C on heating. On cooling the transition could not be completed at room temperature. The hysteresis is again very large and the reason can be the same as $\text{Fe}_{75}\text{Ni}_{25}$ alloy.

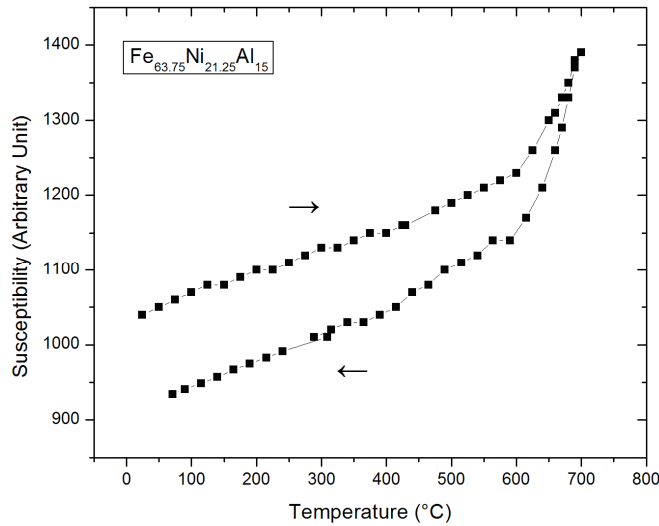


Figure 3.3: $\chi - T$ curve of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$

A sharp peak occurs at around 600°C which implies a magnetic phase transition is starting, but it cannot be completed at 700°C which is our max temperature. So the curve belongs to the same phase on both heating and cooling.

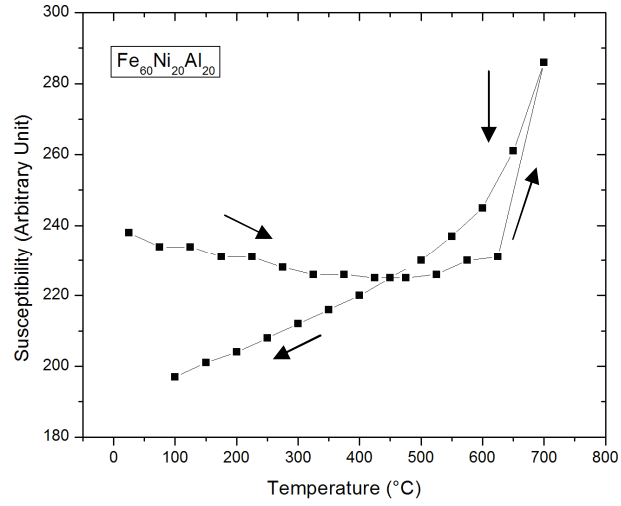


Figure 3.4: $\chi - T$ curve of $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$

The sharp peak starting at around 650°C implies a magnetic phase transition is starting, but it could not be completed due to temperature limitation of the system.

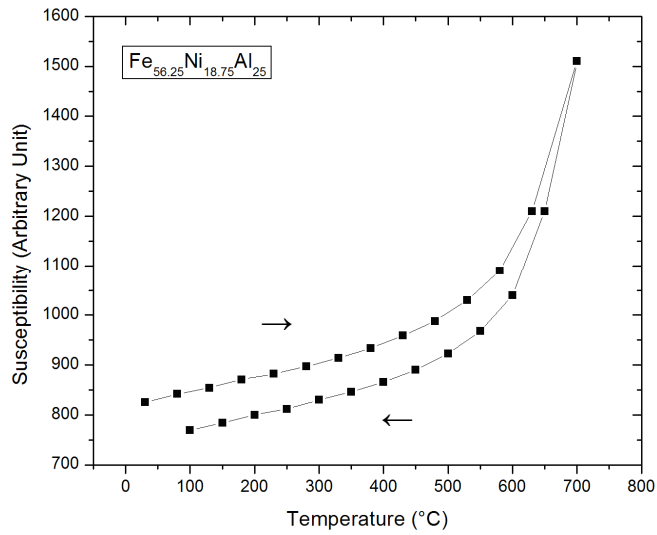


Figure 3.5: $\chi - T$ curve of $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$

Again, the sharp peak at around 600°C implies the start of a magnetic phase transition, but the Curie temperature is above 700°C . The curve obtained here belongs to the same magnetic phase.

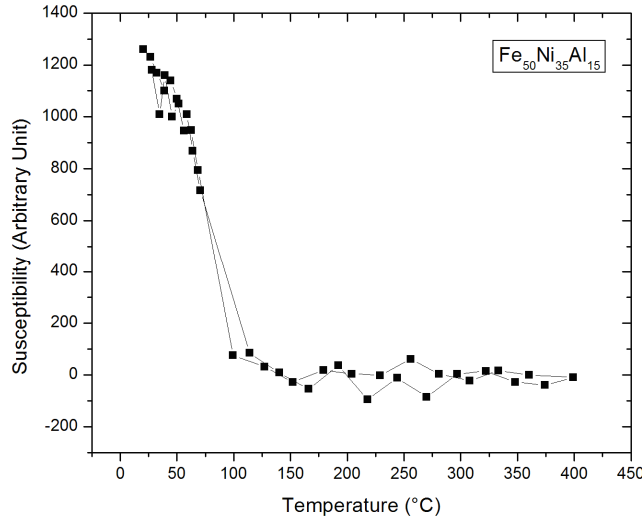


Figure 3.6: $\chi - T$ curve of $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$

Magnetic phase transition occurs at 80°C on both heating and cooling, thus no hysteresis is observed as in $\text{Fe}_{75}\text{Ni}_{25}$ alloy.

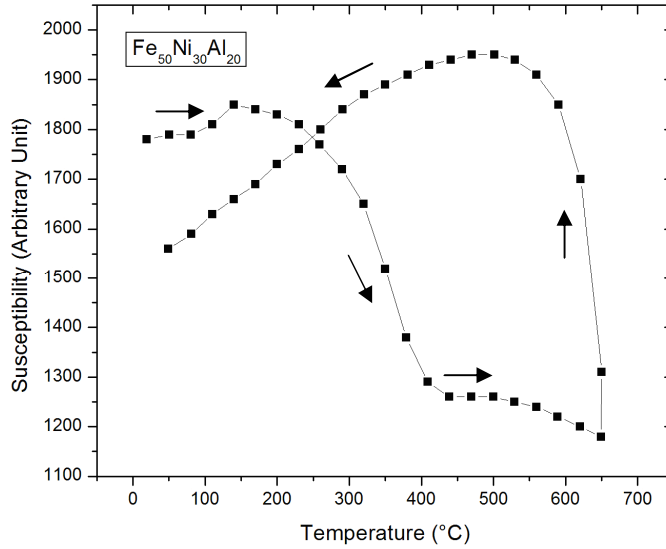


Figure 3.7: $\chi - T$ curve of $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$

The behaviour of the $\chi - T$ curve of $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ is interesting. A magnetic phase transition starts at around 150°C and it is completed at 430°C which is ferro-to-paramagnetic phase transition. On further heating the susceptibility does not decrease to zero which shows that there is a second ferromagnetic phase. On cooling, the curve jumps back to the ferromagnetic phase (the susceptibility value increases), which is an interesting property we have not observed with the other alloys and it needs further investigation to be explained. In general we can say the $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ system has 2 ferromagnetic phases.

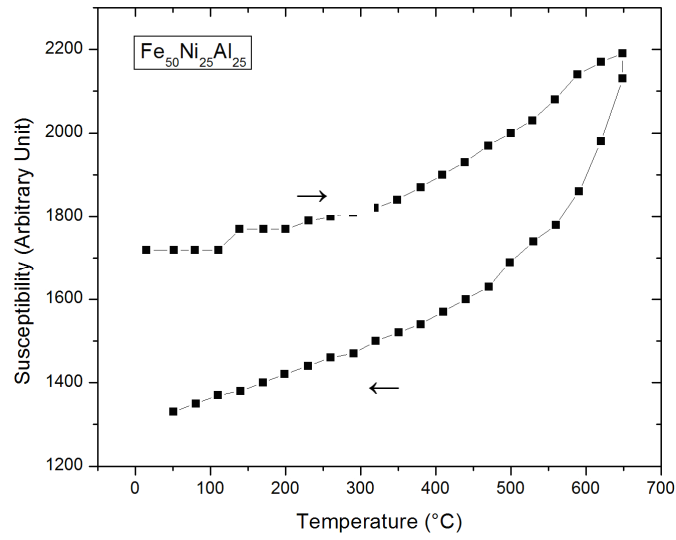


Figure 3.8: $\chi - T$ curve of $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$

The sharp peak starting at around 350°C implies a magnetic phase transition. On cooling the curve does not go back to the starting susceptibility value and it seems to make a hysteresis, so we say a magnetic phase transformation is observed from ferro to paramagnetic state.

The Curie temperatures of the studied materials are summarized in Table 3.1.

Table 3.1: The Curie temperatures of the studied materials

Sample	T _c (°C)
Fe ₇₅ Ni ₂₅	580°C
Fe _{67.5} Ni _{22.5} Al ₁₀	≈700°C
Fe _{63.75} Ni _{21.25} Al ₁₅	Above 700°C
Fe ₆₀ Ni ₂₀ Al ₂₀	Above 700°C
Fe _{56.25} Ni _{18.75} Al ₂₅	Above 700°C
Fe ₅₀ Ni ₃₅ Al ₁₅	80°C
Fe ₅₀ Ni ₃₀ Al ₂₀	≈700°C
Fe ₅₀ Ni ₂₅ Al ₂₅	Above 700°C

Fe:Ni ratio for Fe₇₅Ni₂₅, Fe_{67.5}Ni_{22.5}Al₁₀, Fe_{63.75}Ni_{21.25}Al₁₅, Fe₆₀Ni₂₀Al₂₀ and Fe_{56.25}Ni_{18.75}Al₂₅ was kept constant as 3:1. As Al was added, the Curie temperatures of the samples increased. T_c of Fe₇₅Ni₂₅ is 580°C, but the addition of Al (which means the decrease of Fe and Ni contents) in Fe_{67.5}Ni_{22.5}Al₁₀ alloy resulted in a higher temperature of around 700°C. The Curie temperatures of Fe_{63.75}Ni_{21.25}Al₁₅, Fe₆₀Ni₂₀Al₂₀ and Fe_{56.25}Ni_{18.75}Al₂₅ alloys were above 700°C.

Fe:Ni ratio was not kept constant for Fe₅₀Ni₃₅Al₁₅, Fe₅₀Ni₃₀Al₂₀ and Fe₅₀Ni₂₅Al₂₅ alloys. Fe concentration was kept constant and the Fe:Ni ratio increased as Ni concentration was decreased. The Curie temperature is very low for Fe₅₀Ni₃₅Al₁₅ alloy (80°C). When the Fe content was kept constant, as Ni concentration was decreased and Al concentration was increased (as Fe:Ni ratio and Al increased) the Curie temperatures of the materials increased.

As another discussion, it can be seen that for the same Al contents, let's say for Fe_{63.75}Ni_{21.25}Al₁₅ and Fe₅₀Ni₃₅Al₁₅ alloys, there is a big difference in their Curie temperatures. The higher Curie temperature could be a result of higher concentration of Fe where the T_c of Fe alone is 770°C.

Also, the susceptibility-temperature curve of $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ system shows 2-phase characteristics. The first ferromagnetic phase made magnetic transition at around 400°C . The second transition temperature was above 700°C .

The last and maybe one of the most important conclusion is, $\text{Fe}_{75}\text{Ni}_{25}$ system seemed to go through a structural phase transition related to the magnetic transition and this transformation has been reported as martensitic transformation in many studies [2, 7, 12, 28]. The similar behaviour was seen for the $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ alloy too.

3.2 M-H Measurement

The M-H curves of the materials are measured by a home made model VSM in a magnetic field of maximum 8 kOe with a sensitivity of 10^{-5} emu along the long axes of the materials at room temperature. Some samples did not reach saturation magnetization, so M values at The results are given below for each sample.

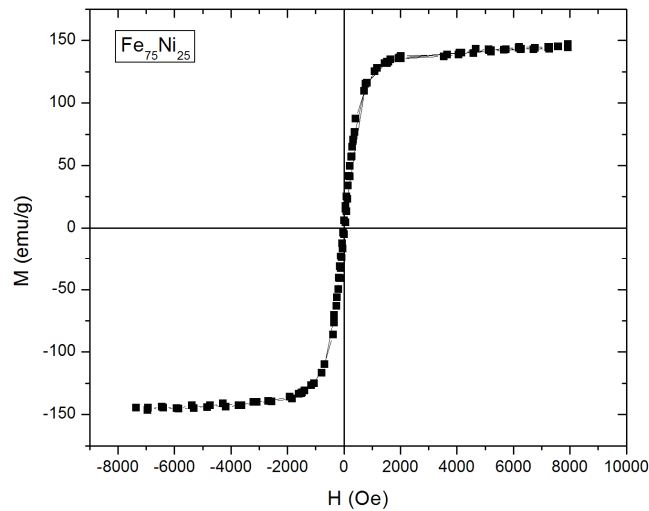


Figure 3.9: M-H curve of $\text{Fe}_{75}\text{Ni}_{25}$

The measured and calculated values for $\text{Fe}_{75}\text{Ni}_{25}$ alloy are given below;

$M_s = 146.94 \text{ emu/g}$, $H_c = 11.97 \text{ Oe}$, $M_r = 2.92 \text{ emu/g}$.

No considerable hysteresis observed. The material reaches the saturation magnetization sharply which suggests that it is ferromagnetic.

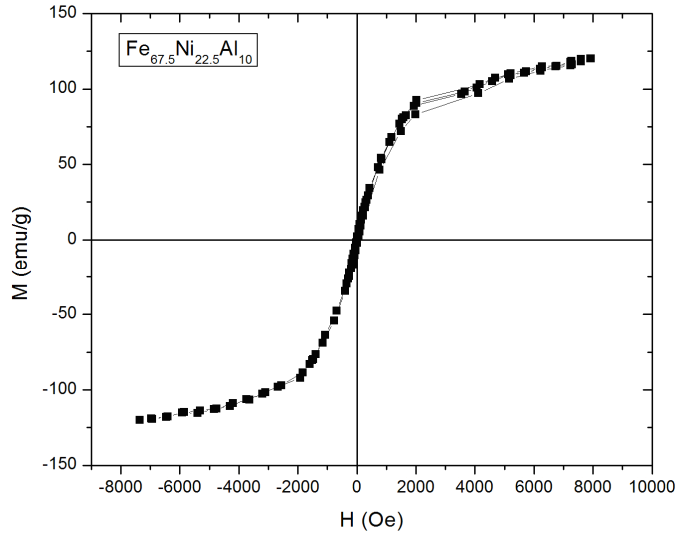


Figure 3.10: M-H curve of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$

$M_s = 120.03 \text{ emu/g}$, $H_c = 11.15 \text{ Oe}$, $M_r = 1.11 \text{ emu/g}$

No hysteresis observed.

The linear behaviour of the curve may be due to both demagnetization and random orientations of the grains or due to some paramagnetic contribution at high field.

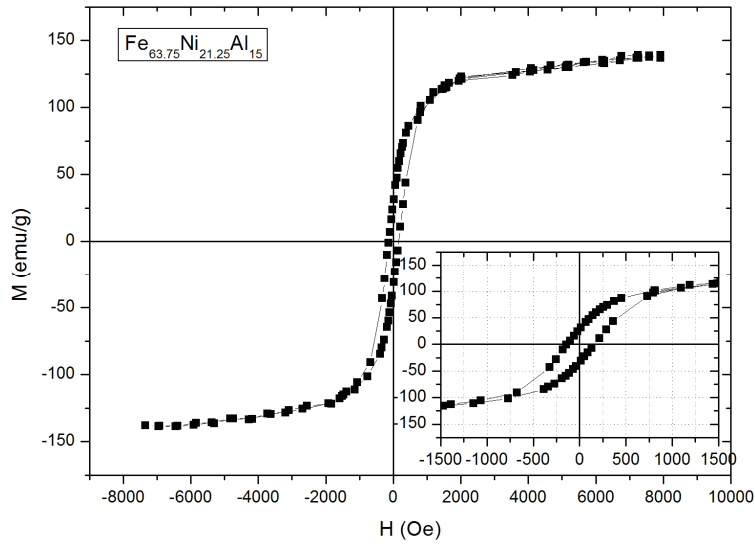


Figure 3.11: M-H curve of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$

$M_s = 139.04 \text{ emu/g}$, $H_c = 138.09 \text{ Oe}$, $M_r = 28.86 \text{ emu/g}$

Very small hysteresis observed and saturation is reached implying the ferromagnetic character of the material.

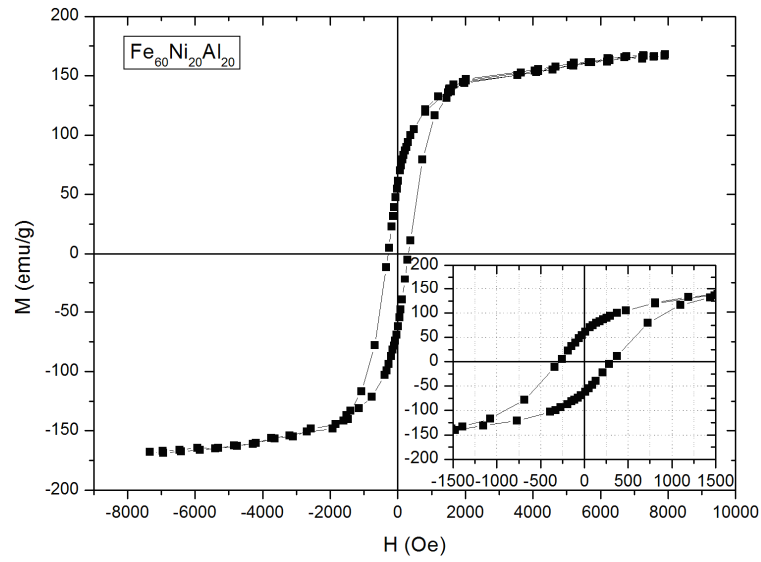


Figure 3.12: M-H curve of Fe₆₀Ni₂₀Al₂₀

$M_s = 167.26$ emu/g, $H_c = 280.97$ Oe, $M_r = 59.21$ emu/g

Some small hysteresis observed.

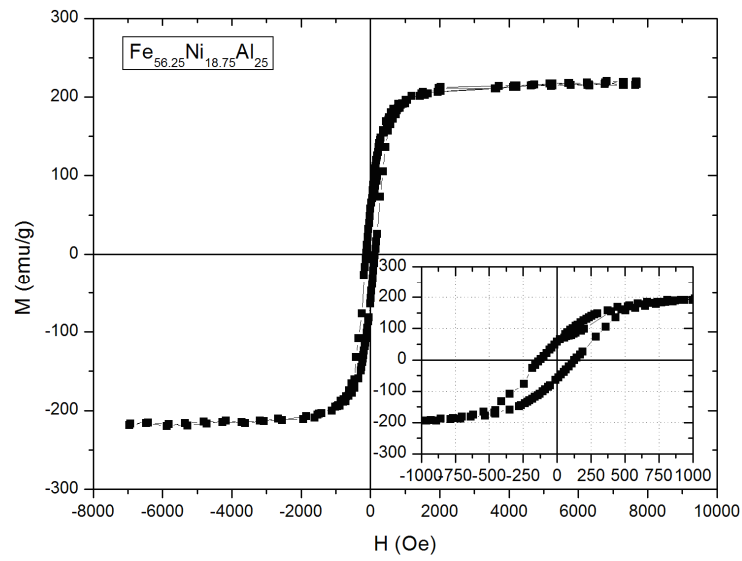


Figure 3.13: M-H curve of Fe_{56.25}Ni_{18.75}Al₂₅

$M_s = 219.92$ emu/g, $H_c = 124.82$ Oe, $M_r = 57.74$ emu/g

Very small hysteresis is observed.

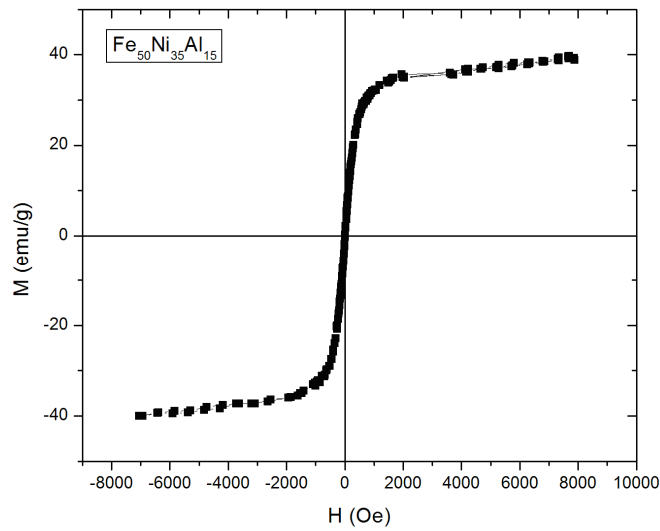


Figure 3.14: M-H curve of $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$

$M_s = 39.76$ emu/g, $H_c = 3.98$ Oe, $M_r = 0.43$ emu/g

Very small hysteresis is observed.

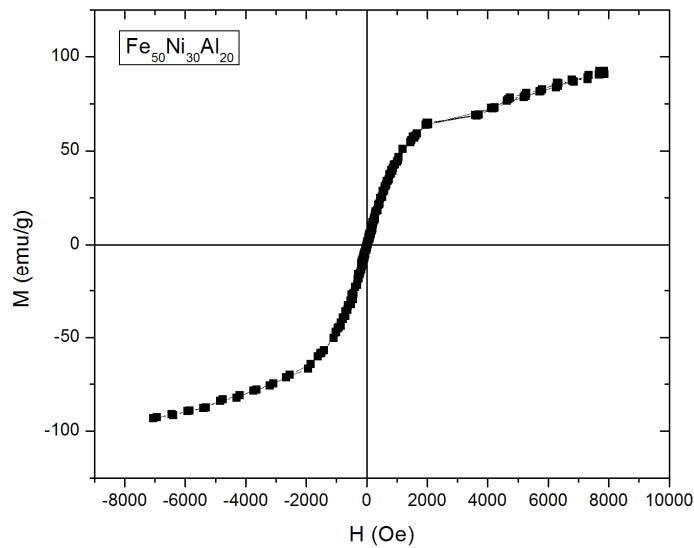


Figure 3.15: M-H curve of $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$

$M_s = 92.47$ emu/g, $H_c = 3.69$ Oe, $M_r = 0.17$ emu/g

No considerable hysteresis is observed.

The linear dependence of M on H at high field implies some paramagnetic contribution.

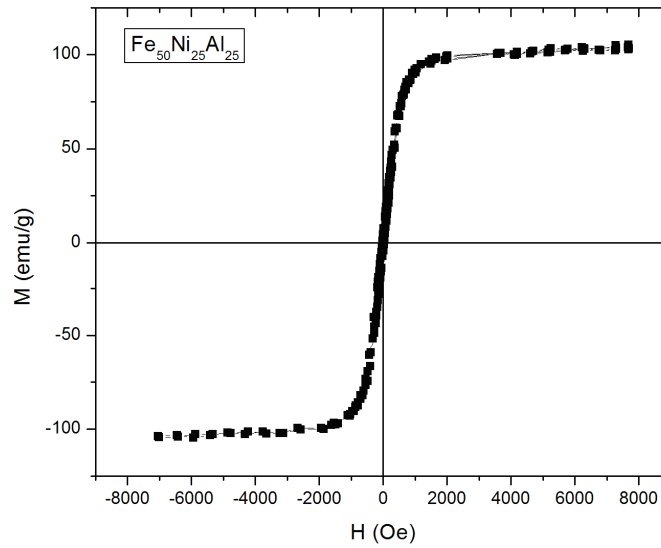


Figure 3.16: M-H curve of $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$

$M_s = 105.32 \text{ emu/g}$, $H_c = 28.31 \text{ Oe}$, $M_r = 4.49 \text{ emu/g}$

No considerable hysteresis is observed.

The results are given in Table 3.2 as follows;

Table 3.2: The M_s , H_c and M_r values of the studied materials

Sample	M_s (emu/g)	H_c (Oe)	M_r (emu/g)
$\text{Fe}_{75}\text{Ni}_{25}$	146.94	11.97	2.92
$\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$	120.03*	11.15	1.11
$\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$	139.04	138.09	28.86
$\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$	167.26	280.97	59.21
$\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$	219.92	124.82	57.74
$\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$	39.76	3.98	0.43
$\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$	92.47*	3.69	0.17
$\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$	105.315	28.304	4.494

The samples marked with * showed linearity at high field and they did not reach saturation. The max magnetizations they reached at the applied field were given in table. The ternary $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18}$ alloys have higher M_s values than the binary $\text{Fe}_{75}\text{Ni}_{25}$ alloy. Fe:Ni ratio in these alloys are constant. As more Al is added (as Fe and Ni concentrations were decreased and more Al was added) the M_s values of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys increased linearly. We have the highest M_s value for $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloy.

For the last 3 alloys with constant Fe, M_s is the lowest for the sample with maximum Ni and minimum Al (with minimum Fe:Ni ratio and Al). As the Ni content was decreased and Al was increases, the M_s values increased linearly.

The very low values of H_c implies that no permanent magnetism was detected. H_c values for $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys are relatively higher, but when these values are compared to the H_c values of permanent magnets, it is seen that they are still very small.

In accordance to H_c , M_r values also showed the same characteristic. For $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys, the M_r values were relatively bigger than other alloys.

One interesting result of the M-H curves is that the $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ and $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ systems show linearity which may be due to some contribution from a paramagnetic phase or demagnetization of grains.

3.3 TEM

TEM examination was carried out by a CM20 model TEM with LaB6 electron gun with 200 keV at room temperature.

3.3.1 Indexing diffraction patterns and finding the lattice parameter

First of all, in order to be able to index the pattern correctly, it is important to obtain a diffraction pattern in zone axis. A zone axis can be recognized as a pattern of symmetrically placed spots with a brightest undiffracted beam in the middle.

The next step will be measuring the distance between the main reflection and 3 different spots. These spots should be in 3 different directions from the central one. Then the ratios between these 3 distances and the angles between these 3 spots are

measured. The measured values can then be compared to a list of standard or calculated patterns. When there is a match, we can start indexing the spots and they will be represented with the h, k and l Miller indices.

The d-spacing is calculated from the equation (2.8) since the camera constant is known now. After determining the d-spacing, a is calculated from the formula for cubic systems;

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (3.1)$$

where “a” stands for the lattice constant (lattice parameter). A lattice in three dimensions has three different lattice constants. But in the special case of cubic systems all three lattice constants are equal to each other.

These steps should be applied to all 3 spots in different axes and an average should be taken to find the lattice parameter of the pattern.

As an example the following pattern from the Fe₇₅Ni₂₅ sample is used (only focus on the brightest spots):

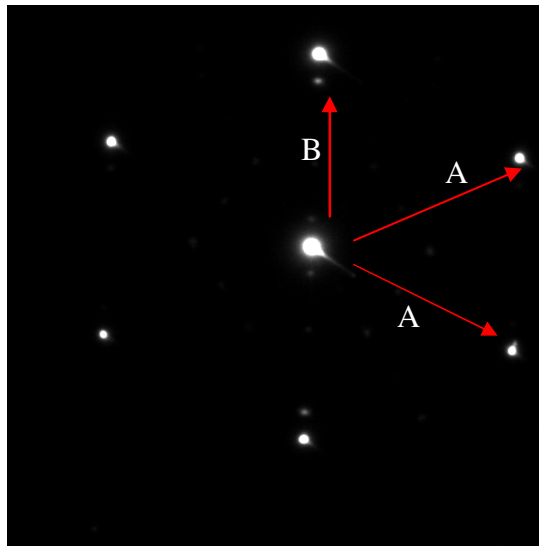


Figure 3.17: Diffraction pattern of Fe₇₅Ni₂₅

The distances are given in Table 3.3.

Table 3.3: The distances to the central spot and the ratio between them

A (mm)	72 ± 0.5 mm
B (mm)	62 ± 0.5 mm
A/B	1.17 ± 0.35

And the measured angles are 65° and $51^\circ \pm 1^\circ$. Comparing the angles and the ratio to the standard patterns, it is seen that this sample is in FCC $\left[\bar{1}44 \right]$ zone axis where in the standard pattern the ratio is 1.173 and the angles are 64.76° and 50.48° .

So now the spots can be indexed as in this standard pattern. We get;

1)

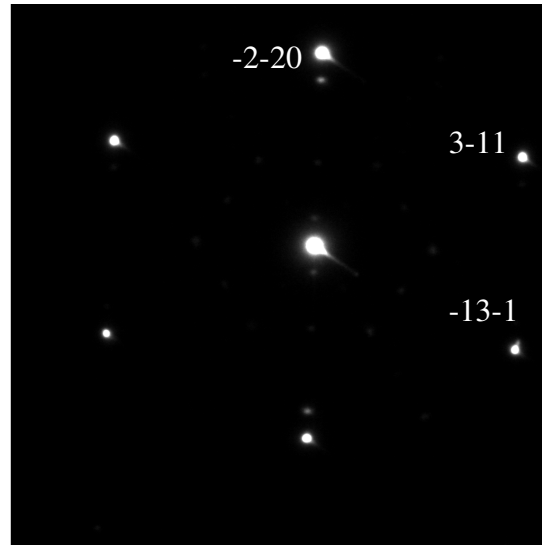


Figure 3.18: Diffraction pattern of $\text{Fe}_{75}\text{Ni}_{25}$ in FCC $\left[\bar{1}44 \right]$ zone axis

After indexing, we can now start calculating the lattice parameter of the pattern. Since we know r and C , the d -spacing can be calculated easily for each spot from the equation (2.8):

$$rd = C$$

$$d_{hkl} = \frac{C}{r} \quad (3.2)$$

And the lattice parameter for cubic systems is given as;

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \quad \text{from the Eq 3.1.}$$

Now these steps can be applied to the Fe-Ni sample having the FCC structure.

For the length A (r=72 ± 0.5 mm and h=3, k=1, l=1);

$$d_{311} = \frac{75.3467 \pm 0.35}{72 \pm 0.5} = 1.0465 \pm 0.0076 \text{ mm and}$$

$$a_1 = \sqrt{3^2 + 1^2 + 1^2} d_{311} = (3.3166 \pm 0.0001)(1.0465 \pm 0.0076)$$

$$a_1 = 3.4705 \pm 0.0077 \text{ Å.}$$

For the length B (r=62 ± 0.5 mm and h=2, k=2, l=0);

$$d_{220} = \frac{75.3467 \pm 0.35}{62 \pm 0.5} = 1.2153 \pm 0.0098 \text{ mm and}$$

$$a_2 = \sqrt{2^2 + 2^2 + 0} d_{220} = (2.8284 \pm 0.0001)(1.2153 \pm 0.0098)$$

$$a_2 = 3.4374 \pm 0.0099 \text{ Å.}$$

The two lattice parameter values are very close to each other as they should be. Now all we have to do is to take the average of them.

$$a = \frac{a_1 + a_2}{2}$$

$$a = 3.4541 \pm 0.0124 \text{ Å.}$$

The same procedure was applied to all other diffraction patterns, so after this, the calculations will be skipped and images will be given with their zone axes and calculated lattice parameters.

2)

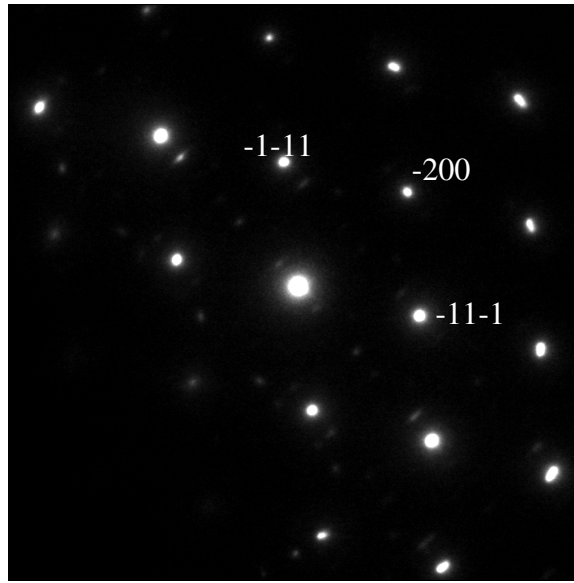


Figure 3.19: Diffraction pattern of $\text{Fe}_{75}\text{Ni}_{25}$ in FCC $[011]$ zone axis

The pattern shows FCC $[011]$ with a lattice parameter of $a = 3.4722 \pm 0.0062 \text{ \AA}$. We can see some additional weak spots around the main spots which are possibly reflected from neighbouring grains. In this pattern we focused on the main reflections.

$\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ sample:

1)

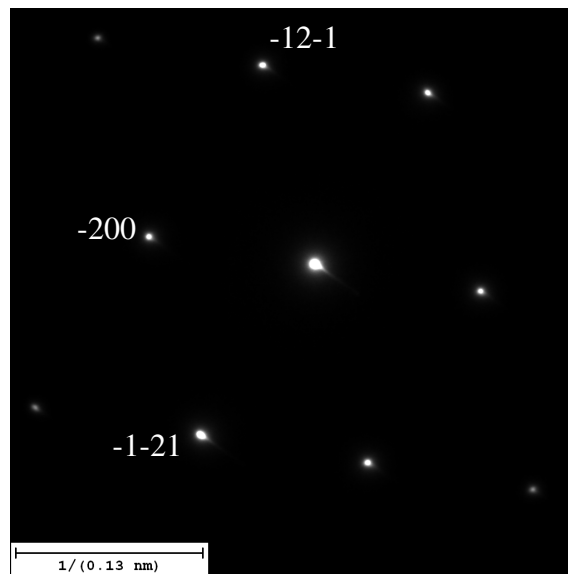


Figure 3.20: Diffraction pattern of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ in BCC $[012]$ zone axis

The pattern shows BCC[012] structure with a lattice parameter of $a = 2.9539 \pm 0.0090 \text{ \AA}$.

2)

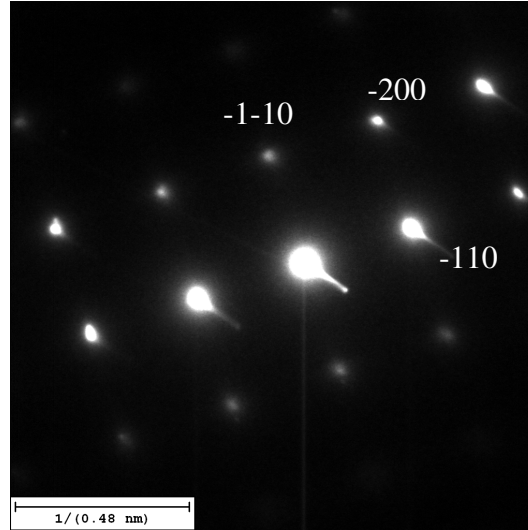


Figure 3.21: Diffraction pattern of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ in BCC [001] zone axis

The pattern shows BCC[001] with $a = 2.8849 \pm 0.0159 \text{ \AA}$.

3)

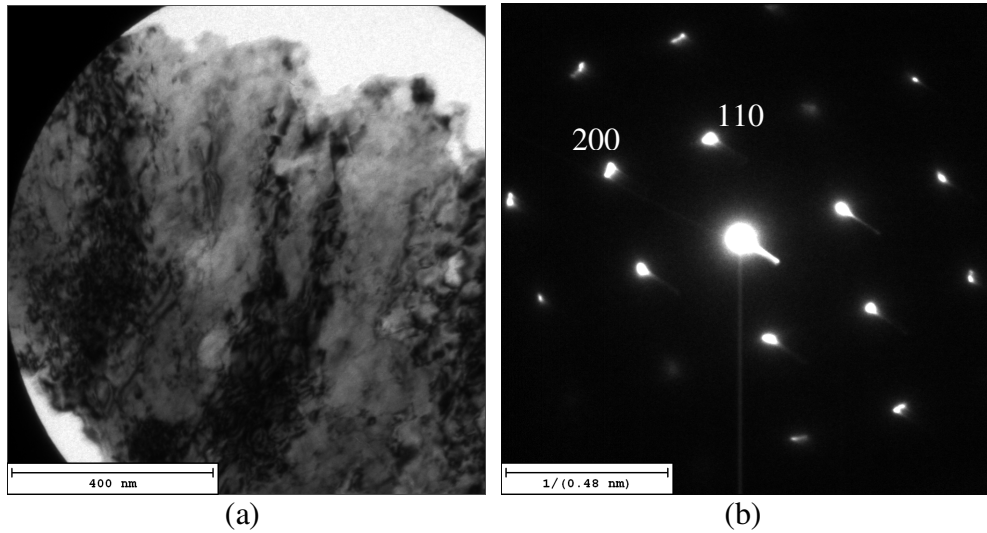


Figure 3.22: Bright field image (a) and diffraction pattern (b) of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ in BCC [012] zone axis

The diffraction pattern above is in BCC[001] structure with $a = 2.8833 \pm 0.0159 \text{ \AA}$.

4)

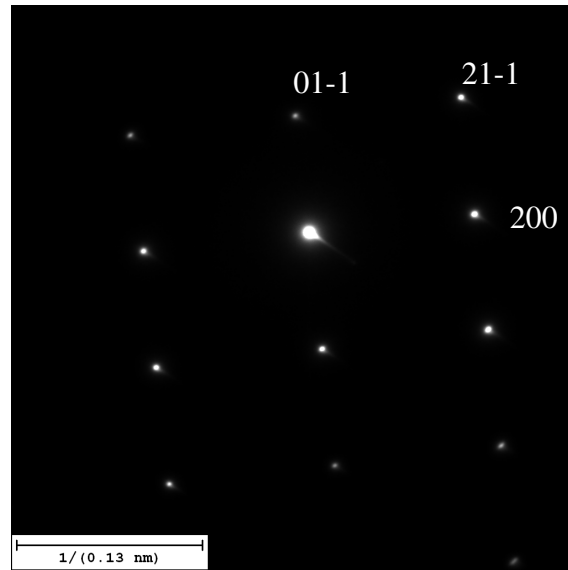


Figure 3.23: Diffraction pattern of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ in BCC $[011]$ zone axis

Above pattern has BCC $[011]$ structure with $a = 2.9639 \pm 0.0157 \text{ \AA}$.

5)

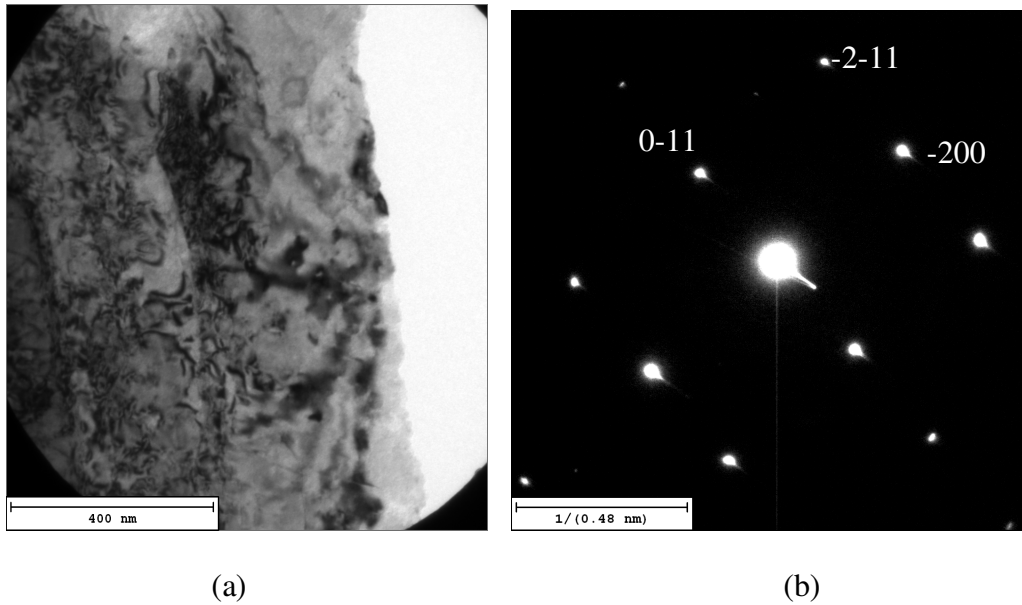


Figure 3.24: Bright field image (a) and diffraction pattern (b) of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ in BCC $[011]$ zone axis

The pattern with BCC $[011]$ structure has a lattice parameter of $a = 2.7089 \pm 0.0133 \text{ \AA}$.

$\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ sample:

1)

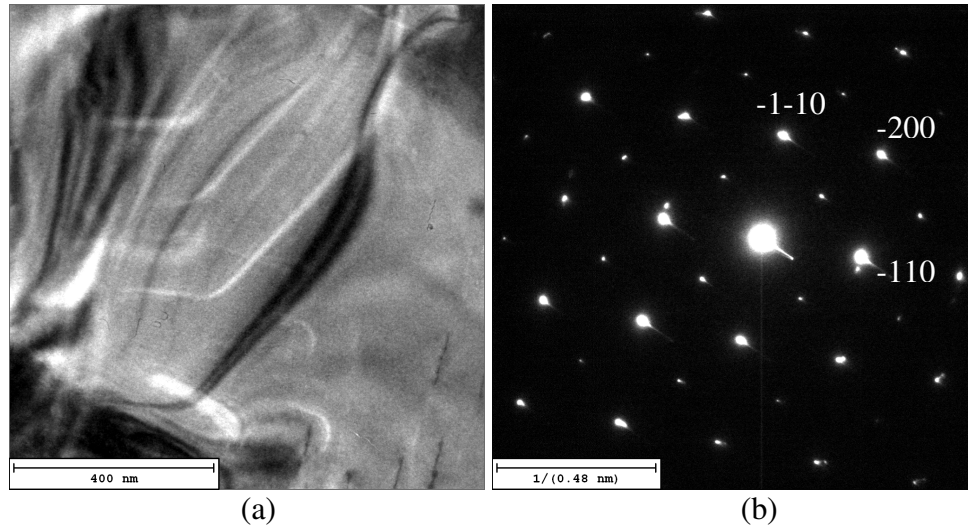


Figure 3.25: Bright field image (a) and diffraction pattern (b) of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ in B2 $[001]$ zone axis

Bright field image and diffraction pattern are given for the $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ alloy. In addition to the main spots (which are bigger and brighter) we can see smaller spots positioned symmetrically between them. This structure tells that the system is ordered. After determining the lattice parameter and comparing it and the structure with literature data, it is seen that the ordered structure is B2 (ordered bcc) type in $[001]$ zone axis with a lattice parameter of $a = 2.8792 \pm 0.0160 \text{ \AA}$.

2)

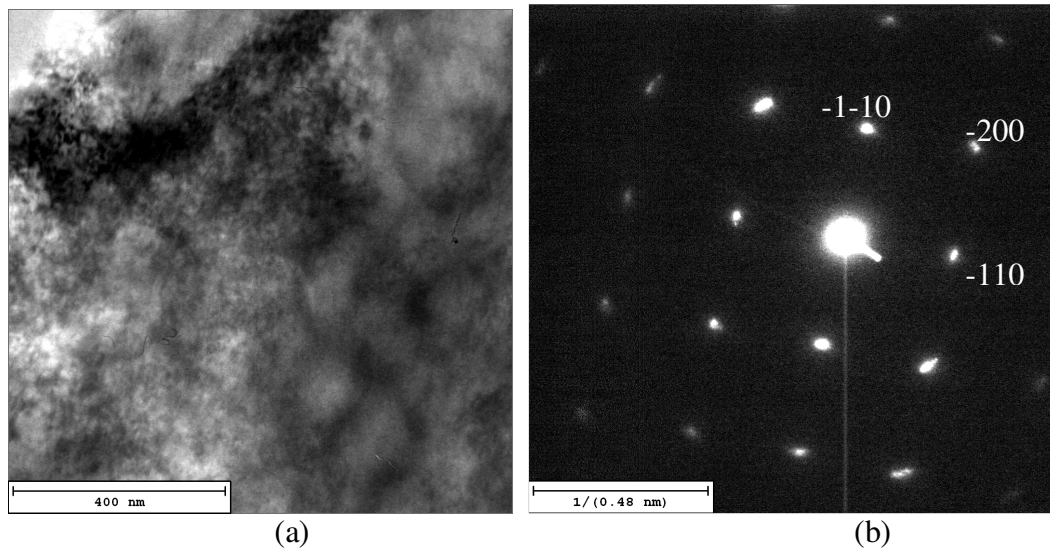


Figure 3.26: Bright field image (a) and diffraction pattern (b) of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ in BCC [001] zone axis

Above pattern with BCC [001] structure and $a = 2.8890 \pm 0.0100 \text{ \AA}$ lattice parameter is in the same zone axis as in the ordered one. The bright field image is blurry but it is given to show the difficulty of obtaining a sharp clear image due to the effect of magnetism.

3)

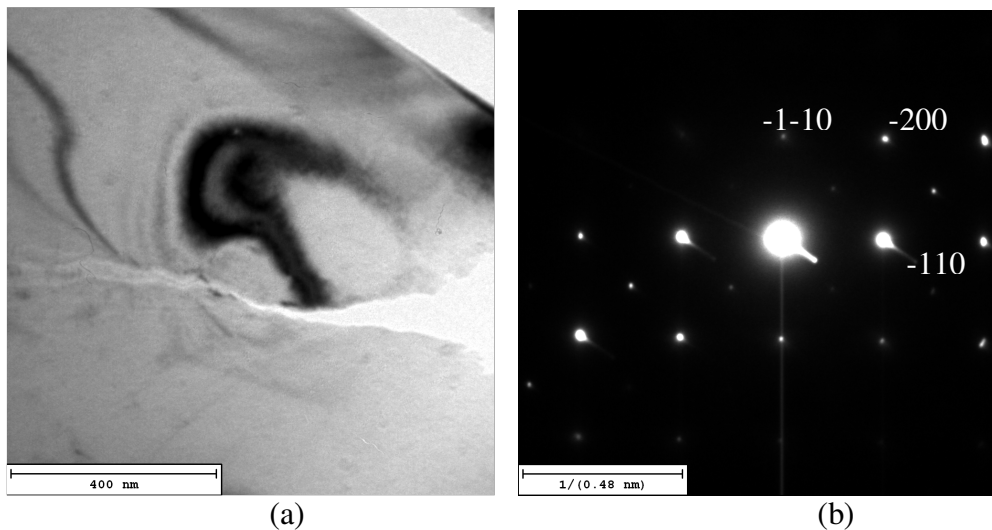


Figure 3.27: Bright Field Image (a) and diffraction pattern (b) of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ in B2[001] zone axis

This pattern was taken from the dark area in the center of the bright field image. It is again an ordered structure (B2 type) in [001] zone axis with $a = 2.9720 \text{ \AA}$.

4)

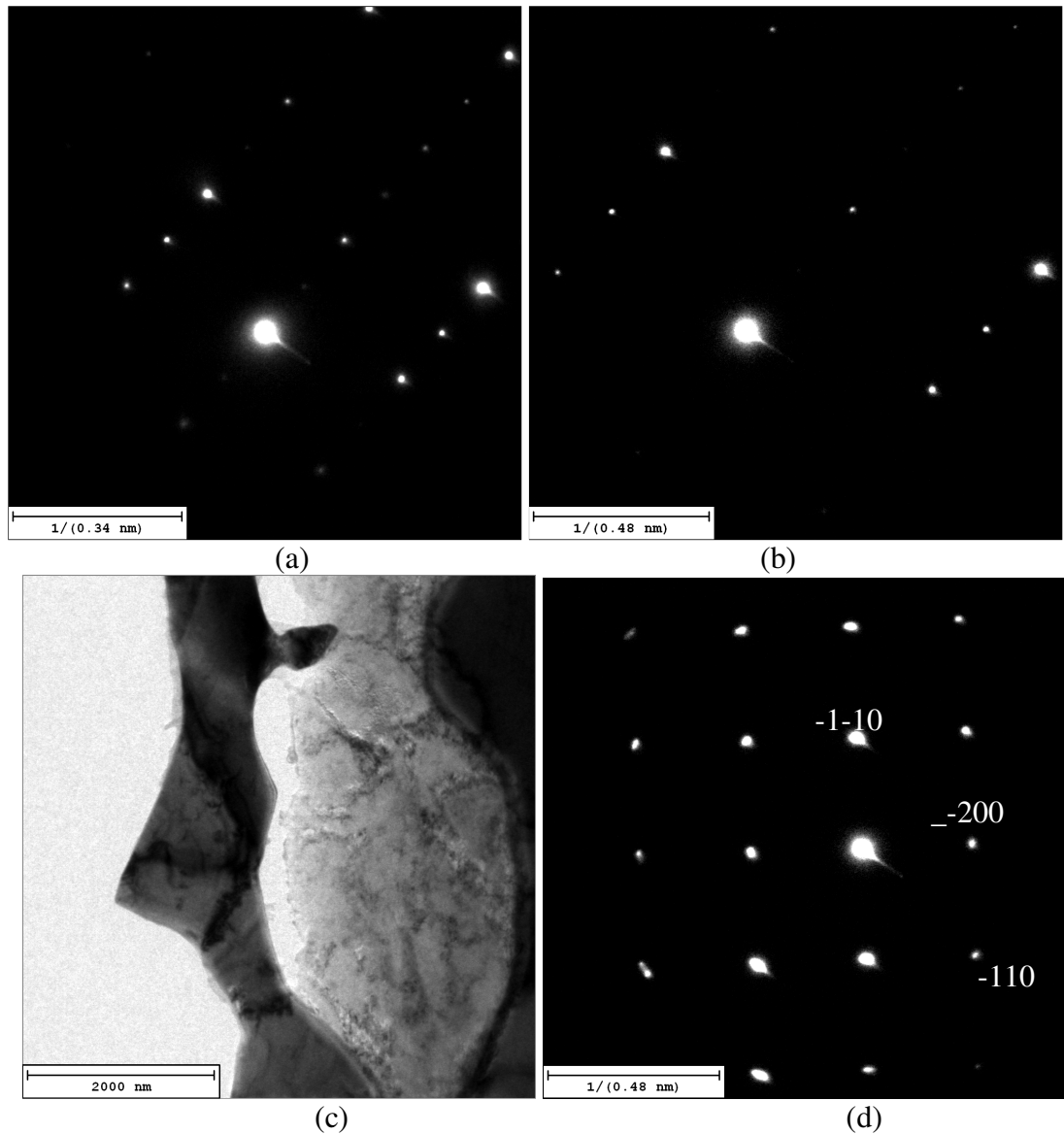


Figure 3.28: Bright field image (c) and diffraction patterns of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ from thick regions (a) (b) and from thin region (d) the latter BCC $[001]$ zone axis

The bright field image shows there are two regions, one thick and one thin. The first two diffraction patterns belong to the thick region and the pattern in (d) belongs to the thin region. The thin region is in BCC $[001]$ structure with $a = 2.9086 \pm 0.0203 \text{ \AA}$.

Due to the effect of magnetism, TEM study was difficult with the bulk materials, especially with the ones that had 15 and 25% Al. In order to eliminate the effect of magnetism, we decided to work on FIB (focused ion beam) samples for these alloys.

5) FIB

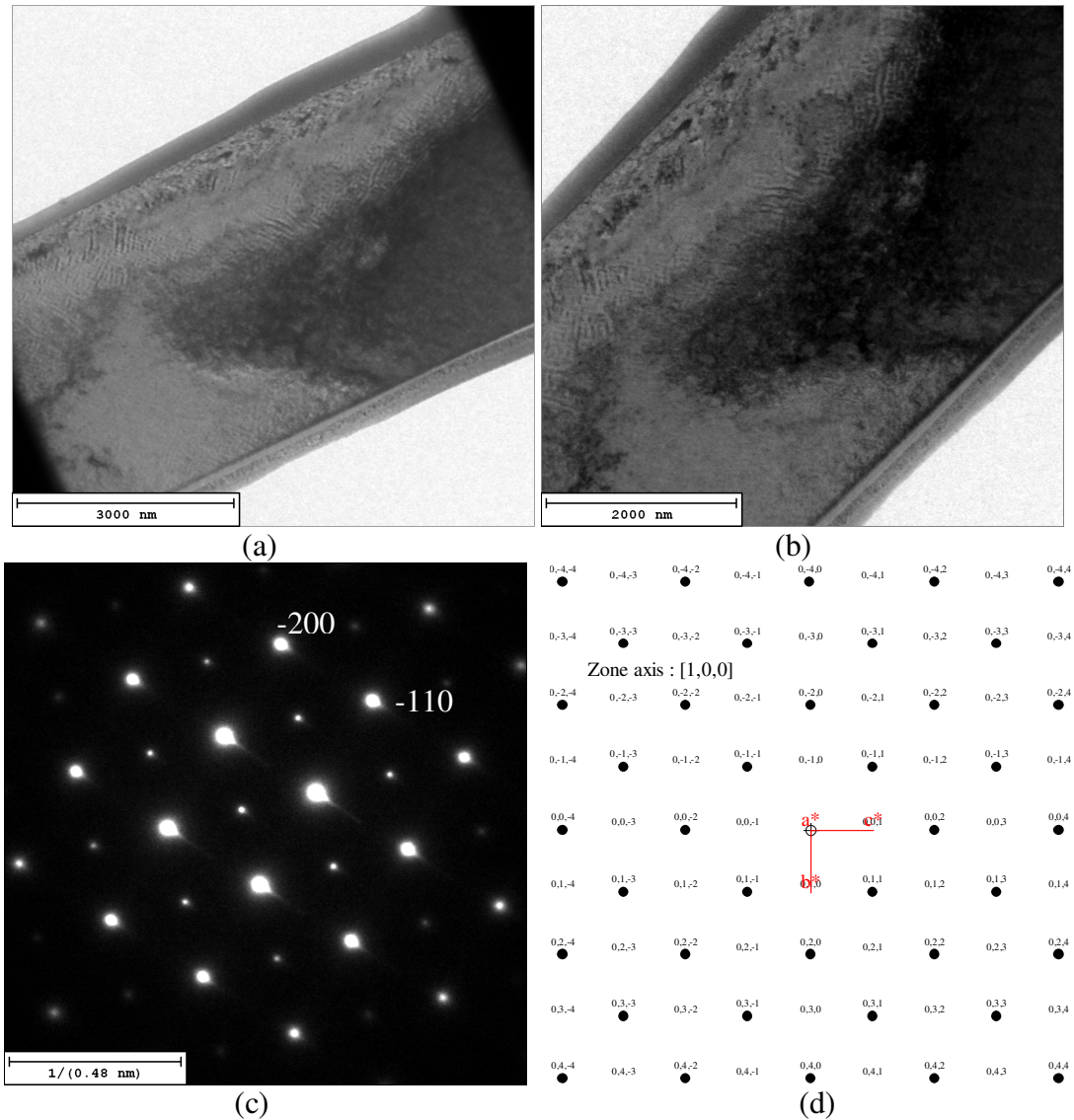


Figure 3.29: Bright field images (a) (b), diffraction pattern (c) and simulated pattern by Carine (d) of FIB $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ in B2 [001] zone axis

The FIB sample gave the same diffraction pattern everywhere in the sample, and it is an ordered structure (B2 type). In order to confirm the result, the diffraction pattern was constructed by Carine software and it is seen that we have a match. Here we have a B2 [001] structure with a lattice parameter of $a = 2.9720 \pm 0.0216 \text{ \AA}$.

From the diffraction patterns of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, we can see both the BCC and B2 structures are in [001] zone axis.

$\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ sample:

1)

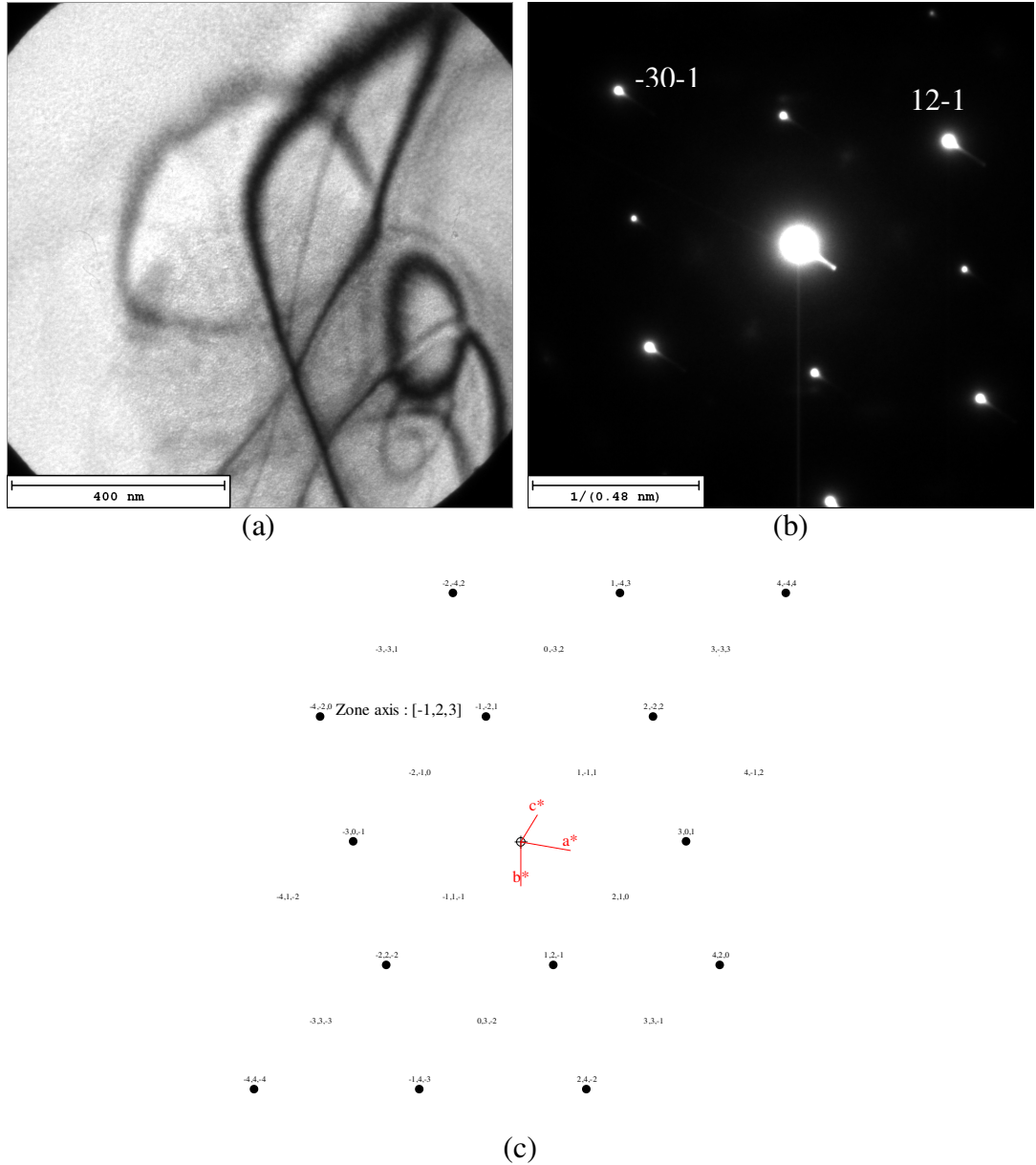


Figure 3.30: Bright field image (a), diffraction pattern (b) and simulated pattern by Carine (c) of $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ in B2 $[\bar{1}23]$ zone axis

The structure of the above pattern was found to be B2 in $[\bar{1}23]$ zone axis with a lattice parameter $a = 2.9592 \pm 0.0060 \text{ \AA}$.

2)

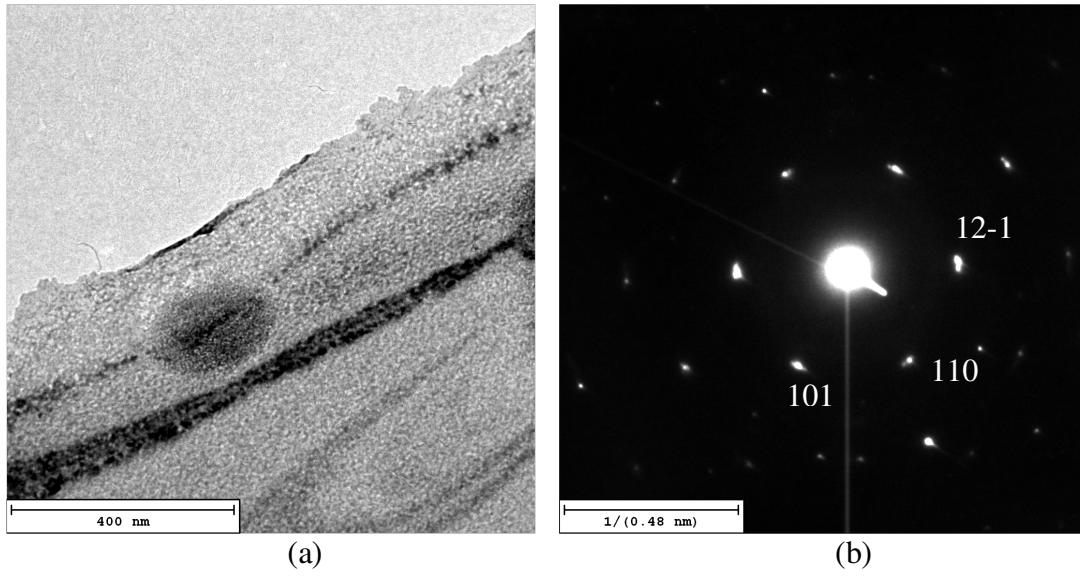


Figure 3.31: Bright field image (a) and diffraction pattern (b) and of

$\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ in BCC $\left[\bar{1}11\right]$ zone axis

The diffraction pattern is in BCC $\left[\bar{1}11\right]$ structure with $a = 2.9193 \pm 0.0288 \text{ \AA}$.

3) FIB Sample

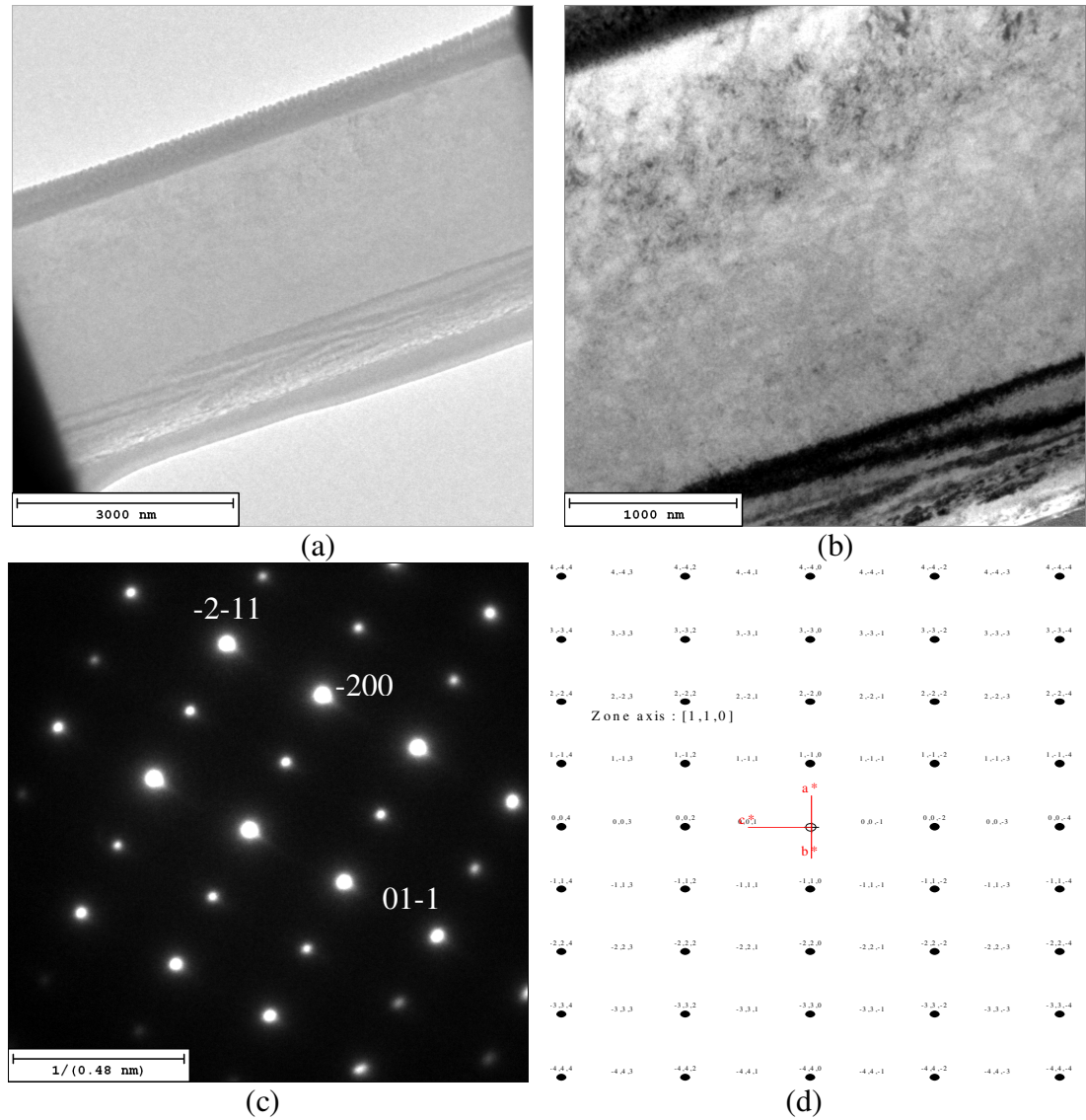


Figure 3.32: Bright field image (a) (b), diffraction pattern (c) and simulated pattern by Carine (d) of $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ in B2 $[011]$ zone axis

A FIB sample was also produced for $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ because of the magnetism effect. The structure is again ordered (B2 type) in $[011]$ zone axis. The lattice parameter is $a = 2.9564 \pm 0.0157 \text{ \AA}$. The pattern was constructed by Carine in order to confirm and the TEM pattern matches the constructed Carine pattern.

Then we average all lattice parameters found from the same sample and the results are given in Table 3.4

Table 3.4: Average lattice parameters of the studied samples

Sample	Lattice parameter (a) Å
Fe ₇₅ Ni ₂₅	3.4631±0.0069 (FCC)
Fe _{67.5} Ni _{22.5} Al ₁₀	2.8786±0.0140 (BCC)
Fe _{63.75} Ni _{21.25} Al ₁₅	2.8988±0.0113 (BCC)
	2.9256±0.0134 (B2)
Fe _{56.25} Ni _{18.75} Al ₂₅	2.9193±0.0288 (BCC)
	2.9578±0.0084 (B2)

3.3.2 EDX

An EDX study was also done for the ternary alloys in order to obtain the atomic percentages of the contents in the sample. Only Fe_{67.5}Ni_{22.5}Al₁₀, Fe_{63.75}Ni_{21.25}Al₁₅ and Fe_{56.25}Ni_{18.75}Al₂₅ samples were examined by EDX. The results are given in Table 3.5.

Table 3.5: EDX data of the studied samples

	Fe _{67.5} Ni _{22.5} Al ₁₀		Fe _{63.75} Ni _{21.25} Al ₁₅		Fe _{56.25} Ni _{18.75} Al ₂₅	
	Bulk		Bulk		FIB	FIB
	BCC [011]	BCC [-113]	Thin	Thick		
Fe (at. %)	70.613	71.847	77.755	49.490	68.527	64.628
Ni (at. %)	20.997	20.953	16.165	34.460	19.230	19.532
Al (at. %)	8.3850	7.1967	6.0850	16.050	12.242	15.842

When the table is compared to the Table 1.2 that shows the nominal atomic percentages in the original samples, it can be seen the results are close to the original ones. Taking the Al percentage as a reference, it increases parallel as in the original

samples. There is around 8% Al where there has to be 10, 12% Al where there has to be 15 and 15% where there has to be 25.

In general, we saw FCC structure in the Fe₇₅Ni₂₅ alloy. When aluminum was added we saw BCC structures and even ordering. In Fe_{63.75}Ni_{21.25}Al₁₅ alloy in thinner regions the structure was disordered BCC. But in thicker regions we ended up in ordered structures (B2) where weaker spots were seen in addition to the main reflections. This is also supported by the EDX data. The thickness difference is due to preferential polishing for the different structures in the electropolishing. The structures and lattice parameters match the data given in literature and it is shown in the Figure 3.33 below. In addition, from the diffraction patterns of Fe_{63.75}Ni_{21.25}Al₁₅, we can see both the BCC and B2 structures are in [001] zone axis. It suggests we do not have different structures but we have ordering mechanism in the same structure in other regions. The ordered structures have bigger lattice parameters than the disordered ones within the same material.

Phase ^a	Pearson symbol	Space group	Strukturbericht designation	Prototype	Composition range ^b	Solubility of 3rd element	Lattice parameters
Fe–Al					at% Al	at% Ni	(Å)
α-Fe, δ-Fe	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	0 to ~45	~20	0–25 at% Al: 2.867–2.911 [19]
γ-Fe	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	0–1.3	100	
Fe ₃ Al (D0 ₃)	<i>cF16</i>	<i>Fm</i> $\bar{3}m$	D0 ₃	BiF ₃	~23 to ~34		5.790 [20]
FeAl (B2)	<i>cP2</i>	<i>Pm</i> $\bar{3}m$	B2	CsCl	23.3 to ~55	100	2.907 [21]
ε ^c	<i>hR26</i>	—	—	Al ₈ Cr ₅	~58 to ~65		
FeAl ₂	<i>aP18</i>	P1	—	Al ₂ Fe	66–66.9	~3	<i>a</i> = 4.878, <i>b</i> = 6.461, <i>c</i> = 8.7476 [22] α = 87.927°, β = 74.452°, γ = 83.11°
Fe ₂ Al ₅	<i>oC16</i>	<i>Cmcm</i>	—	—	70–73	~2	
Fe ₄ Al ₁₃	<i>mC102</i>	<i>C2/m</i>	—	—	74.5–76.6	~7	<i>a</i> = 15.492, <i>b</i> = 8.078, <i>c</i> = 12.471, β = 107.66° [23]
(Al)	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	~100		
Ni–Al					at% Al	at% Fe	(Å)
γ-Ni	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	0–21.2	100	3.5486 [24]
γ'-Ni ₃ Al	<i>cP4</i>	<i>Pm</i> $\bar{3}m$	L1 ₂	Cu ₃ Au	24–27	~15	3.5695 [24]
Ni ₃ Al ₃	<i>oC16</i>	<i>Cmmm</i>	Ga ₃ Pt ₅	—	~32–36		
NiAl (B2)	<i>cP2</i>	<i>Pm</i> $\bar{3}m$	B2	CsCl	30.8–58	100	2.877 [25]
Ni ₂ Al ₃	<i>hP5</i>	<i>P</i> $\bar{3}m1$	D5 ₁₃	Al ₃ Ni ₂	59.5–63.2	~4	57–60 at% Al: <i>a</i> = 4.442–4.036, <i>c</i> = 4.895–4.915 [26] 60–23 at% Al: <i>a</i> = 4.036–4.053, <i>c</i> = 4.895–4.902 <i>a</i> = 6.5982, <i>b</i> = 7.3515, <i>c</i> = 4.8021 [27] 4.025 [28]
NiAl ₃	<i>oP16</i>	<i>Pnma</i>	D0 ₁₁	Fe ₃ C	~23–26		
(Al)	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	99.89–100	~2	
Fe–Ni					at% Ni	at% Al	(Å)
α-Fe	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	0–5.5	40	2.860 [29]
δ-Fe	<i>cI2</i>	<i>Im</i> $\bar{3}m$	A2	W	0–3.5		
γ-(Fe,Ni)	<i>cF4</i>	<i>Fm</i> $\bar{3}m$	A1	Cu	0–100	1.95	3.587 [29]
γ'-FeNi ₃	<i>cP4</i>	<i>eq14</i>	L1 ₂	AuCu ₃	63–85	~12	3.5550 [30]
Al–Fe–Ni					at% Al	at% Ni	(Å)
Al ₉ FeNi	<i>mP22</i>	<i>P2₁/c</i>	D8 ₄	Al ₉ Co ₂	82–83	7–14	<i>a</i> = 8.598, <i>b</i> = 6.271, <i>c</i> = 6.207, β = 94.76° [31]
Al ₁₃ Fe ₃ Ni	<i>hP28</i>	<i>P6₃/mmc</i>	D8 ₁₁	Al ₅ Co ₂	70–73	55–60	
Al ₁₀ FeNi ₃ ^d	—	—	—	—	—	—	

Figure 3.33: Solid phases in Fe-Ni-Al system and their lattice parameters [4]

It is seen that the lattice parameter of FeNi alloy is given as 3.587 Å and the lattice parameters of B2 structures are given as 2.907 Å and 2.877 Å. These values are very

close to what was found during this study. Also, in many more studies it is pointed out that ordering mechanism and B2 structures are expected in Fe-rich ternary Fe-Ni-Al system [4, 9, 10, 11].

3.5 XRD

The X-ray diffraction (XRD) was applied to bulk plates with an X ray source of Cu K_{α} in the range of $2\theta=10-120^{\circ}$ with a scan speed of $1^{\circ}/\text{min}$ and step increment of 0.02 at room temperature by GBC-MMA model XRD device. Only $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloy was examined by a Bruker axs-D8 advance model XRD in the same conditions.

For $\text{Fe}_{75}\text{Ni}_{25}$ alloy, it is expected to find Fe-Ni phase with a lattice parameter of $3.587 \text{ \AA}$ [4] and/or Fe phase. Ni alone is not expected.

For the alloys that have Al content, FeAl or NiAl phases are expected together with some Fe or Fe-Ni. In the TEM study, for alloys with 15 and 25% Al, B2 structures are observed. Literature studies guide us to the result that these B2 structures should be FeAl or NiAl phases with a lattice parameter of $2.907 \text{ \AA}$ or $2.877 \text{ \AA}$ [4].

The expected phases and their lattice parameters are also given in Table 1.3 and Table 1.4.

The XRD results together with susceptibility measurement suggest that only kamacite phase (BCC) is observed in $\text{Fe}_{75}\text{Ni}_{25}$ alloy. If there was an Fe phase in extra, we would have seen this ferromagnetic phase after the 550°C where the ferro-to-para phase transition occurs since the Curie temperature of Fe is 770°C . This result is not in accordance with TEM study because in TEM, an FCC Fe-Ni phase with a lattice parameter of $3.4631 \pm 0.0069 \text{ \AA}$ was found. On the other hand, literature data and our susceptibility-temperature curve suggest that a structural transition might have occurred in Fe-Ni system, therefore the phase we detect by XRD could be the ferromagnetic BCC phase. At room temperature there is a possibility of mixture of FCC and BCC phases.

For the other alloys with Al, XRD results suggest that FeAl or NiAl and kamacite phases exist. The lattice parameters are in good accordance with TEM results and literature.

For the last three alloys with constant Fe content (50 at%) no TEM study was done, so the phases were determined by only XRD.

The XRD results of the studied materials are given below.

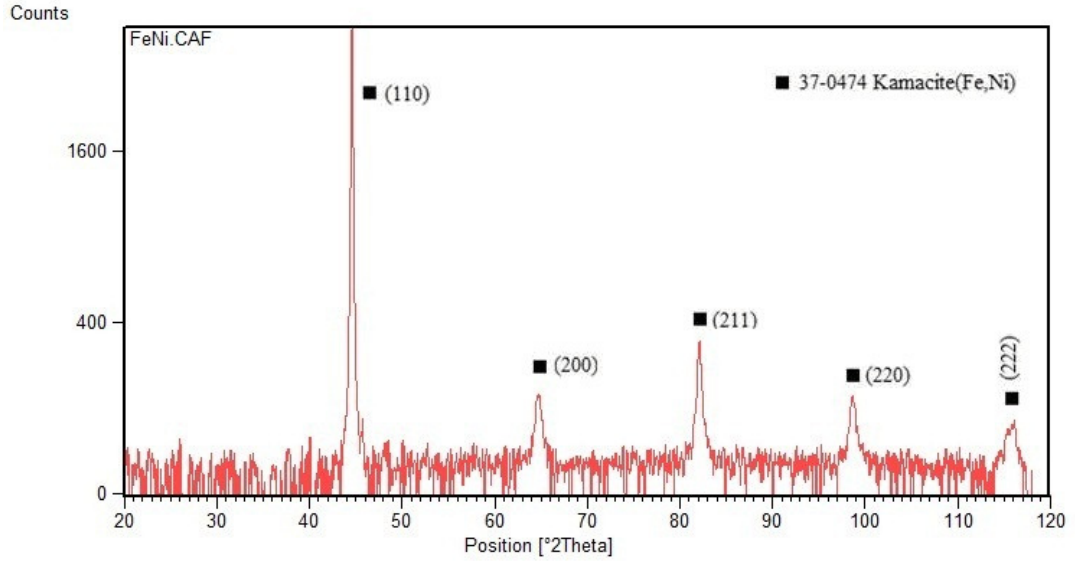


Figure 3.34: XRD result of Fe₇₅Ni₂₅

As mentioned above, only one phase exists for the binary alloy and it is kamacite with a lattice parameter $a=2.8680 \text{ \AA}$.

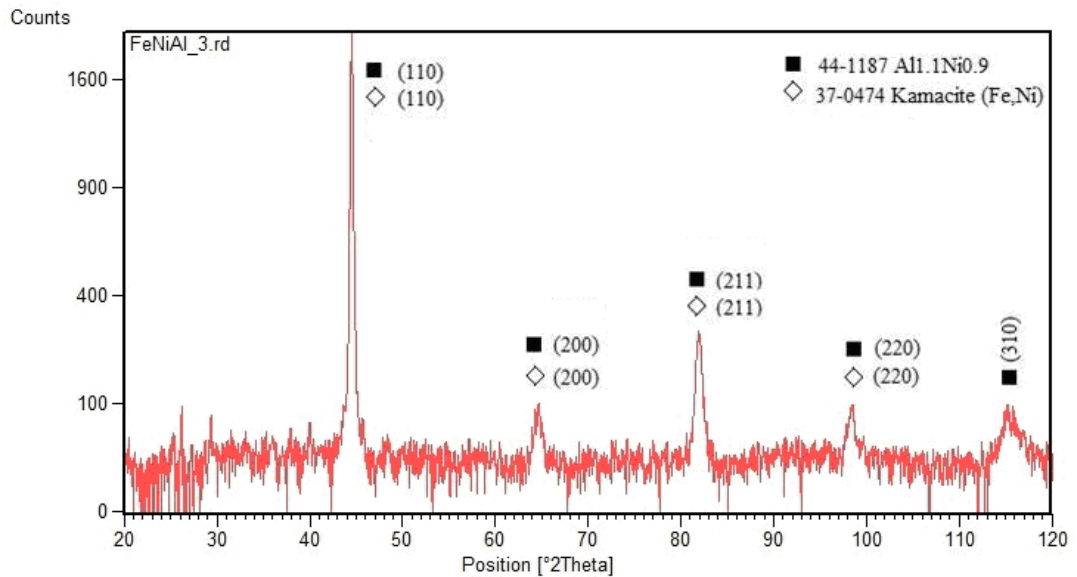


Figure 3.35: XRD result of Fe_{67.5}Ni_{22.5}Al₁₀

Fe_{67.5}Ni_{22.5}Al₁₀ alloy has Al_{1.1}Ni_{0.9} and kamacite phases. The lattice parameter of Al_{1.1}Ni_{0.9} is $a=2.8666 \text{ \AA}$.

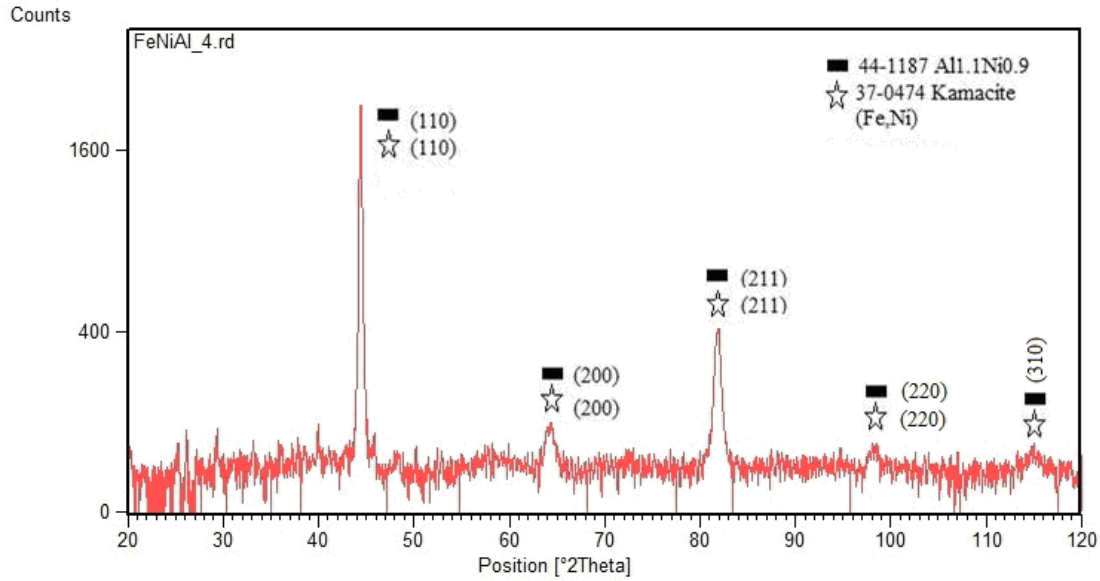


Figure 3.36: XRD result of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$

The XRD result of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ is the same with $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$. we have Al_{1.1}Ni_{0.9} and kamacite phases.

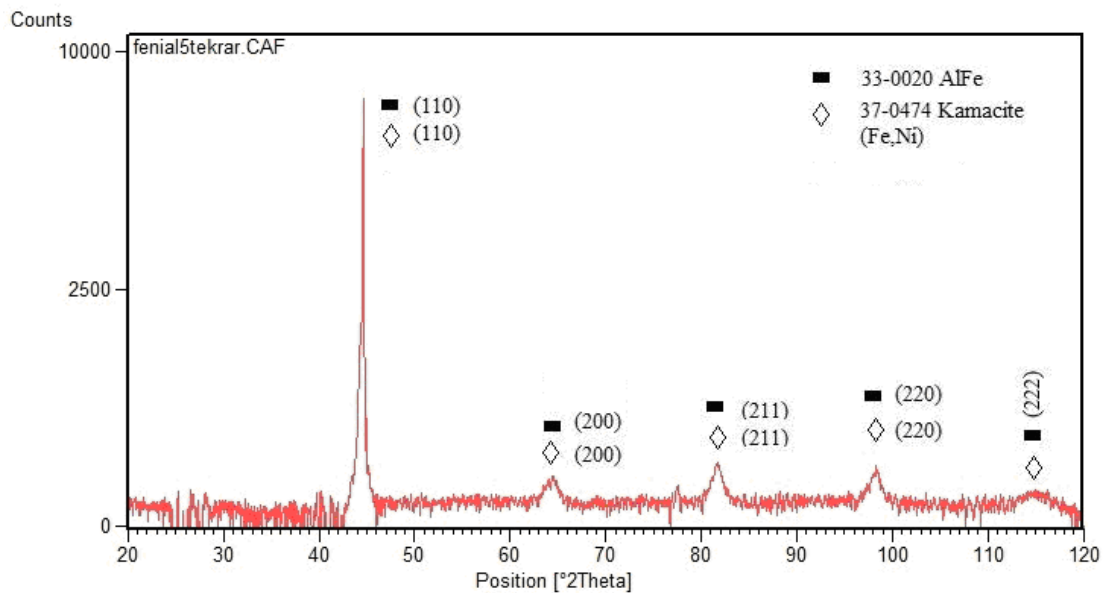


Figure 3.37: XRD result of $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$

AlFe and kamacite phases were found for $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$. The lattice parameter of AlFe is $a=2.8954 \text{ \AA}$.

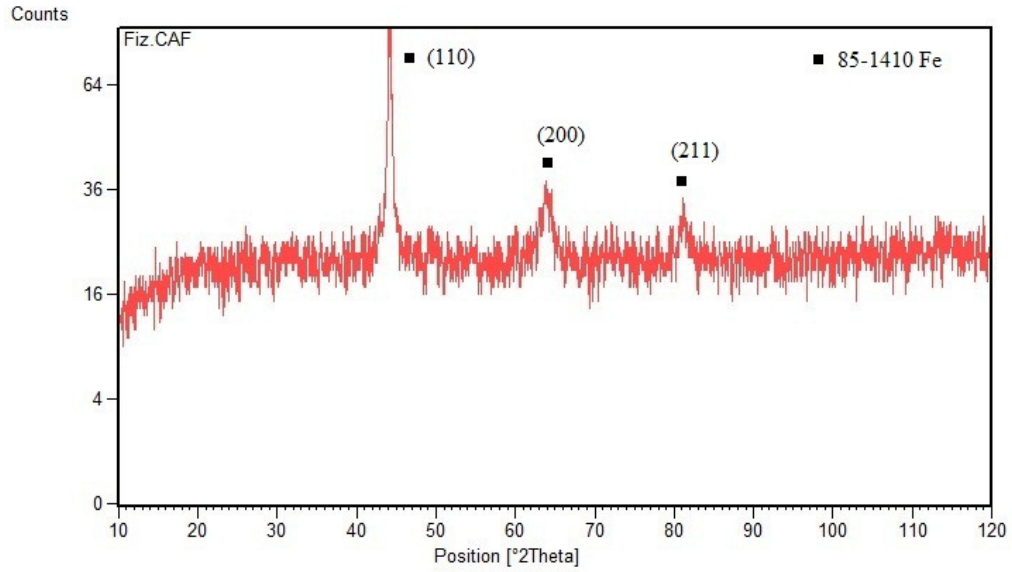


Figure 3.38: XRD result of $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$

For the $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloy we could only see the Fe phase. This is possible that due to the low counts of measurement the other peaks we saw in the other samples could not be detected.

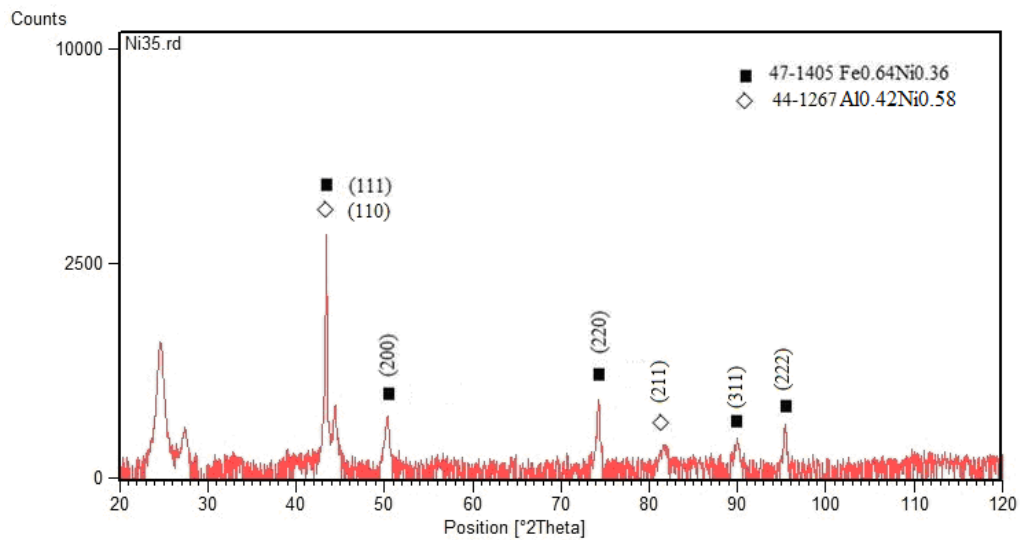


Figure 3.39: XRD result of $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$

For the $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$ alloy we found $\text{Fe}_{0.64}\text{Ni}_{0.36}$ with lattice parameter $a=3.5922 \text{ \AA}$ and $\text{Al}_{0.42}\text{Ni}_{0.58}$ with $a=2.8710 \text{ \AA}$.

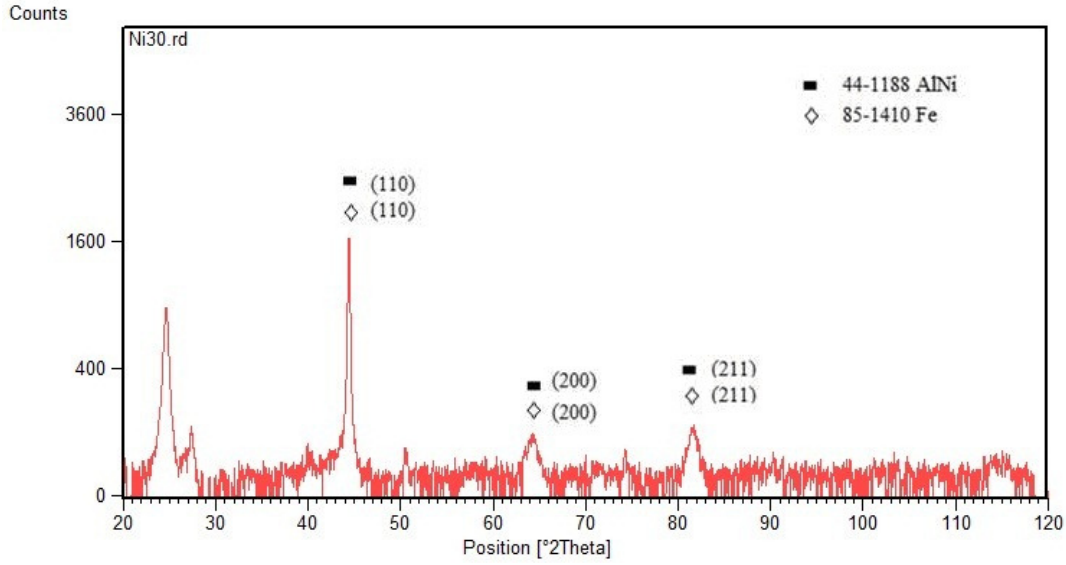


Figure 3.40: XRD result of $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$

AlNi and Fe phases were found for $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$. The lattice parameter of AlNi is $a=2.8880 \text{ \AA}$ and the lattice parameter of Fe is $a=2.8860 \text{ \AA}$.

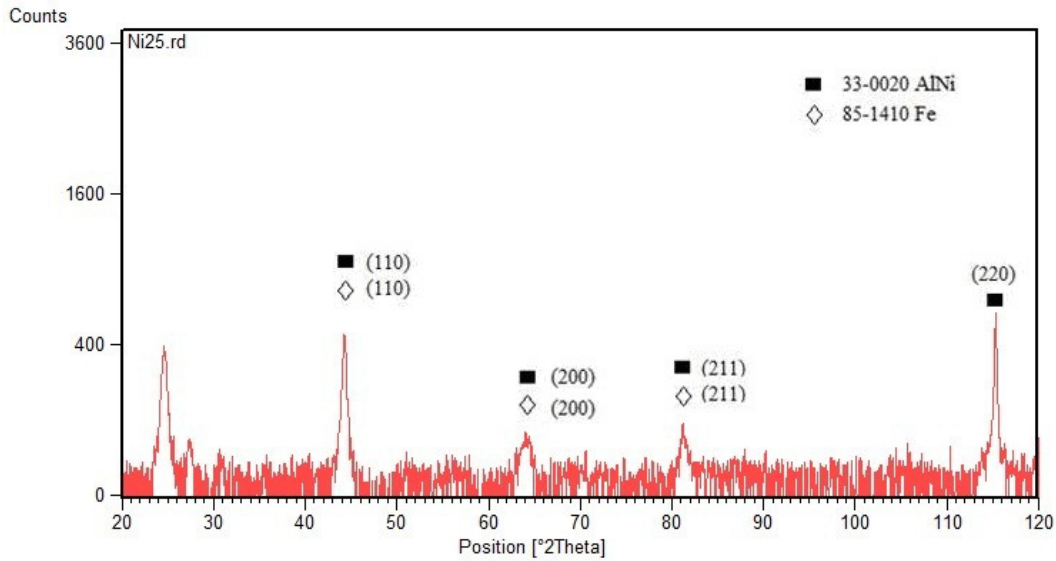


Figure 3.41: XRD result of $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$

Similarly AlNi and Fe phases were found for $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$. the related lattice parameters are $2.8880 \text{ \AA}$ and $2.8860 \text{ \AA}$.

All the phases are cubic. For the $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys, XRD results match TEM results where AlNi or AlFe phases were expected with the similar lattice parameters. The results are also supported by EDX. In summary, the phases are listed in Table 3.6.

Table 3.6: XRD results of the studied materials

Sample	Phases
Fe ₇₅ Ni ₂₅	Kamacite (Fe,Ni)
Fe _{67.5} Ni _{22.5} Al ₁₀	Al _{11.1} Ni _{0.9} , Kamacite
Fe _{63.75} Ni _{21.25} Al ₁₅	Al _{11.1} Ni _{0.9} , Kamacite
Fe ₆₀ Ni ₂₀ Al ₂₀	AlFe, Kamacite
Fe _{56.25} Ni _{18.75} Al ₂₅	Fe
Fe ₅₀ Ni ₃₅ Al ₁₅	Fe _{0.64} Ni _{0.36} , Al _{0.42} Ni _{0.58}
Fe ₅₀ Ni ₃₀ Al ₂₀	AlNi, Fe
Fe ₅₀ Ni ₂₅ Al ₂₅	AlNi, Fe

Looking back at VSM we were expecting to find paramagnetic phases in Fe_{67.5}Ni_{22.5}Al₁₀ and Fe₅₀Ni₃₀Al₂₀ systems and TEM results suggested that we were looking for AlNi (or FeNi). AlNi is paramagnetic at room temperature, so the XRD results support VSM and TEM results.

For ternary alloys we found 2-phase systems. For Fe_{56.25}Ni_{18.75}Al₂₅ alloy only Fe phase could be detected. This sample was examined by a different model of XRD so the reason that only Fe could be detected can be due to low counts of the system.

For Fe₇₅Ni₂₅ alloy, only Fe-Ni phase (kamacite) in BCC structure exists. In TEM examination Fe-Ni phase in FCC structure was found for the same sample. This may be due to structural transformation as mentioned in Figure 3.1. Kamacite is an alloy of iron and nickel and it is usually in the proportions of 90:10 to 95:5. At room temperature it is ferromagnetic. Kamacite with 3% Ni has a Curie temperature of approximately 760 °C [26].

XRD results show that AlNi phases were found for Fe_{63.75}Ni_{21.25}Al₁₅, Fe₅₀Ni₃₀Al₂₀ and Fe₅₀Ni₂₅Al₂₅ alloys. Kamacite (Fe-Ni) is ferromagnetic at room temperature and AlNi is paramagnetic. This may be the reason why we were not able to see the Curie temperatures of these alloys because the T_c of kamacite is above 700°C and our temperature range was 24-700°C.

The Curie temperature of FeAl was also reported as above 627°C [9].

4. CONCLUSION

This thesis focused on the investigation of magnetic and structural properties of Fe-Ni-Al alloys.

Fe-Ni alloys with low Ni concentration are known to go through martensitic transformation on heat treatment. As martensitic transformation can lead to a special property called shape memory effect, we investigated a binary $\text{Fe}_{75}\text{Ni}_{25}$ alloy. We kept Fe:Ni ratio constant and then added different percentages of Al in order to see how the magnetic and structural properties are affected. $\text{Fe}_{75}\text{Ni}_{25}$, $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ samples were produced in an arc-melting furnace with tungsten as electrode. This was done in an argon atmosphere and all samples were re-melted three times. $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$, $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ and $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ samples where Fe concentration was kept constant were produced from powders under argon atmosphere in a glove box system. After being pressed in the glove box, arc-melting and induction melting were applied to the samples. All the 8 bulk samples were homogenized at 1050°C for 12 hours. Magnetic susceptibility and VSM measurements were taken in order to characterize the magnetic properties of the materials. TEM and XRD examinations were carried out in order to characterize the structural properties of the samples. Magnetic susceptibility, VSM and XRD measurements were done for all samples. TEM study was applied only for $\text{Fe}_{75}\text{Ni}_{25}$, $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$.

1) Susceptibility Measurement

Susceptibility measurement was carried out to determine the Curie temperatures of the samples in order to find their magnetic transition points. The Curie temperatures (T_c) of the materials were measured from χ -T curves in the temperature range of 24 - 700°C .

i) The Curie temperature of $\text{Fe}_{75}\text{Ni}_{25}$ sample was measured as 580°C from Figure 3.1. $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ sample started to make a magnetic phase transition before 700°C . The other $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ samples made sharp peaks right around 700°C which implies that there is a possible magnetic phase transition above 700°C . In general the addition of Al (which means the decrease of Fe and Ni contents) resulted in increasing Curie temperatures.

ii) When we look at the last three alloys with constant Fe ($\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$, $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$, $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$) the Curie temperature of $\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$ alloy is very low (80°C). As Ni content was decreased and Al content was increased for the following alloys, the Curie temperatures of these materials increased. $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ alloy was characterized to have 2 ferromagnetic phases. One phase made a transition at around 400°C and the other transition is above 700°C .

iii) A large hysteresis was observed for the binary $\text{Fe}_{75}\text{Ni}_{25}$ alloy. Martinez-Blanco et al [12] reported that the Fe-Ni system goes through MA (from martensite to austenite) transformation between $367\text{-}647^\circ\text{C}$ and on cooling the reverse transformation does not happen until below 127°C . They also reported that ferro-to-paramagnetic phase transition occurred between $427\text{-}667^\circ\text{C}$. Our system made the magnetic transition between $450\text{-}630^\circ\text{C}$ and the reverse transformation happened below 120°C . Therefore, we get a conclusion that our system went through a structural transformation as well as the magnetic transition and the reason of the large hysteresis is that the reverse transformation does not happen until the sample is cooled below 120°C where the system recovers ferromagnetism.

iv) The similar behaviour was observed from the susceptibility-temperature curve of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$.

v) As a result, we can say the $\text{Fe}_{75}\text{Ni}_{25}$ and $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ alloys go through structural transformation between room temperature and Curie temperature and this transformation is expected to be martensitic transformation that could lead us to shape memory effect which needs to be explored.

2) M-H measurement

Hysteresis curves were obtained in order to determine the magnetic behaviours of the materials by a home made VSM in a magnetic field up to 8 kOe with a sensitivity of 10^{-5} emu at room temperature along the long axes of the samples.

- i) The M-H data shows that all of the samples are soft magnets since they showed no noticeable hysteresis and they reached saturation by small applied fields. $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys showed some hysteresis but it is very small. In accordance, the H_c and M_r values were also very small.
- ii) The saturation magnetization value decreased when the Fe and Ni contents were lowered and Al was added to the binary alloy. M_s of $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ is lower than $\text{Fe}_{75}\text{Ni}_{25}$. But as more Al was added (which means the Fe and Ni contents were lower) the M_s values of the $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys increased. We have the lowest M_s value for $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ and the highest M_s value for $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloy.
- iii) Considering the alloys with constant Fe ($\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$, $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$, $\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$), M_s is the lowest for the sample with maximum Ni and minimum Al ($\text{Fe}_{50}\text{Ni}_{35}\text{Al}_{15}$). As the Ni content was decreased and Al was increased, the M_s values increased linearly.

3) TEM

The TEM measurements were done by a CM20 model TEM at room temperature. The TEM study focused on diffraction patterns and structures of the samples were investigated. Only $\text{Fe}_{75}\text{Ni}_{25}$, $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ samples were examined by TEM. The samples were magnetized within the device due to the current. This made the materials harder to work by TEM. Bright field images could not be sharp enough due to the focusing problems which were caused by the magnetism effect. For the same reason, it was very difficult to tilt the sample. As a result, the study was focused on diffraction patterns which gave structural information on samples. The study showed that all the examined samples have cubic structures. This result supports VSM results because all the samples are soft magnets and cubic structures are known to be soft magnets.

i) The $\text{Fe}_{75}\text{Ni}_{25}$ alloy was characterized to have FCC structure with a lattice parameter of $a=3.4631\pm0.0069 \text{ \AA}$. $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$ was in BCC structure with $a=2.8786 \text{ \AA}$. In $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, both BCC and B2 structures were observed. In the thinner regions the system was disordered. But in the thicker regions we had ordered structures possibly due to some diffusion mechanism. This was supported by EDX where there were less Fe, Ni and Al in thinner regions and more Fe, Ni and Al in thicker regions. In $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ both BCC and B2 structures were observed. The given EDX data also relatively matched the original atomic percentages of produced samples.

ii) The ordered and disordered regions of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys are in the same zone axes ([001]). This fact suggests that some ordering mechanism exists within the same structure. The ordered structures have bigger lattice parameters than the disordered ones within the same material.

iii) In $\text{Fe}_{75}\text{Ni}_{25}$ alloy FCC structure was observed. With the addition of Al, in $\text{Fe}_{67.5}\text{Ni}_{22.5}\text{Al}_{10}$, $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$ and $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ alloys BCC structures and even ordering in these structures were observed. This is an expected fact given in many literature data. The lattice parameter for Fe-Ni match the literature. The lattice parameters found for Fe-Ni-Al alloys match the lattice parameters of either FeAl or NiAl phases with B2 structures in literature.

4) XRD

The XRD results suggest that all the alloys were 2-phase systems except $\text{Fe}_{75}\text{Ni}_{25}$. All the systems have cubic structures and the lattice parameters of the alloys match the lattice parameters found by TEM study. Kamacite (BCC) phase was found for $\text{Fe}_{75}\text{Ni}_{25}$ alloy while an FCC phase was found by TEM study. This may support the conclusion where a structural transformation (from BCC to FCC) exists. The expected paramagnetic phases from VSM study were found as NiAl phases by XRD study. NiAl and FeAl phases were detected by XRD and these phases were expected from the phase diagrams and TEM study.

In general our studied materials were characterized to be magnetically soft. The calculated lattice parameters and susceptibility values match the values in literature. The EDX data confirmed the atomic percentages of Fe, Ni, Al contents in the samples. Curie temperatures of $\text{Fe}_{63.75}\text{Ni}_{21.25}\text{Al}_{15}$, $\text{Fe}_{60}\text{Ni}_{20}\text{Al}_{20}$, $\text{Fe}_{56.25}\text{Ni}_{18.75}\text{Al}_{25}$ and

$\text{Fe}_{50}\text{Ni}_{25}\text{Al}_{25}$ were above 700°C . $\text{Fe}_{50}\text{Ni}_{30}\text{Al}_{20}$ has two ferromagnetic phases. One magnetic transition happened at around 400°C but the second transition was above 700°C . The addition of Al (the decrease of Fe and Ni contents) resulted in increasing Curie temperature and saturation magnetization. For the alloys with constant Fe, the addition of Al (decrease of Ni) resulted in increasing Curie temperature and saturation magnetisation. The phases found by TEM and XRD supported each other and magnetic measurements were also in accordance. For $\text{Fe}_{75}\text{Ni}_{25}$ alloy, FCC structure was found by TEM and BCC structure was found by XRD. This may support the fact that the Fe-Ni system went through a structural transformation from BCC to FCC. The sample studied by TEM was stabilized in FCC phase due to rapid cooling of the sample after annealing.

The expected paramagnetic phases in VSM study were found as NiAl phases by XRD study. NiAl and FeAl phases were detected by XRD and these phases were expected from the phase diagrams and TEM study.

Future studies:

Susceptibility measurements will be taken in a larger temperature range in order to see the behaviours of the samples above 700°C and below 24°C . Possible shape memory effect will be investigated and tested. Dilatometry studies will be carried out.

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