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Aging Heat Treatment of Additive Manufacturing Maraging Steels in Nitrogen Containing Atmospheres

Master of Science in Materials Science and Engineering Department

by
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Aging Heat Treatment of Additive Manufacturing Maraging Steels in Nitrogen Containing Atmospheres

Abstract

Additive Manufacturing (AM) is a manufacturing method that pushes the limits of imagination and eliminates the question of whether complex industrial products can be produced that cannot be obtained with traditional manufacturing methods. In this study, microstructure and mechanical properties of maraging steels produced by DMLS method and aged in different durations (6 and 9 hours) and atmospheres (Air, N_2 and N_2/H_2) were investigated. When the SEM images were examined, it was observed that the molten pool boundaries did not disappear completely but became blurred with increasing temperature. Coaxial cellular structures and bands are seen in all samples. XRD results show martensite and gamma phases for all atmospheres. In addition, Ɛ-Fe_3N phase was detected at N_2-490-9 hours. In the hardness test, the sample with the highest hardness value is found in Air-490-6 hours. Increasing aging duration decreases hardness. In the tensile test results, the strength values of all samples were quite close to each other, the sample with the lowest strength is N_2-490-6. In the abrasion test, the sample with the worst abrasion resistance is Air-490-6. Increasing time also has a negative effect on wear resistance. In the corrosion results, the nitrogen atmosphere gave more positive results than the air atmosphere. When we look at the Archimedes test results, it can be said that the density values of the samples are very close to the values in the literature, and we can say that they are produced successfully by the additive manufacturing method.

Keywords: Additve Manufacturing, Maraging Steel, Nitriding, Mechanical Properties, Aging Heat Treatment.

Eklemeli İmalat Maraging Çeliklerinin Azot İçeren Atmosferdeki Isıl İşlemi

Öz

Eklemeli İmalat (Eİ), geleneksel olarak bilinen ve kullanılan imalat yöntemleri ile elde edilemeyen karmaşık endüstriyel ürünlerin üretilip üretilemeyeceği sorusunu ortadan kaldıran, hayal gücünün sınırlarını zorlayan bir imalat yöntemidir. Bu çalışmada, Eİ yöntemlerinden DMLS yöntemi ile üretilen maraging çeliklerinin farklı zamanlarda (6 ve 9 saat) ve atmosferlerde (Hava, N_2 ve N_2/H_2) mikroyapı ve mekanik özellikleri incelenmiştir. SEM görüntüleri incelendiğinde, erimiş havuz sınırlarının tamamen kaybolmadığı ancak artan sıcaklıkla bulanıklaştığı gözlemlendi. Tüm örneklerde koaksiyel hücresel yapılar ve bantlar görülmektedir. XRD sonuçları, tüm atmosferlerde martensit ve gama fazlarını gösterir. Ek olarak, N_2-490-9 saatlerinde Ɛ-Fe_3N fazı tespit edildi. Sertlik testinde en yüksek sertlik değerine sahip numune Air-490-6 saatte bulunur. Artan süre ile sertlik azalmaktadır. Çekme testi sonuçlarında tüm numunelerin mukavemet değerleri birbirine oldukça yakın çıkmıştır, mukavemeti en düşük numune N_2-490-6'dır. Aşınma testinde aşınma direnci en kötü olan numune Air-490-6'dır. Artan süre, aynı zamanda aşınma direncini de olumsuz yönde etkilemiştir. Korozyon sonuçlarında nitrojen atmosferi hava atmosferine göre daha olumlu sonuçlar vermiştir. Arşimet testlerine baktığımızda örneklerin yoğunluk değerlerinin literatürdeki değerlere çok yakın olduğunu ve eklemeli imalat yöntemiyle başarılı bir şekilde üretildiğini söyleyebiliriz.

Anahtar Kelimeler: Eklemeli İmalat, Maraging Çeliği, Nitrürleme, Mekanik Özellikler, Yaşlandırma Isıl İşlemi.

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List of Abbreviations

Al	Aluminium
AM	Additive Manufacturing
Ar	Argon
AT	Age treatment
α-Fe	Alpha-ferrite
BCC	Body-centered cubic
BCT	Body-centered tetragonal
C	Carbon
CAD	Computer-assisted Design
Co	Cobalt
DAT	Direct aging treatment
DED	Directed Energy Deposition
DMLS	Direct Metal Laser Sintering/Doğrudan Metal Lazer Sinterleme
EBM	Electron Beam Melting
EBW	Electronic BeamWelding
Ecorr	Electrochemical corrosion potential
ECP	Electrochemical corrosion potential
EDX	Energy-dispersive X-ray spectroscopy
e.g	exempli gratia(for example)
Eİ	Eklemeli İmalat

FCC	Face-centered cubic
FDM	Fused Deposition Modelling
Fe	İron
H_2	Hydrogen
İKÇÜ	İzmir Katip Çelebi Üniversitesi
LENS	Laser Engineered Net Shaping
LOM	Laminated Object Manufacturing
L-PBM	Laser powder melting
Mo	Molybdenum
Ni	Nickel
OM	Optical Microscope
SAT	Solution – age treatment
SEM	Scanning Electron Microscopy
SLA	Stereolithography
SLM	Selective Laser Melting
SLS	Selective Laser Sintering
ST	Solution treatment
T6	Thermal cycle consists of a solution heat treatment followed by a water quenching and then an age hardening (or precipitation hardening).
Ti	Titanium
XRD	X-Ray Diffrection

List of Symbols

°C	Celsius degree
h	hours
HV	Hardness Vickers
kV	Kilo-volt
g/cm3	gram per cubic centimetre is a unit of density
J	Joule
%	Percentage
Ksi	Kilopound per square inch
W	Watt
K	Kelvin
m	meter
Kg	kilogram
MPa	Mega-Pascal
in	inch
mm	milimeter
°F	Farad
HRC	Hardness Rockwell
μ	micron
mm/s	Millimeters Per Second

l/min	Litres per Minute
ml	milliliter
N/mm^2	newtons per square millimetre

Chapter 1

1. Introduction

In engineering studies, how the part can be manufactured should be considered together with the design. A designed piece becomes meaningful when it is transformed into a real product. A made design can be manufactured with a series of manufacturing techniques, each step of which follows the next step. Additive Manufacturing (AM) is a production method that pushes the limits of imagination and eliminates the question of whether complex industrial products can be produced that cannot be obtained with traditionally known and used manufacturing methods. AM provides a great advantage to manufacturers in product development in terms of time, cost and raw materials. It is a manufacturing method that allows a product to be obtained in 3D by using metal, plastic and composite materials and various methods such as melting, bonding and material stacking. Additive manufacturing method is one of the most important sub-branches of industry 4.0 with rapidly developing technology.Thus, additive manufacturing is used in many areas from food to health, from automotive to construction.

In this thesis, heat treatments of maraging steels produced by Direct Metal Laser Sintering (DMLS) method which is one of the popular AM methods were performed. The aim of this research is to age maraging steel samples produced by selective laser melting technique at a single temperature, but at two different durations (6 and 9 hours) and in two controlled atmospheres and to examine the effect of atmospheres used in this aging process on the final properties.

1.1 Aim and Objective of the Thesis

Today, one of the most innovative production methods for metallic materials is Additive Manufacturing (AM) technology. This technology encompasses the production of parts in layers and offers freedom of design (3D design), zero waste, reduction in expensive tool material and improved mechanical properties. Maraging steels produced with additive manufacturing technology are widely used in aircraft industry, aviation field and molding applications due to their high strength, high toughness, good weldability and dimensional stability during aging heat treatment [1]. The reason for this research is; when we look at the literature, there is not enough information about the duration of use and increasing the performance of maraging steel. In addition, there is no information regarding to what extent the atmosphere used for these heat treatments will affect the wear and corrosion resistance desired from the material. With this project, it is aimed that the phases within the structure will contribute to the product with the effect of different heat treatment, and the second is to realize improvements such as surface hardness, wear resistance and corrosion resistance with the help of atmospheric environment.

In some cases, very rapid cooling after laser part production may eliminate the solutionizing step and make only the aging treatment sufficient, so a T6 heat treatment is not required [2]. Many appliance and powder manufacturers also recommend direct aging. Therefore, in this research project, an aging heat treatment was chosen rather than solution taking. Another reason for the application of aging heat treatment is to increase the hardness by converting the austenite phase formed in the structure after the DMLS process into a martensitic structure.

The aim of this study is to age maraging steel samples produced by selective laser melting technique at a single temperature, for two different durations (6/9 hours) and in two controlled atmospheres (NH_3 and N_2 gases), and then to examine the effect of atmospheres used in this aging process on maraging steel. The hardness value of maraging steel before the aging process is between 280-320 (HV) [3]. After applying the aging heat treatment at 490 °C for 6 and 9 hours, it reaches the maximum hardness value of 560 (HV). Based on the information in the literature, the heat treatment temperature was determined as 490 ° C and the duration was 6 and 9 hours. The atmospheres to be used are N_2 and N_2/H_2 gases. In the aging processes to be carried out in N_2/H_2 and N_2 atmosphere, it is aimed to improve the hardness and wear properties by diffusing nitrogen to the maraging steel sample. The nitriding process is expected to give a minimum of 53 HRC hardness and thus improve the wear properties. Thus, the corrosion properties would improve without changing the wear properties.

1.2 Theoretical Background

1.2.1 Additive Manufacturing

Today, almost all of the products that can be imagined are designed in a computer environment by means of various programs. However, one of the most important criteria is that the part can be manufactured while designing [4]. Some designed products cannot be manufactured because they have various processing or manufacturing restrictions. With the developing technology, can a product with additive manufacturing design be "manufactured?" removes the question. Additive manufacturing (AM) is the layer-by-layer manufacturing of the part to be manufactured using materials such as metal, plastic, ceramic or composite from the 3D model data, contrary to traditional manufacturing methods . The advantages of Additive Manufacturing [5];

- Design limitlessness – AM can produce even the most complex shapes.
- Free complexity – Increasing object complexity will only have a marginal impact on production costs.
- Lightweight design – AM enables weight reduction through topological optimization
- Elimination of production steps – The most complex structure can be produced with a single step

The part that is planned to be manufactured begins with the acquisition of 3D data in the computer environment, as seen in Figure 1.1. These data are obtained as an original design with 3D scanning systems with deep-sensing cameras, ready-made design over the internet or computer aided drawing programs. These obtained data are converted into a format that can be transferred to other programs by dividing the geometric structure surface into many triangles and saving as "stl" extension representing the part [5]. After this step, first slicing is applied using different softwares and then the manufacturing parameters are determined. The file prepared with this software is converted into a format that the device can read and transferred to the additive manufacturing device and the manufacturing process is started [6]. Finishing processes such as cleaning, separation, firing, sintering and infiltration are applied to the finished part, and the production of the part is completed.

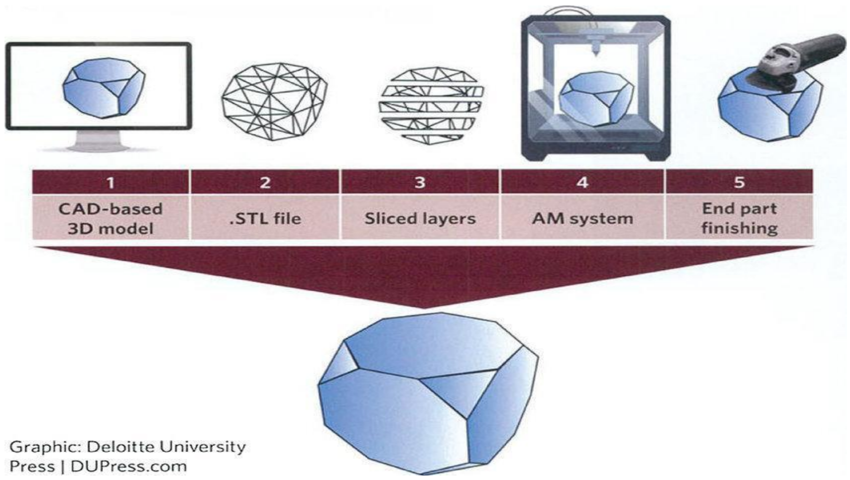


Figure 1.1: Additive manufacturing process steps [7]

An unrestricted manufacturing means that all the parts that can be designed are manufactured. In other words; it allows the layer-by-layer fabrication of parts that cannot be manufactured by traditional means, such as the manufacture of functionally assembled parts or evacuated parts [8]. Thus, large material wastes that occur in traditional manufacturing methods are prevented.

Thus, manufacturing for every field such as automotive, aircraft and space industry, prosthesis, implant, organ and personalized applications has begun to push the limits of imagination [9]. So much so that in the rapidly developing and digitizing new century, with this manufacturing method, it is very easy to manufacture parts designed even at home, such as ordinary printers, without the need for an expert.

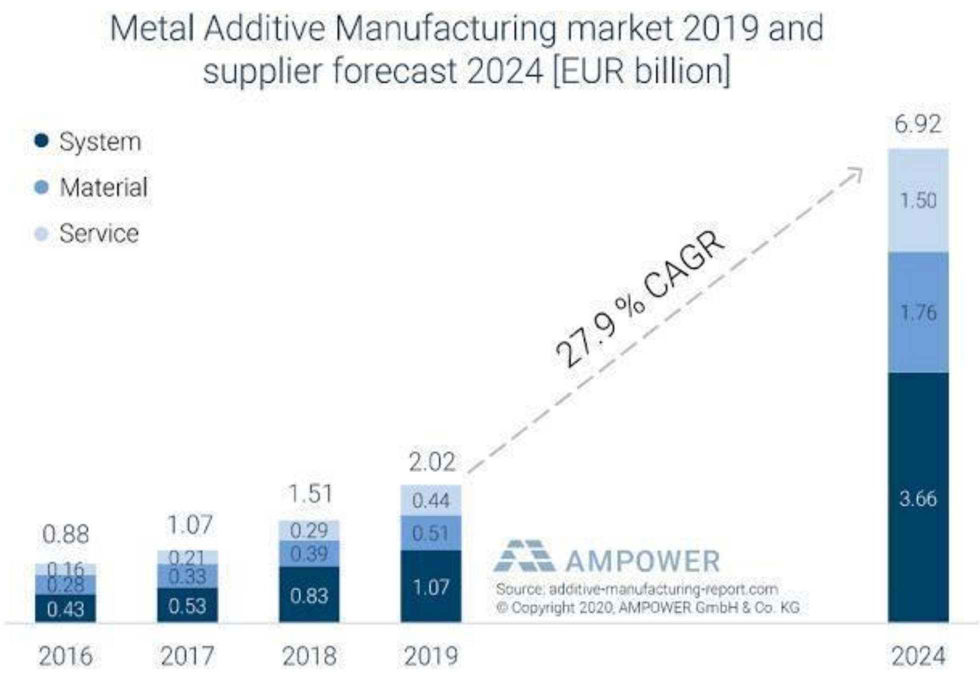


Figure 1.2: Metal Additive Manufacturing market size by 2016 [10]

Additive manufacturing has grown and continues to grow its market share by realizing a serious growth every year. These results are concrete findings showing that companies are confident in their AM production methods and plan to continue their growth.

1.2.2 Classification of Additive Manufacturing

Additive manufacturing varies in classification according to the energy source, method and material used. Some of them are as follows; classification according to the type of operation performed (e.g. laser, extrusion, etc.) or classification according to the raw material used (eg; powder raw material, liquid raw material, filament raw material) [11]. According to ASTM F42 standard, additive manufacturing is divided into 7 main categories. The classification made is given in Table 1.1, respectively.

Table 1.1: Classification of Additive Manufacturing [11]

CATEGORIES	TECHNOLOGIES	PRINTED 'INK'	POWER SOURCE	STRENGTH/ DOWNSIDES
Material Extrusion	Fused Deposition Modelling (FDM)	Thermoplastics Ceramic slurries Metal pastes	Thermal Energy	• Inexpensive extrusion machine
	Contour Crafting			
Powder Bed Fusion	Selective Laser Sintering (SLS)	Polyamides/ Polymer	High-powered Laser Beam	• High Accuracy and Details • Fully dense parts • High specific strength • Powder handling & recycling • Support and anchor structure • Fully dense parts
	Directed Metal Laser Sintering (DMLS)	Atomized metal powder, ceramic powder		
	Selective Laser Melting (SLM)			
	Electron Beam Melting (EBM)		Electron Beam	
Vat Photopolymerization	Stereolithography (SLA)	Photopolymer , ceramics	Ultraviolet Laser	• High building speed • Good part resolution
Material Jetting	Polyjet/Inkjet Printing	Photopolymer, Wax	Thermal Energy	• Multi-material printing • High surface finish
Binder Jetting	Indirect Inkjet Printing (Binder 3DP)	Polymer, Ceramic, Metal Power	Thermal Energy	• Full-color objects printing • Wide material selection
Sheet Lamination	Laminated Object Manufacturing (LOM)	Plastic Film, Metallic Sheet, Ceramic Tape	Laser Beam	• High surface finish
Directed Energy Depositon	Laser Engineered Net Shaping(LENS)	Molten metal powder	Laser Beam	• Repair of damaged/worn parts • Require post-processing

1.2.2.1 Material Extrusion

The material in the form of filaments is pushed to the nozzle by the heating chamber with the material extrusion method,. Then the material is melted according to a certain layer thickness. It is deposited on the production table by melting the material from the nozzle. Thus, according to the part geometry, this process is repeated without interruption and continues until the last layer [12].

1.2.2.2 Powder Bed Fusion

The additive manufacturing method has a great importance in the production of complex metallic parts that cannot be produced with traditional manufacturing methods. In the manufacture of a metal part, various machining processes such as turning and milling are required, and the additive manufacturing method can produce the part in a single operation, in contrast to this method. The Powder Bed Fusion process contents: Selective laser sintering (SLS), Selective laser melting (SLM), Electron beam melting (EBM) and Direct metal laser sintering (DMLS).

Selective laser melting technique uses metal, polymer, ceramic and composite based powders as raw materials. The powder, which is laid on the production table in Figure 1. 3 as much as the layer thickness, allows the powders to be combined by penetrating each other with the laser beam. This process continues until the last piece is obtained in the same way for each layer of the piece [13]. The most important parameter required for this method is to provide the correct energy density. The most important parameters of energy density are laser power and scanning speed. Thus, the production of the part is completed by sintering the powder grains in accordance with the layer shape of the part with the energy density created by selecting the appropriate scanning speed and laser power according to the material type [14].

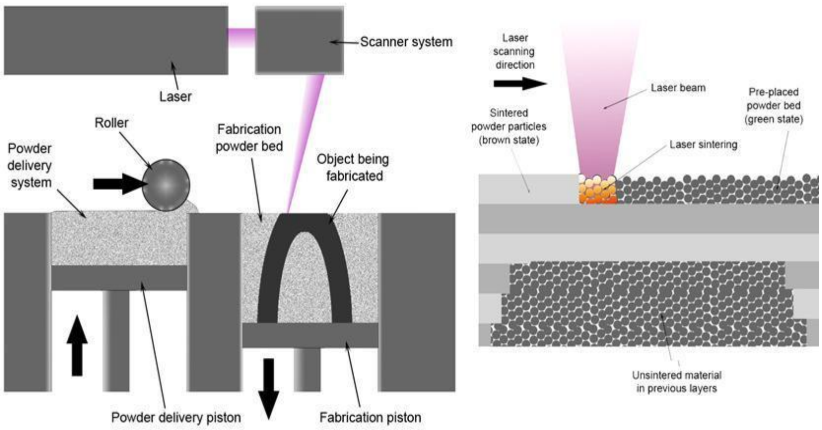


Figure 1.3: Selective Laser Melting method [14]

The electron beam melting process is very similar to the laser melting process. The difference is that in this method, metal powder is melted with an electron beam instead of using laser energy. This difference can be seen when Figure 1. 1.6 and Figure 1. 4 are looked at respectively. Metal powders are melted with an electron beam operating at high voltage (30-60kV) [12].

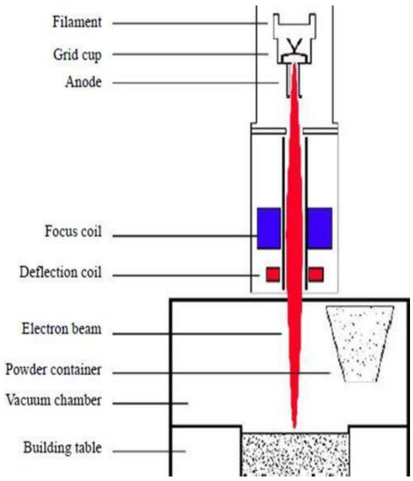


Figure 1.4: Electron Beam Melting method [12]

Direct Metal Laser Sintering (DMLS) is one of the powder bed fusion technology that can be used for manufacturing functional metal components, stainless steels, high grade steels, and nickel and cobalt based super alloys.3D metal parts with DMLS manufacturing method can be produced in detail. A laser mounted on an arm moves horizontally melting powder to build up material as a bed moves vertically. In the production phase, the shape of the samples to be produced first will be created in a three-dimensional CAD model. However, the limited strength and dimensional accuracy of the manufactured parts and poor surface properties are the disadvantages of rapid prototype manufacturing methods. In their studies, they were able to improve the dimensional accuracy and sintering quality of the part by creating optimum process parameters. In the DMLS manufacturing method, parts with high density (95% theoretical density) could be produced by optimizing process parameters such as laser scanning distance and scanning pattern. There are many input parameters in the DMLS process and these parameters can be controlled to obtain different mechanical properties of parts manufactured with DMLS [15].

There are different laser parameters (laser power, laser scanning range), different metal powder properties (powder size, alloy percentage of the material) and different powder melting laser parameters (layer thickness, scanning speed). Depending on these input parameters, different mechanical properties of the parts; output parameters such as hardness, density, strength, porosity ratio can be obtained. In additive manufacturing technologies, manufacturing speed, part quality, dimensional accuracy of the part and material properties gain importance and studies continue to improve these properties. In particular, studies are carried out to make the parts manufactured with these technologies suitable for end use without applying any additional processes [15] .

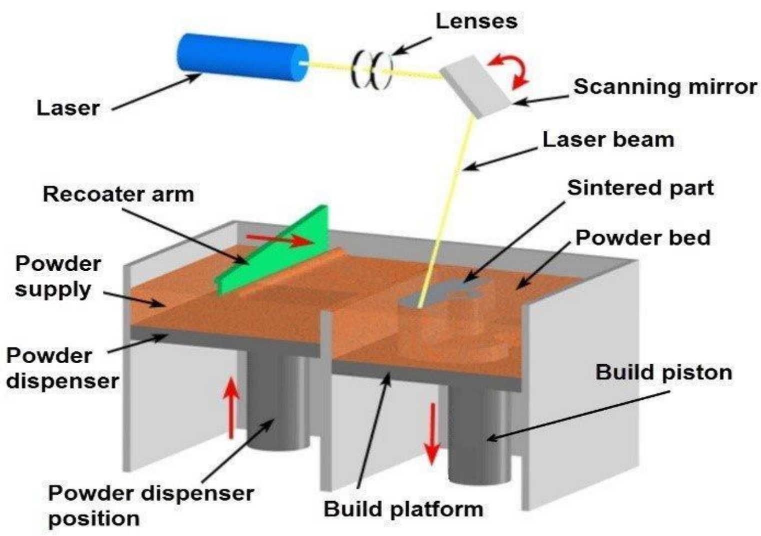


Figure 1.5: Direct Metal Laser Sintering method [15]

1.2.2.3 Vat Photopolymerization

The SLA method is the curing of the photopolymer (liquid) resin layer at room temperature with the help of an ultraviolet laser beam. SLA technology is faster than other methods. Therefore, functional parts can be produced faster. Highly detailed, complex shaped parts and surfaces that are difficult to produce with other methods can be produced with this method [12].

1.2.2.4 Material Jetting

Material Jetting (MJ) sprays material in droplets through a small diameter nozzle which is then layered onto a UV light cured build platform. [11].

1.2.2.5 Binder Jetting

Binder Jetting is used in two methods as liquid binder and powder base material. The powder is spread into the chamber in equal layers. A sticky material is sprayed out by the nozzle, thus binding the powders together. After the process is finished, the dust is cleaned [11].

1.2.2.6 Sheet Lamination

Sheet lamination processes contains laminated object manufacturing (LOM) and ultrasonic additive manufacturing (UAM). The UAM process uses ribbons or sheets of metal, which are bound together using ultrasonic welding. LOM uses a similar layer by layer approach but adhesive is preferred as material. [5].

1.2.2.7 Directed Energy Depositon (DED)

It is based on the principle that a raw material feeder and energy source mounted on the robot arm melt the material and deposit the molten material on the layer. The larger parts can be produced compared to SLM and SLS technologies. [11].

1.2.3 Maraging Steels

Maraging steels are steels (iron alloys) that are known for toughness without losing ductility and possessing superior strength. Maraging steels are the diffrent for special group of low carbon high strength steels. The high strength they have is not due to the amount of carbon they contain, but to the intermetallic phases in the structure. Maraging steels generally contain 17- 19% Ni, 8- 12% Co and up to 5% Mo and 0.2 - 1.6% Ti. High strength in these steels is obtained by martensitic transformation and subsequent precipitation hardening. Aging refers to the extended heat-treatment process[16].

Figure 1.6: Maraging Steel [16]

Its chemical compositon is generally high in nickel, molybdenum and cobalt. The carbon content in the composition is considered an impurity in these alloys. Therefore, it is usually kept at values below 0.03 percent. [17]. The composition grades of maraging steels are shown in Table 1.2.

Table 1.2: The compositon and grades of maraging steels [17]

Grade	Composition (%)(1)				
	Ni	Mo	Co	Ti	Al
18Ni (200)	18	3.3	8.5	0.2	0.1
18Ni (250)	18	5.0	8.5	0.4	0.1
18Ni (300)	18	5.0	9.0	0.7	0.1
18Ni (350)	18	4.2(2)	12.5	1.6	0.1
18Ni (Cast)	17	4.6	10.0	0.3	0.1
(1) All grades have a maximum content of 0.03 %C **(2)** Some manufacturers use the combination of 4.8% Mo and 1.4% Ti					

Typical physical and thermal property values of the standard 18 Ni (18% Nickel) maraging steels are presented in the Table 1.3. Mechanical properties of different 18 Ni maraging steel grades are shown in Table 1.4.

Table 1.3: Physical and thermal properties of 18 Ni Maraging Steel [17]

18 Ni Maraging Steel	
Property	**Value**
Density	8.2 g/cm^3 at 20℃
Coefficient of thermal expansion	1.3x10^{-5}/K at 20℃
Melting point	1425-1505 ℃
Specific heat capacity	440J/(kg*K) at 20℃
Thermal conductivity	20-25 W/(m*K) at 20℃

Table 1.4: Mechanical properties of different 18 Ni maraging steel grades.[17]

Grade	Tensile Strength MPa (ksi)	Yield Strength MPa (ksi)	Elongation 2 in or 50 mm (%)	Reduction of area (%)	Heat Treat-ment(1)
18Ni (200)	1500 (218)	1400 (203)	10	60	A
18Ni (250)	1800 (260)	1700 (274)	8	55	A
18Ni (300)	2050 (297)	2000 (290)	7	40	A
18Ni (350)	2450 (355)	2400 (348)	6	25	B
18Ni (Cast)	1750 (255)	1650 (240)	8	35	
Cobalt -free					
200/250/300	1895 (275)	1825 (265)	11.5	58.5	C

There are many different application areas of maraging steels are presented in Table 1.5.

Table 1.5: Different application areas of maraging steels.

Production tools	Aerospace and aircraft parts
Carbide die holders Casting and forging dies Aluminium and zinc dies Extrusion press rams, dies, and containers	Gimbal ring pivots Rocket motor cases Anchor rails Arresting hooks Load cells
Military	Others
Lightweight portable military bridges Cannon recoil springs Rocket motor cases	Pump impellers and casings Auto-racing car parts Uranium enrichment plants parts

Due to their properties and wide range of applications, including widespread use in the aerospace industry, maraging steels have recently been demonstrated to be suitable for the fabrication of parts via 3D printing [17]. Maraging steels produced by 3D printing presented in Figure 1.7.

Figure 1.7: Maraging steels produced by 3D printing

1.2.4 Heat Treatment Process

Heat treatment is the known of the processes applied to improve the mechanical properties of metals. It is one of the type of metallurgical process. The metal is then cooled abruptly so that the granules (grain) are trapped in a phase that is not thermodynamically stable at room temperature. This phase is usually one in which the material exhibits superior mechanical properties. Although the theory of heat treatment is not well known, its practice was known and applied long before the industrial era. For example, it is a simple heat treatment for blacksmiths to freeze swords by immersing them in water after forging to strengthen them. Similar applications; it has also happened with some other metal items where sharpness, hardness, resistance to abrasion is required [18].

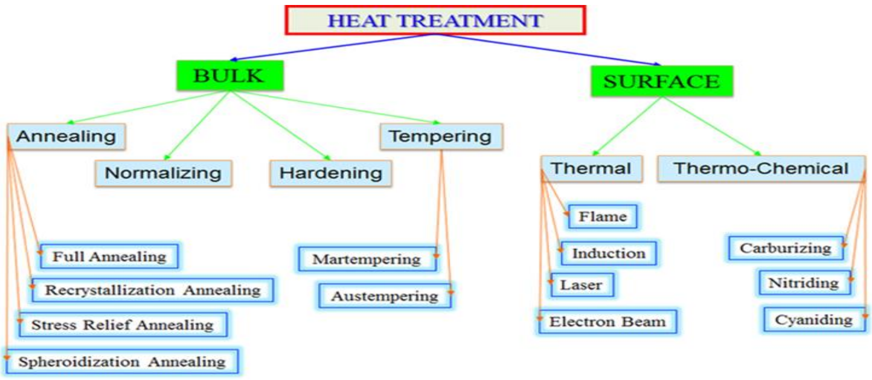


Figure 1.8: Classification of heat treatment techniques [18]

In work hardening (also called strain hardening) the material is stretched beyond its yield limit. As the ductile metal is physically deformed, it hardens and becomes stronger. Plastic stretching creates new dislocations. The greater the dislocation density, the more dislocation movement becomes difficult because the dislocations block each other, which increases the material stiffness[18].

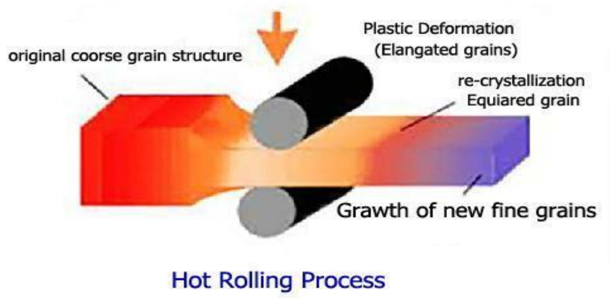


Figure 1.9: Hot rolling, which is one of the work hardening hardening method [18]

Age hardening (Precipitation hardening) is a process in which a second phase that begins in solid solution with the matrix metal is precipitated out of solution with the metal as it quenches and particles of this phase are dispersed in the metal to resist shear dislocations[18].

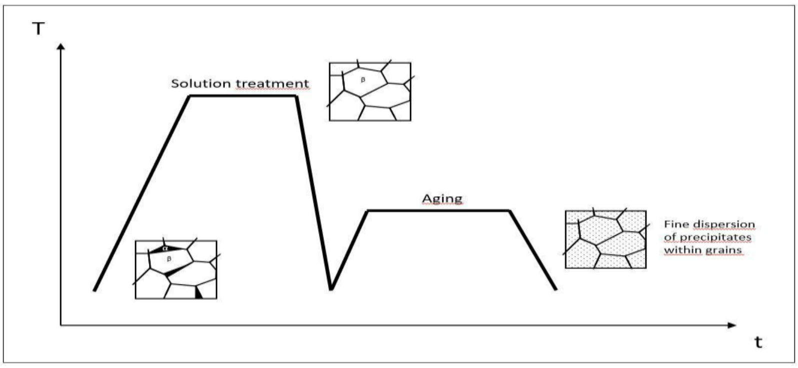


Figure 1.10: Schematic diagram of the age-hardening process

Martensitic transformation, known as tempering and quenching, is a steel-specific hardening process. Maraging steel is the formation of the iron phase by transforming from ferrite to austenite. Therefore, it is the transformation of the crystal structure from HMK (volume-centered cubic) to FMC (surface-centered cubic) by heating to a certain temperature. Diffusion is not needed because the cooling rate is so fast, so that the carbon does not have time to form carbide precipitates. This is called the martensitic transformation. Due to the supersaturation of the solid solution carbon, the crystal lattice becomes HMD (Volume-centered quadrilateral). This phase is called martensite [18].

1.2.5 Nitriding Methods

Nitriding is an important surface hardening treatment with different application areas in the industry. In bending and torsion loading, the highest stresses occur on the surface, and the surface of the materials is exposed to friction and chemical effects. The purpose of surface hardening methods is to improve the surface properties in the desired direction to prevent or delay a damage that may start from the surface. At the end of the process, a hard layer is formed on the surface and the properties of the part such as wear resistance, corrosion resistance, and fatigue resistance are improved, while ductility is preserved since no change occurs in the interior. Nitriding in steel and cast iron is based on the solubility of nitrogen in iron and diffusion of nitrogen onto the surface of steel and cast irons. The smaller diameter of nitrogen than carbon makes it easier to penetrate the iron cage. Nitriding takes place in the ferrite region of the ironcarbon phase diagram. Thus, phase changes will occur when high temperatures are not reached [19].

The important factors in the use of nitriding are; the hardness of the inner part of the material is not affected, it takes place at lower temperatures than other surface hardening methods, and the process parameters are controllable and the distortion is low [20].

Nitriding is a surface hardening process performed by diffusion of nitrogen to the surface at a temperature between 500 – 700 °C. Unlike other thermochemical surface hardening processes, nitriding is performed at lower temperatures, which is one of the biggest advantages of the method. In this way, high hardness values are achieved on the material surface, while minimal distortion and excellent dimensional stability are achieved [21]. With this method, it is possible to reach a surface hardness of 1200 HV while obtaining a hard layer up to 1 mm on the steel surface.

When the nitriding process is studied, the Fe-N equilibrium diagram in Figure 1.11 can be used. At conventional nitriding temperatures, nitrogen dissolves in iron, but by a very small percentage of 0.1%. Nitrogen content greater than this ratio forms γ nitride with the chemical formula Fe4N. If the nitrogen content exceeds 6%, γ nitride starts to transform into ε nitride [22].

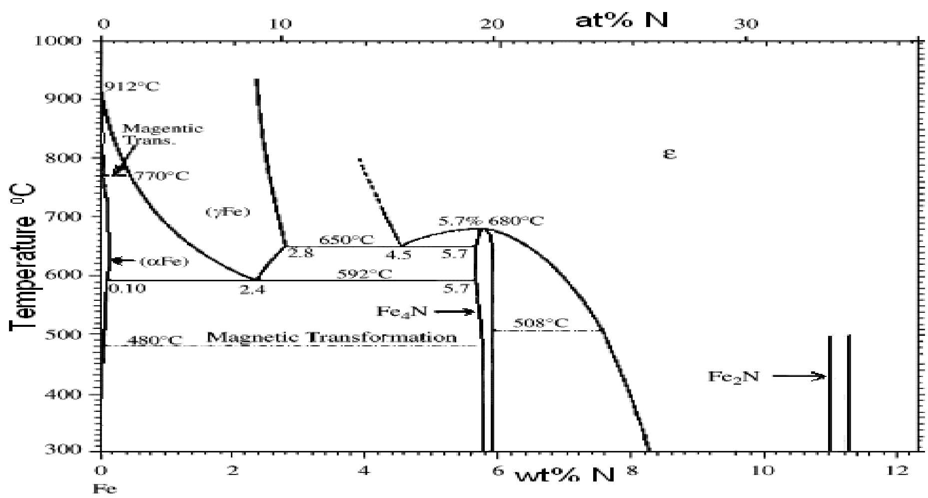


Figure 1.11: The Fe-N equilibrium diagram

According to the phase diagram, the solid solution formed by nitrogen in α-iron is the α phase and has a nitrogen solubility of 0.42% at eutectoid temperature (591℃) and approximately 0.015% at room temperature. If nitriding is carried out at a temperature lower than the eutectoid temperature of 591°C, solution α is formed first, followed by the γ phase, and finally the ε phase. In other words, as the surface is enriched with nitrogen, the phase formation from the core to the surface takes the form of α, γ, ε, respectively [21].

After the nitriding process, the steel acquires the following properties;

- High surface hardness,
- High-temperature hardness,

The most important factor in nitriding is the structure's type and amount of alloying elements.. The effective elements are aluminium, titanium, chromium, molybdenum, vanadium and nickel. When these alloying elements are present in a certain amount in the structure, they form alloy nitrides, which are thin and very hard, due to their affinity for nitrogen. In addition to nitridability, factors such as temperature, gas mixture, time, pressure, tension are also important factors [23].

It is possible to perform the nitriding process using many different methods. These methods are generally grouped under four main headings [21]. These are;

- Gas nitriding in a furnace or fluidized bed,
- Nitriding in a salt bath,
- Powder nitriding,
- Plasma ion nitriding.

1.2.5.1 Gas Nitriding

Gas nitriding is a surface hardening method that is made by diffusing nitrogen to the material surface at a temperature suitable for the process(500 - 550 °C), usually in an atmosphere containing ammonia gas [23]. Figure 1.12 shows schematically a furnace used for gas nitriding.

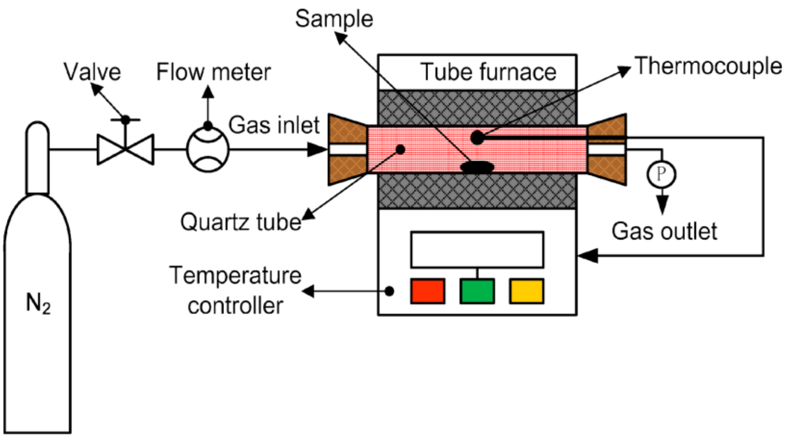


Figure 1.12: A Schematic of a furnace used for gas nitriding

At the end of the gas nitriding, the fast cooling process used in steels is not required for hard surface formation. Since the process is performed at lower temperatures than other surface hardening processes, less distortion and deformation occur as a result of nitriding. Although there is an increase in volume as a result of the process, these dimensional changes are relatively small [20].

1.2.5.2 Nitride Layer Formation

In the nitriding process, various diffusion zones and layers are formed from the surface to the inner region, depending on the nitrogen concentration, alloying elements and temperature. The first zone is the hard layer that acquires a new internal structure appearance after nitriding and occurs at a certain thickness from the outer surface. The second region is the core part, which preserves the materials's internal structure before nitriding and is located under the hard layer. The hard layer is divided into two: the white (compound) layer and the diffusion layer in terms of nitrogen binding and diffusion. In figure 1.13, the layer structure formed on the surface of nitrided steel is shown schematically. These layers are briefly described below.

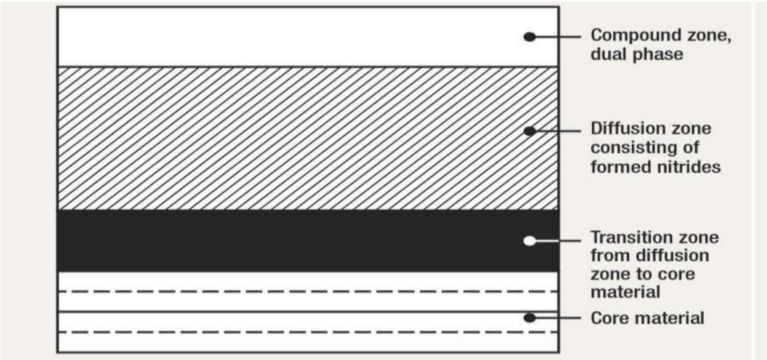


Figure 1.13: The layer structure formed on the surface of nitrided

1.2.5.3 Preliminary Preparations Before Nitriding Process

The following processes should be applied to the steel before the nitriding process;

- The parts to be nitrided must be cleaned very well before the process and ensure that there is no dust or scale on the part's surface.

- If the part is prepared by hot forging or machining on a lathe, attention should be paid to surface smoothness. An uneven surface can cause some problems after nitriding. These problems are; (a) there may be results such as exfoliation and (b) cracking of the white layers can occur.

- Heat treatment, hardening and tempering should provide the desired strength values. Care should be taken not to increase the grain size during heat treatment. Otherwise, a very rough, ready-to-crack structure may occur after the nitriding process.

- After the heat treatment, the desired shape should be given to the steel and the surface roughness should be minimized.

1.2.5.4 Advantages and Disadvantages of Nitriding Method

The advantages of the nitriding method are given below;

- Since the material surface is directly hardened by nitriding, there is no need for annealing, tempering and hardening of the material after the treatment.

- The internal structure of nitrided parts is tough, the surface is very hard and resistant to abrasion. They also have high sliding abilities.

- Nitrided parts show high resistance to corrosion.

- The layer thicknesses formed by nitriding remain the same without losing their properties even if they are heated up to 500°C.

- In steels hardened by nitriding process, minimum distortion and excellent dimensional stability are achieved because lower temperatures are applied compared to other methods.

However, the disadvantage of the nitriding method is; high surface stresses (loadings) cause the hard layer to flake off. High forces should not be applied to the material surface to prevent this.

1.2.5.5 Application Areas of the Nitriding Process

All kinds of drive gears, crankshafts, connecting rods, camshafts, transmission and gear gears, and other parts that work in environments where power transmission is made and molds made with plastic metal injection molds are commonly subjected to nitriding process. The nitriding process is frequently used in the surface hardening of the spinning press-forming processes and its use is becoming widespread day by day. In addition, working parts; rotation, buckling, friction, welding, etc. Since it is desired to work with resistance in environments, it is desired to be covered with hard layered surfaces since the surfaces that are in contact with the friction working surfaces are faced with abrasion. In this way, nitriding should be done to prevent abrasion of the working surface and the parts that are heated by friction [20].

1.3 Literature Overview

One of the most innovative production methods for metallic materials today is Additive Manufacturing (AM) technology. This technology encompasses the production of parts in layers and offers the 3D design, improved mechanical properties , reduced need for expensive tool materials and zero waste. Maraging steels are alloys that have nano-sized intermetallic precipitates homogeneously dispersed in a martensitic matrix as a microstructure, thus gaining high toughness-high strength mechanical properties. [24] .

Selg et al. investigated the microstructure and molybdenum nitride growth kinetics for maraging steel by gas nitriding at temperatures between 440˚C and 520˚C and in an NH_3/H_2 atmosphere for both solution-annealed and precipitationhardened samples. When looking at the nitrogen content, molybdenum content and the equilibrium solubility of nitrogen in the nitrided zone, more than expected nitrogen content was observed. The excess nitrogen removed showed finer and more consistent nitride formation in solution annealed samples than in aging samples. The results obtained showed, it was observed that it contained a large amount of Mo_2N, which caused a strong increase in both the inner zone hardness and the surface hardness. In addition, it was observed that a harder layer was formed on the surface [25].

Generally, heat treatments are applied to maraging steel parts produced with AM technology, which is one of the secondary processes. Another important issue to consider is the heat treatment conditions to be applied after AM. Because the heat treatment parameters greatly effect on the microstructure of the AM materials and therefore the product performance, and especially nowadays, the studies on this subject are increasing rapidly. Considering the studies made with aging heat treatment; Yasa et al.studied the effect of SLM parameters on the obtained surface quality, density and hardness was investigated. In addition, various aging heat treatments (different combinations of time and maximum temperature) were applied to SLM parts to achieve high hardness values. Microstructural examination, hardness test, impact toughness and tensile tests were applied to Maraging300 steel samples produced by the SLM process and applied an appropriate aging process, and compared with the results obtained using traditional manufacturing techniques. Macro hardness results showed that porosity reduces hardness. Different aging durations and temperatures were tried to find the best combination of process parameters. Heat treatment at 480°C for 5 hours was found to provide high hardness in a relatively short time [26].

Mooney et al. investigated the effect of heat treatment on the plastic anisotropy of maraging steel parts. Various heat treatments were applied to evaluate the microstructure, hardness, tensile properties and plastic stress behaviors of maraging steel . The combination of time and temperatures of heat tratment evaluate its effect on plastic anisotropy and mechanical properties. As a result of this; It was found that 6 hours in the 490°C heat treatment plan were not optimal in terms of strength, hardness, ductility and anisotropy properties, while the 8-hour aging plan at 525°C was the best combination in terms of improving mechanical properties [27].

In Jägle and Choi's study, AM maraging steel was aged at 480oC/5 hours and achieved maximum hardness (53 HRC; 32 HRC when produced with L-TYE). After aging, new phases were formed inside and at the cell borders. The precipitates in the sample that reached the highest hardness are mainly of two types. These; Ni_3X-type precipitates and Fe_7Mo_6 type precipitates (μ-phase precipitates). Figure 1.14 shows both the sample produced by DMLS microstructure and the heat treatment microstructure including the precipitates [28].

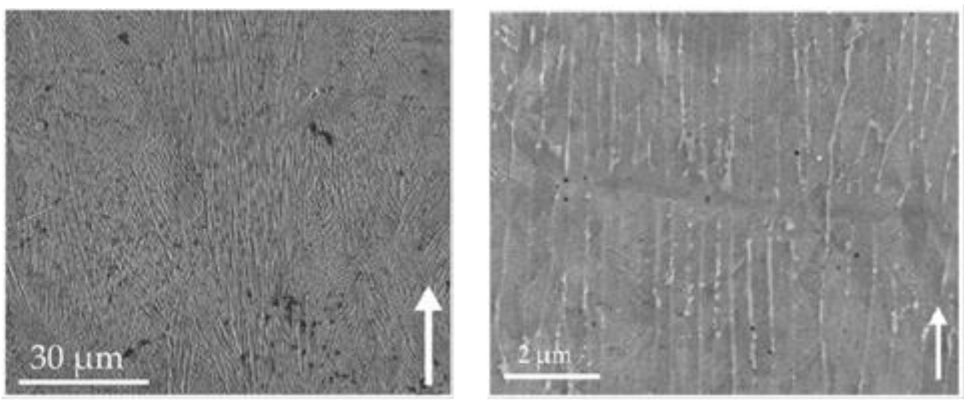


Figure 1.14: Microstructure of (a) sample produced with DMLS and (b) aging heat treated sample [28]

Among the heat treatments, there are studies in which heat treatments similar to the T6 process (including the aging process steps after the solution treatment process) are applied. Song et al. investigated the effect of heat treatment on the microstructure and mechanical behavior of 18Ni-300 maraging steel produced by selective laser melting. After pouring into solution at 840°C for 2 hours in the study, yield strength and Vickers hardness decreased slightly. However, yield strength and vickers hardness reached their maximum values after the samples were exposed to aging at 490°C for 2 hours. Also, in terms of the anisotropy of the production directions, the tensile behavior of horizontally constructed samples was found to be slightly higher than that of vertically constructed samples [29].

In the study of Tuck et al., Maraging steel parts produced with SLM were aged for 3 hours at 490°C, following the solution process, which includes waiting for 5 hours at 960°C and 2 hours at 820°C and cooling in air. After heat treatment, annealed martensitic Fe-Ni(Co) microstructure replaced the welded structures formed in additive manufacturing.Thus, superior mechanical properties such as high strength and toughness are obtained [30]. Again, Kucerova et al. they applied a similar T6 process and as a result, they found that the strength and hardness values (1800 MPa, 665 HV) of the heat-treated parts doubled compared to the part produced with the DMLS technique [31].

Yao et al. studied the effect of heat treatment on the mechanical properties of 18Ni300 produced by Directed Energy Deposition (DED). In the study, aging processes were applied at 490°C for 1 hour, 4 hours, 7 hours and 10 hours, respectively, after one hour of solid solution treatment at 830°C, and the effects of different heat treatments on microstructure development and mechanical properties were investigated. The solid solution and aging process significantly increased the microhardness of the forming parts. The microhardness increased slightly with increasing aging time. After the heat treatments, the strength values of the samples increased greatly, while the elongation values decreased slightly. It was also found that the tensile strength and elongation of the samples increased continuously with increasing aging time [32].

When the types of processes (aging process and T6 process) are compared; Mutua et al. investigated the effects of various process parameters on the densification behavior, mechanical ,surface morphology, microstructure and properties of maraging steel produced by SLM technique. While only aging heat treatment was applied to some samples, solution treatment at 820°C for 1 hour was applied to some samples and then 0.5–24 hours of aging at 460-600°C. As a result of the studies, solution uptake/aging led to the removal of the austenite phase and the formation of intermetallic precipitates in the martensite matrix. There was no difference between the heat treatments in terms of mechanical properties when compared with the samples that were only aged [33].

According to the study of Casati et al. , only aging heat treatment and T6 heat treatment provide similar properties (Figure 1.15 a). In addition, the effect of aging temperature on material hardness can be seen in Figure 1.15 b. Optimal aging time – considering the maximum hardness achieved, an aging temperature of 490°C appears to be optimal [34].

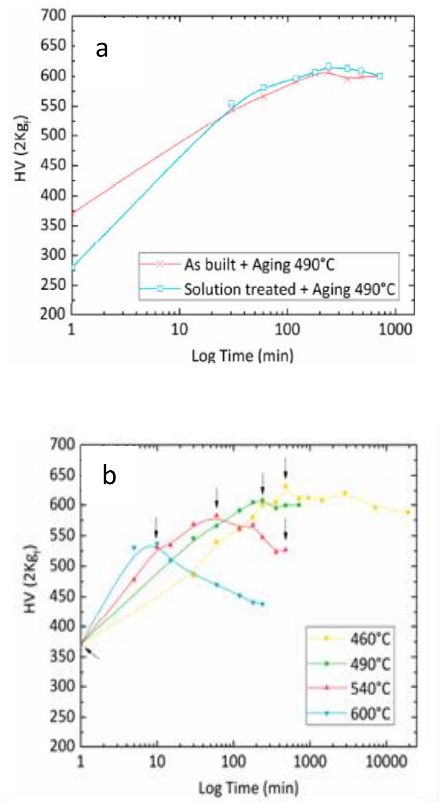


Figure 1.15: (a) T6 and aging heat treatment hardness values of samples produced with DMLS, (b) aging temperature – Vickers hardness [34]

Influence of gas nitriding on maraging steel fatigue resistance is discussed in the article by K. Hussain at al. Metallographic processed maraging steel samples with different volume fractions of austenite were subjected to gas nitriding at 450°C for 8 h in <35% dissociated ammonia gas atmosphere. When the results are examined, it shows that the nitrided ones contain 12% by volume and the unnitrided ones contain 24% by volume retained austenite. A decrease in hardness was observed. As shown in Figure 1.16, it was 55 and 35 mm in material containing 12 and 24 vol% austenite, respectively [35].

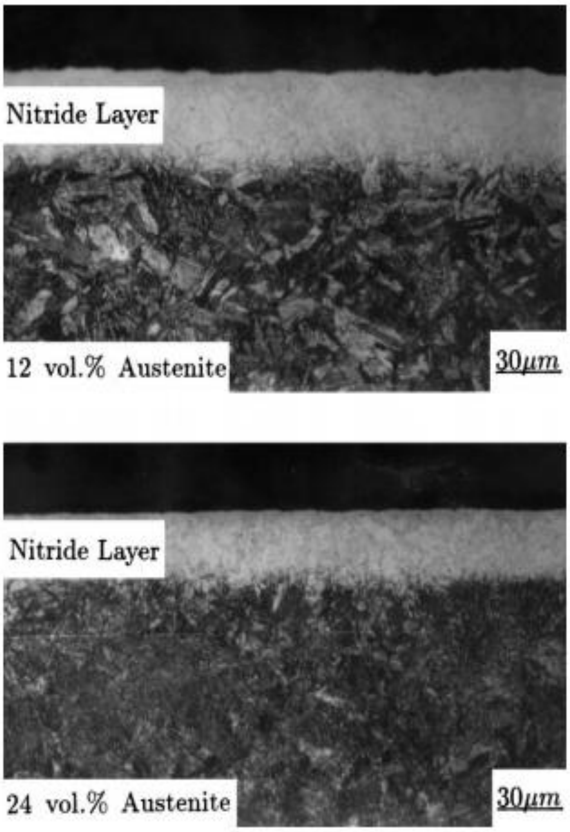


Figure 1.16: Growth of the nitride layer in the material with 12 and 24% retained austenite [35].

Chapter 2

2. Experimental Procedure

2.1 Materials

This study used commercially available gas-atomised Maraging 300 steel powder obtained from EOS company. The powder morphology is spherical and the particles werein the range of 15–45 µm size. The chemical composition, including the amounts of impurity elements, is shown in Table 2.1[16].

Table 2.1: The chemical composition of Maraging-300 steel powder [16].

Element	Content (%)
Fe	67
Ni	18.5
Co	9
Mo	4.8
Ti	0.6
Al	0.1
Si	0.10
Mn	0.10
C	0.030
Zr	0.01
P	0.010
S	0.010
B	0.0030

2.2 Production Process

Maraging 300 steel cubic samples were produced by DMLS method of additive manufacturing. The production parameters were as follows; scanning speed was 360mm/s, laser power was 280 Watt and layer thickness was 30 µm. These parameters are within the values recommended by the device manufacturer EOS and are also compatible with theliterature-related studies

The production method contains the steps below [30];

- DMLS technology, like other AM technologies, follows the basic sequence of processes: print model, slice and layer by layer. After the 3D model is created and sliced with the appropriate software, the code required for the printer to make the part is given to the printer, and the physical process is started.

- To start, the DMLS printer hopper is filled with the desired metal powder. The temperature setting is adjusted according to the sintering range of the powder. During these processes, an inert gas is used to protect the printer part.

- After the powders are laid on the production table, they are scanned by the laser and deposited layer by layer.

Figure 2.1: DMLS device at FSMVU/ALUTEAM.

The 2 cube samples with a side of 13mm (Figure 2.2a) and 15 cylindrical shaped tensile test samples with a length of 46mm and a diameter of 8 mm (Figure 2.2b) were produced with the DMLS technique of Fatih Sultan Mehmet Waqif University (FSMVÜ). Support structures were used during the DMLS process. The produced samples were subjected to the metallographic preparation process. Tensile test samples were prepared according to ASTM E8 standard. Tensile tests were performed on at least three samples of each parameter. Since the maraging steel samples have a very high hardness value and wear the jaw parts of the tensile test devices, a problem has been encountered in the tensile tests. Therefore, after forming the tension rod form with the dimensions in accordance with the standard as in figure 2.3a, the holder ends were turned into the shape in figure 2.3b by unscrewing and tensile tests were carried out with the screw system.

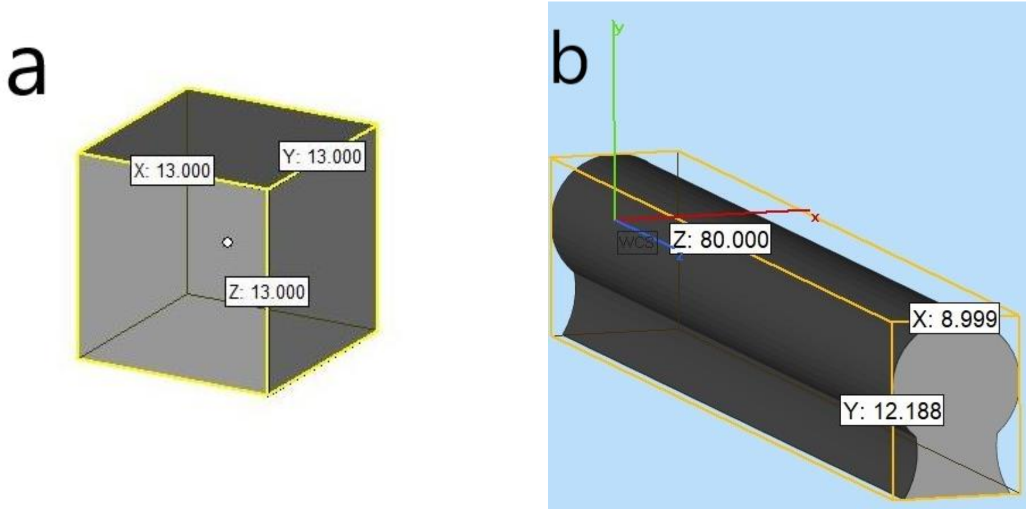


Figure 2.2: A shematic of a) cube sample b) tensile sample drawşng for the DMLS process

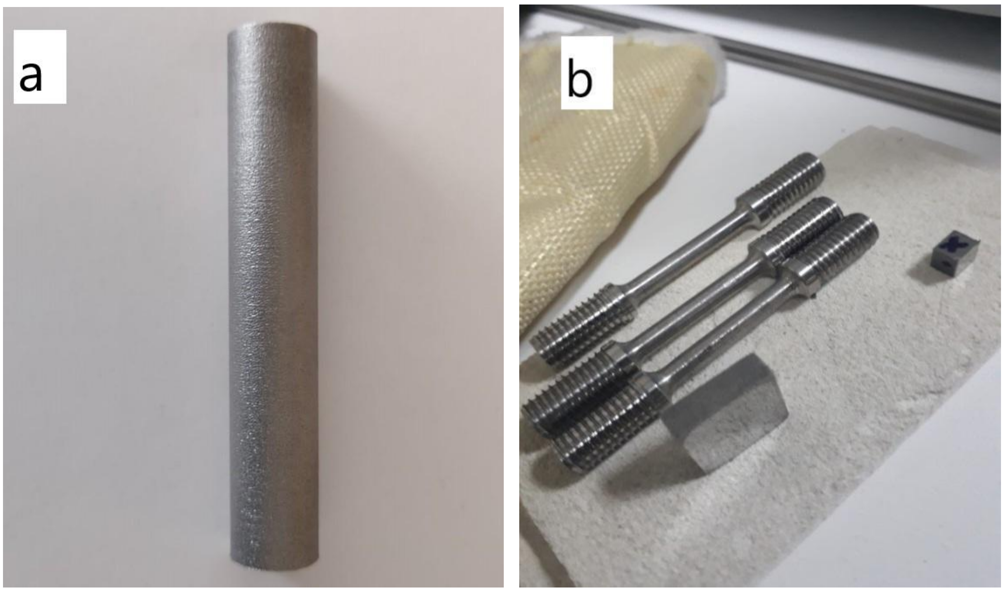


Figure 2.3: Samples produced after DMLS a) before turning b) after turning

2.3 Nitriding Process

The surface of the cube-shape DMLS Maraging 300 steel samples were polished and then made ready for nitriding. Atmosphere controlled tubular furnace was used for aging heat treatment. A glass tube made of quartz was used as the tube. The heating rate was set at 8°C per minute. Two different atmospheres were used as atmosphere; these are N_2/H_2 gas and N_2 gas. The temperature was 490°C and the aging processes were applied in two different periods of 6 and 9 hours. The applied gas pressure during the process was controlled by a manometer and a pressure that exceeded atmospheric conditions was avoided. The most important point is that, the flow rate of the gas passing through the tube was kept constant as 2-3 lt/min. The samples produced with the DMLS technique will be subjected to aging heat treatment at different durations and in different atmospheres. In all heat treatments, the tube furnace of İzmir Katip Çelebi University (İKÇU) (in Figure 2.4) were done by N_2 and N_2/H_2 atmospheres. The aging process parameters are shown in Table 2.2.

Figure 2.4: Tubular furnace used in İKÇU

Table 2.2: Heat treatmentparameters applied to samples

Sample Codes	Nitriding temperature (℃)	Time	Atmosphere	Cooling
N_2/H_2-490-6	490	6	N_2/H_2	Air
N_2/H_2-490-9	490	9	N_2/H_2	Air
N_2-490-6	490	6	N_2	Air
N_2-490-9	490	9	N_2	Air

2.4 Metallographic Preparation

Sample preparation is one of the important in any microscopical technique with interpretation of microstructural features and proper preparation methods facilitating examination. Sample preparation method as follows;

● In order to avoid errors in the procedures to be performed, the samples must be of appropriate size for the analysis. Therefore, the samples were brought to the appropriate size using the cutting process with the metallographic method. During additive manufacturing, cube-shaped samples were cut into 3 equal pieces perpendicular to the scanned surface.

● A flat surface was needed for the small metallographic sample sizes, the examination of the edge region of the sample or the next process. Therefore, the cut sample was molded.

● Sanding and polishing processes were carried out to remove the scratches on the surface during the metallographic sample preparation process. Thus, it was aimed to remove the surface roughness that previously occurred on the sample surface. Sanding was for reducing coarse defects and polishing is for reducing fine defects.

● Lubricant, 0.25 and 3 micron diamond solution was used during the polishing process. During the polishing process, the lubricant reduced friction and prevented the formation of deep scratches. First, a 3 micron diamond solution and a lubricant were used together. Then a 0.25 micron diamond solution and a lubricant were used.

● Thus, the samples were ready for the next procedures to be carried out.

2.5 Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDX)

A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image. SEM is used to obtain information about surface topography and composition. Electrons in the beam interact with the sample, producing various signals. Thus, we get information about the composition. EDX spectroscopy is involved in the determination of the elemental composition of matter using scanning electron microscopy (in figure 2.5).

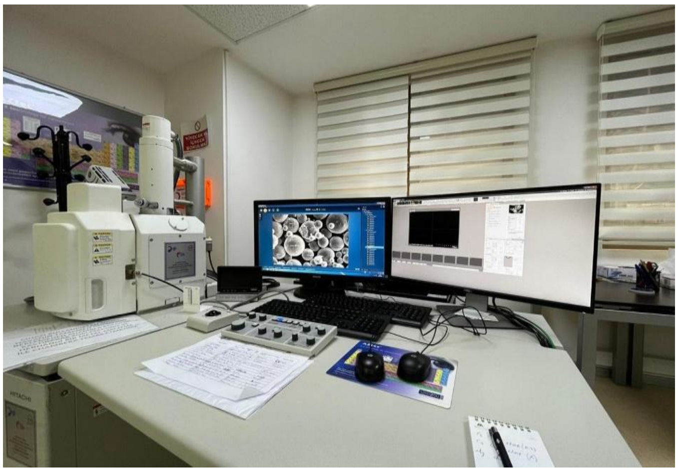


Figure 2.5: Scanning Electron Microscope in FSMVU

2.6 Phase Characterization Study

Phase analysis studies were carried out using the X-ray diffraction (XRD) device in figure 2.5 to determine the phases that may occur in the structures of the heat treatments applied to the maraging steel produced by DMLS technique at 490°C at 6 and 9 hours parameters. XRD analysis is based on the principle that each crystal refracts X-rays in a characteristic pattern, due to the unique atomic arrangement of the phase. These diffraction profiles for each crystal phase fingerprint, identify that crystal. The parameters are as follows; The test was carried out on the copper tube, between 40º and 100º, with the tube's current being 40 mA.

Figure 2.6: XRD device in IKÇU Central Laboratory

2.7 Hardness Tests

Vickers hardness tests were carried out using the hardness device as shown in figure 2.7. Vickers hardness measurement is to measure the resistance of the material to im-mersion of a standard rectangular pyramid tip into the material. Vickers hardness is not load dependent. It is beneficial to increase the load and thus the trace in order to obtain an average value in a heterogeneous structure and to reduce the measurement errors. In this study, it was carried out using a rectangular pyramid tip in a Vickers hardness device under 50 g load for 15 seconds. At least seven hardness measurements were taken from each sample, standard deviation and error functions were calculated.

Figure 2.7: Vicker Hardness Test device

2.8 Tensile Tests

Tensile test is one of the fundemental types of mechanical testing determining how strong a material is and how much it can elongate [50]. Three tensile samples were prepared for each heat treatment parameter (Figure 2.8a). The analyzes of the produced tensile samples were made by 9 Eylül University (DEU) with the Shimadzu brand tensile test device which is shown in Figure 2.8b. Tensile tests were applied with a strain rate of 1 mm/min.


(a)


(b)

Figure 2.8: a) Tensile test samples, b) Tensile test device

2.9 Wear Tests

Wear tests were carried out on a tribometer in accordance with ASTM G-99 standard. In order to examine the wear behavior of the samples obtained as a result of the applied aging heat treatment, wear tests were carried out at room temperature. Wear tests were carried out in a ball-on-disc type wear device using alumina balls, under a load of 5 N, with a speed of 20 cm/sec and a distance of 150 m. The abrasion test device made in Gebze Technical University (GTU) is shown in Figure 2.9a. In Figure 2.9b, the image of the sample after wear is given.

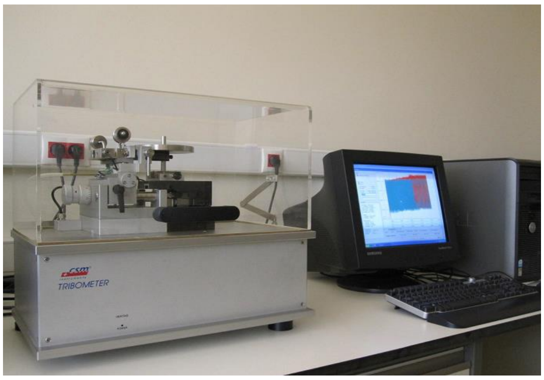


Figure 2.9 a: Tribometer in Gebze Technical University

Figure 2.9 b: Image of the worn sample surface

As a result of the test, the wear value is calculated in this way; before and after the wear test, the weight of each sample is measured, and the weight losses (ΔG) of the sample are calculated. Weight losses during the wear test are calculated using the density measured according to TS 1310 by the pycnometer method [36]:

$$\Delta V = \Delta G / \rho$$

ΔV = Volumetric loss
ΔG = Weight loss
ρ= density

The obtained volumetric loss values are also found from the slope of the diagrams showing the variation of the slip distance (S) of the samples with the wear rate [36].

$W_r = \Delta V / S$

Wr = Wear rate
ΔV = Volumetric loss
S= Sliding distance

2.10 Corrosion Tests

By extrapolating the anodic and cathodic polarization curves to the corrosion potential of the Tafel regions, the corrosion current, that is, the corrosion rate, is determined. When the anodic and cathodic Tafel regions are not obtained together, the corrosion rate can be found by extrapolating only one of them to the corrosion potential. In this study, the electrochemical corrosion behavior of the samples was characterized by potentiodynamic polarization tests according to ASTM G5-14 standard using the IVIUM/Vertex-CompactStat model potentiostat. Cube-shaped samples were prepared by metallographic methods, which were cut perpendicular to the scanned surface during additive manufacturing. The tests were carried out using a 3.5 wt% NaCl solution with a scan rate of 0.5mV/s. The corrosion test was applied to the samples for 30 minutes. Tafel curves were obtained by scanning within the determined potential range using Ag/AgCl reference electrode and platinum cathode. Icorr and Ecorr values were determined from these extracted curves using IviumSoft software, and corrosion rate calculations were made based on these data.

Figure 2.10: A schematic of corrosion test setup

Chapter 3

3. Results and Discussions

3.1 Archimedes Test Results

The results of the Archimedes test in ethanol for the maraging steels produced by the DMLS method, one of the additive manufacturing methods, were aged at 490 degrees and at different durations are shown in Table 3.4. Porosity is an undesirable negative feature in materials. Porosity reduces the mechanical properties of the material such as corrosion, shrinkage and hardness. When the results are examined, the densities of the samples are quite close to the densities in the literature. N_2-490-9 shows a small amount of porosity in the sample. These were also observed in SEM images. This is proof that materials can be produced successfully by additive manufacturing method. In the study of Kempen et al., the relative density was found to be around 99% as a consequence of heat treatment at 480 °C for 5 hours of 18Ni 300 maraging steel produced with similar parameters by the additive manufacturing method [38].

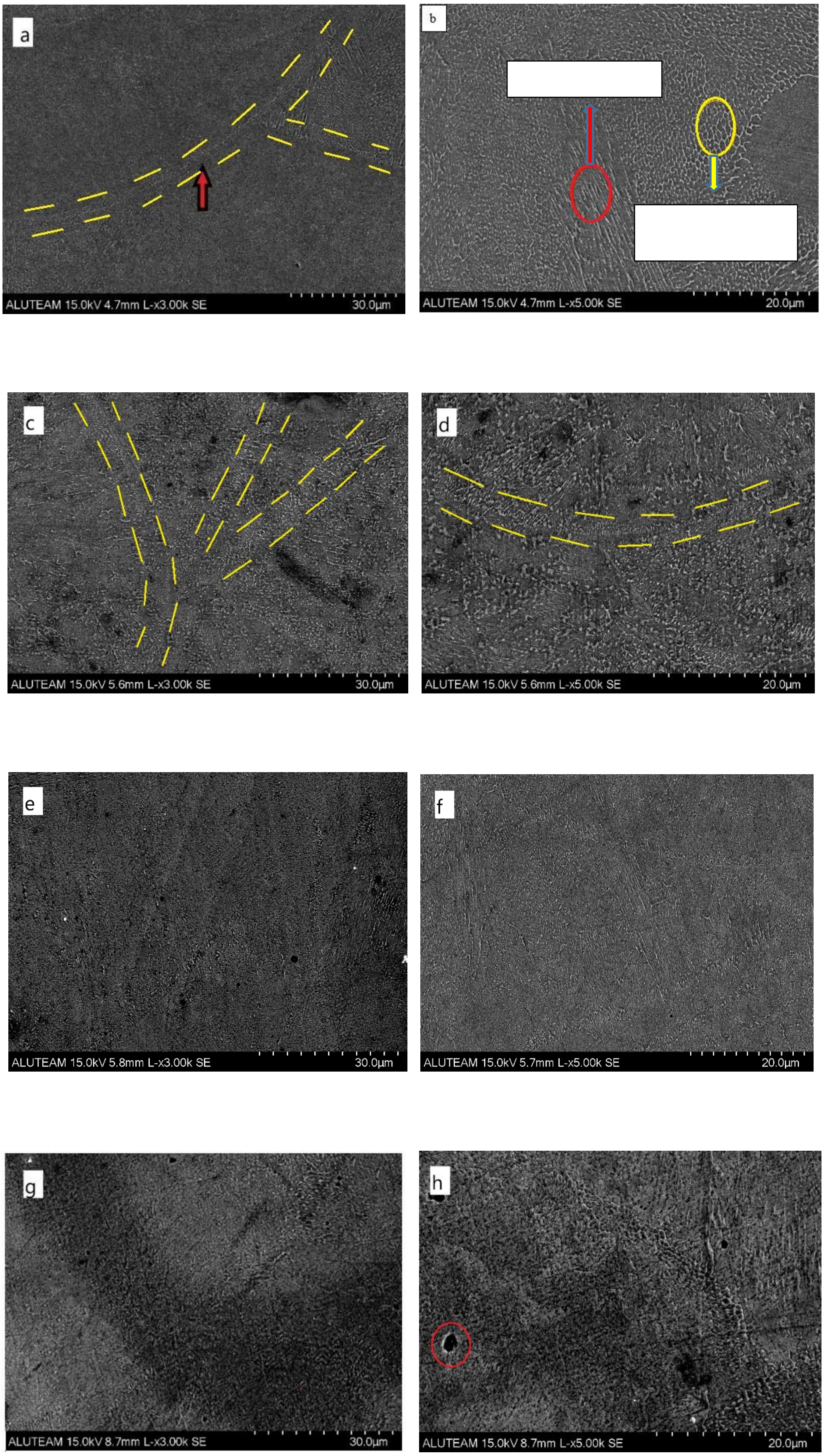
Table 3.1: Archimedes test results of samples aged at different durations and atmospheres

Sample	**Bulk Density (g/cm3)**	**Theoretical Density g/cm^3**	**Open Porosity (%)**
Air-490-6	7.80	8.1	0.08
N_2-490-6	8.02	8.1	0.12
N_2-490-9	7.89	8.1	1.31
N_2/H_2-490-6	8.05	8.1	0.27
N_2/H_2-490-9	7.45	8.1	0.06

3.2 Microstructural Evolution

3.2.1 Scanning Electron Microscopy (SEM) and EDX Analysis

SEM images of samples subjected to aging heat treatment at different atmospheres and hours are presented in the Figure 3.1 (a)-(i). It can be observed from these SEM images that melt pools (red arrow) coming from DMLS process have been depleted for Air-490-6 samples in Figure 3.1 a. It can be said that the temperature of 490℃ for 6 hour for air atmosphere is not enough to remove the traces left by these molten pools. In Figure 3.1b, two different cellular morphologies were observed: equiaxed cellular structures (yellow circle) and stripes (red circle). When we could be examined at the SEM image of the N_2-490-6 sample in Figure 3.1 (c-d), melt pools were seen. Stripes is the region of elongated grains with oriented orientation as a result of competitive growth during solidification. Equiaxed cellular structures is a region of randomly oriented grains in the center of the metal as a result of widespread nucleation [39]. Cellular and striped structures were seen on the front and back of the melt pool. When we compared the N_2-490-6 and N_2-490-9 samples, it was observed that the melt pool boundaries decreased with increasing time. In Figure 3.1e, approximately 2 μm pores were seen. Melt pools were almost not visible in the SEM images of the N_2/H_2-490-6 sample. Approximately 10 μm in size pores appeared on the surface (Figure 3.1(g-h)). Some amount of porosity was also observed in the N_2/H_2-490-9 sample, and it was observed that the pore sizes were similar (Figure 3.1 (ı-i)). In Figure 3.1i, the cellular structures and stripes observed in the Air-490-6 sample were also observed in the N_2/H_2-490-9 sample.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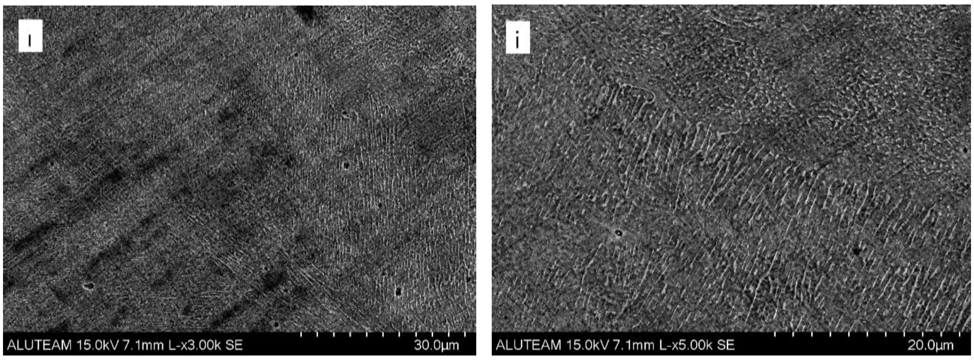


Figure 3.1: SEM images at different magnifications of samples that have been etched after heat treatments; (a-b) Air-490-6, (c-d) N_2-490-6 , (e-f) N_2-490-9 ,(g-h) N_2/H_2-490-6 , (ı-i) N_2/H_2-490-9, respectively.

In a similar study by Aydın, two different cellular morphologies are observed in the SEM images of maraging 300 steel produced by SLM method. These are equiaxed cellular structures around the molten boundary and stripes structures. It was interpreted that the formation of martensite lattice was prevented due to the rapid cooling of these structures during production by SLM method. This study similar to our study.When it was examined the SEM images that he applied aging heat treatment at 490 °C for different durations (4 and 6 hours), it wasobserved that the melt boundaries and cellular structures did not disappear, but only became blurred with increasing time [40].. Riccardo et al. applied heat treatment to 18Ni 300 maraging steel produced by additive manufacturing at different temperatures (460°C, 490°C, 540°C, 600°C) and durations (8 hours, 4 hours, 1 hour 10 minutes). When the SEM images are examined, it was observed that the cell boundaries became visible as the temperature increased or the austenite phase precipitated at the intragranular boundaries with excessive aging [41]. Yao et al.'s 18Ni 300 maraging steel produced by additive manufacturing was subjected to solution heat treatment at 830 °C for 1 hour, followed by aging heat treatment at 490 °C for different durations (1,4,7 and 10 hours). Intense columnar crystal structures were observed in the SEM image of the untreated sample. They observed that these structures did not disappear at low durations after the aging heat treatment, but some secondary phases were observed at the grain boundary and within the grain with increasing time. In the SEM images of the samples that underwent 7 hours of aging heat treatment, they observed that the columnar crystal structures turned into martensite lattices and there was an increase in the precipitated phases. The reason for this is interpreted that the temperature of the solution heat treatment provides the grain growth and homogenization of the austenite phase, but the rapid cooling and subsequent low temperature aging heat treatment prevents the conversion of austenite into martensite form. We can attribute the reason why martensite forms were not formed in our study. In addition, they interpreted that heat treatments can increase dislocation's amount and intensity and promote the second phase's precipitation [42]. When we compare the studies in the literature with the study we have done, it can be said that we have obtained similar results.

3.2.2 X-Ray Diffraction Analysis

The XRD phase analysis results of the aging heat treatment of maraging steel at 490°C in different atmospheres (air, N_2 and N_2/H_2) and at different durations (6 and 9 hours) were shown in Figure 3.2. The diffractograms of samples heat treated in all samples show the characteristic α-Fe peaks at 45° (110) , 65° (200) and 82,5° (211). When the peak densities of the phases formed in Air-490-6, N_2-490-6 and N_2/H_2-490-6 samples were examined, it is seen that they are almost the same. The intensity of the Fe peaks progressively decreased with the increase in nitriding time. Thats why after the nitriding process, the apparition of new peaks at N_2-490-9 sample was observed. In the study of Jun S. et al., it was subjected to rapid cooling by applying solution heat treatment at 840°C for 2 hours in air atmosphere and then aging heat treatment was applied at 490°C for 2 hours. They detected significant martensite (α) phase and found austenite (γ) phase in low density [43]. When we compared their study with our study, it showed similar results with the air atmosphere aged sample.

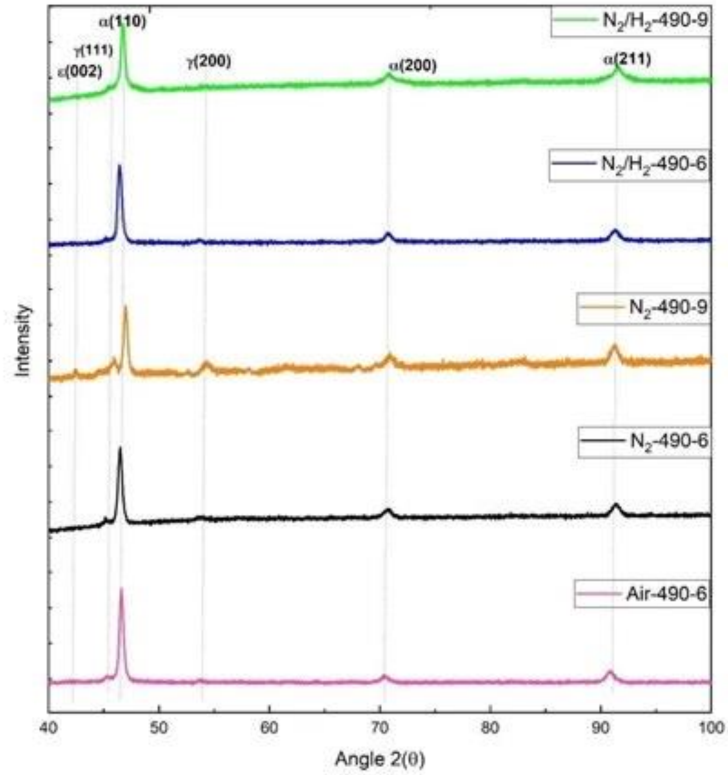


Figure 3.2: XRD analysis results of heat-treated samples.

When examined the results made in N_2 atmosphere, it was observed that new phases were formed in the N_2-490-9 sample with increasing time. In addition, it was investigated that the martensite phases decreased with increasing time compared to the N_2-490-6 sample and austenite phase was formed. In a similar study by Casati R. et al., different heat treatments were applied at different temperatures (460°C, 490°C, 540°C, 600°C) and at different durations (10 minutes, 1, 4 and 8 hours). analyzed their properties. It was observed that the martensite (α) phase decreased with increasing time. They interpreted the reason for this decrease as the transformation of martensite structure into austenite structure with increasing aging time [44]. When we compare this study with our study, the reason for the formation of new phases in the N_2-490-9 sample can be based on this attribution.

It has been observed that the 45˚ peak intensity of the heat treatment samples made in N_2/H_2 atmospheres is lower than the heat treatment samples made in other atmospheres and it decreases further with increasing time. It was also observed that no new phase was formed. In a study by Yan et al., the effect of plasma nitriding of maraging steel on its mechanical properties was investigated at 360°C for 1 to 24 hours in a mixed gas of 25%N_2 + 75%H_2 at low temperature. They stated that the α-Fe (110) peak exhibited lower diffraction with increasing nitriding time, indicating an increase in the amount of solid solution nitrogen element in α-Fe. They also observed that the α-Fe peaks expanded as the nitriding time increased. It was thought that the reason for this widening was nitrogen gradient, residual stresses, grain size reduction and possibly defective structure in the nitrided layers. In this study, the reason can be the decrease in the a-Fe (110) peak of the samples in N_2/H_2 atmospheres with increasing time to the explanations mentioned above [45].

3.3 Mechanical Test Results

3.3.1 Hardness Test Results

The results of the hardness test applied to the samples's section that were heat treated at 490 degrees at different durations and atmospheres, figure 3.2 is shown. Hardness test was carried out in vickers hardness device with 1 kg weight and 10 seconds parameter. When it can be observed at the graph, the highest hardness value belongs to the heat treatment performed in the Air-490-6. The hardness of the heat treatment in air atmosphere was 589 HV. This value was higher compared to both N_2-490-6 and N_2-H2-490-6 samples. The hardness values N_2-490-6 and N_2-490-9 samples were 589 HV and 583 HV, respectively. The hardness values of N_2/H_2 -490-6 and N_2/H_2 -490-9 samples were 587 HV and 579 HV, respectively. The hardness of the 6-hour heat treatment in N_2 and N_2/H_2 atmospheres as slightly higher thatin the same atmospheres at 9-hour. When it can be examined at the heat treatment for 9 hours, it is observed that increasing time affects the hardness negatively.

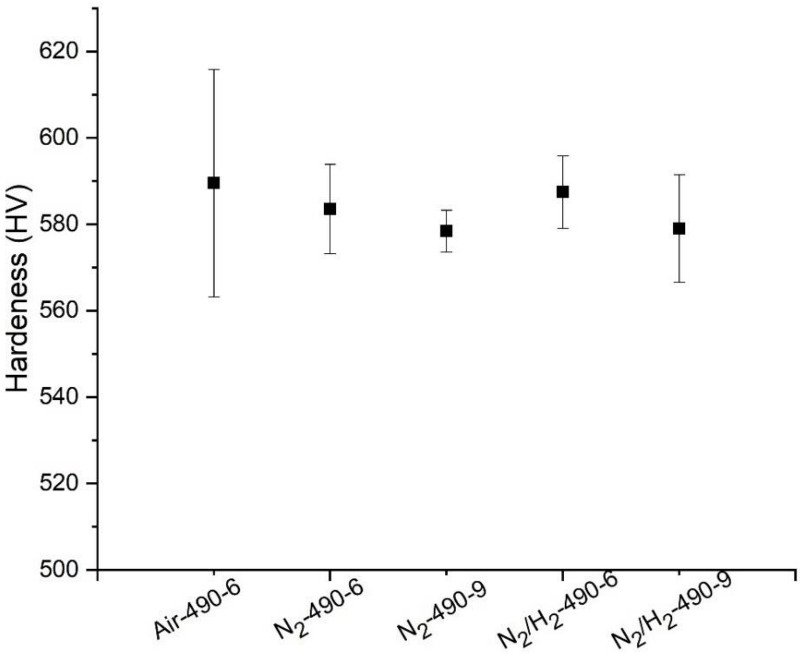


Figure 3.3: The hardness of maraging steel samples heat treated in different atmospheres

In a similar study by Giulia et al., firstly, solution heat treatment was applied to the maraging steels produced by the additive manufacturing method at 940°C for 2 hours. Then, aging heat treatment was applied at different temperatures (450°C, 470°C, 490°C, 510°C 530°C and 550°C) and at different durations (6, 10 and 24 hours). When we examine the hardness results, the hardness value of the heat treatment performed at 490°C for 6 hours is 583 HV [46]. Compared to the work we have done, it shows a similar hardness value with the samples heat treated at 490°C for 6 hours (585 HV). In this case, it was observed that the solution heat treatment had no effect on the hardness results. In a similar study by Zhu H. M. et al., they applied aging heat treatment at 500 °C at different durations (1, 3, 6 and 9 hours) in an argon atmosphere. When they examined the results, they reached the highest hardness value at 6 hours and observed that the hardness value decreased with increasing time [47]. When we compared this study and the studies in the other literature, it can be said that the optimum hardness of maraging steel at 490 °C is 6 hours, which then it deteriorates its mechanical properties by causing excessive aging of the sample with increasing time.

When we examined the heat treatment results of the samples made with N_2/H_2 atmosphere, the increased time did not significantly affect the hardness. In the study of Aydın et al., different heat treatments were applied to 18Ni300 Maraging steel produced by additive manufacturing method. He interpreted the effect of heat treatment applied at 490 °C at different durations (1, 2, 4, 6 and 8 hours) on hardness. It is observed that the hardness increases with increasing time up to 6 hours, and the hardness value decreases as the heat treatment for 6 hours has the highest hardness value. The reason for the increase in hardness with increasing time is that Ni_3Ti intermetallic precipitates and gives hardness to the material. The reason for the decrease in hardeness, it is interpreted after reaching the optimum parameter of 490°C for 6 hours, the conversion of Fe2Mo precipitate in the structure to austenite form by the increasing temperature. As it is known from the literature, austenite is the softest phase of steel [40]. When we examine the results of this study, it supports our findings. In our study, the hardness values decreased after 490°C for 6 hours. When it is compared the hardness results with the XRD phase results, the decrease in α-Fe peaks with increasing time and the transformation from martensite to austenite supports this study.

3.3.2 Tensile Test Results

The stress–strain curves of the- heat-treated maraging steel samples at different parameters are shown in Fig. 3.4. The graphic results of the tensile test are shown in Table 3.1. As shown in Table 3.2, the air atmosphere sample exhibited yield strength (YS) and ultimate tensile strength (UTS) of 2000 MPa and 2005 MPa, respectively. The strength of the sample upon N_2-490-6 was obtained the lowest UTS of 1862 MPa, indicating that heat treatment resulted in a decrease in strength. However, there are obvious improvements in YS and UTS of the samples after aging treatments for N_2/H_2 atmosphere at 490 °C. The YS and UTS are improved to 1974 MPa and 1972 MPa, respectively, after aging heat treatment for N_2/H_2-490-6. The YS and UTS are improved to 1970 MPa and 1968 MPa, respectively, after aging heat treatment for N_2/H_2-490-9. Compared to N_2/H_2 atmosphere heat treatment condition, the N_2-490-6 and N_2-490-9 samplesamples exhibited slightly lower YS and UTS after the heat treatment. When we examine the results of the N_2-490-6 sample, the lowest UTS is 1862 MPa.

In this context, this samplesample results shows there is no improvement of the mechanical properties. It is observed that, as compared to the air atmosphere sample-sample, the nitrided samplesamples for N_2/H_2-490-9 exhibit an increase in ultimate tensile strength (UTS) and 0.2% yield stress (0. 2% YS) and also a decrease in percentage elongation to fracture (%El).

Table 3.2: Tensile properties of the heat-treated Maraging steel samples.

Property	**Air-490-6**	**N_2-490-6**	**N_2-490-9**	**N_2/H_2-490-6**	**N_2/H_2-490-9**
UTS (MPa)	2005±15	1862±15	1973±15	1972±30	1970±63
0.2 % YS (MPa)	2000 ±11	1860±13	1865±8	1974±10	1968±5
% El	5.7±0,3	6.8±0,3	7.6±0,3	6.4 ±0,4	5,2 ±0,5

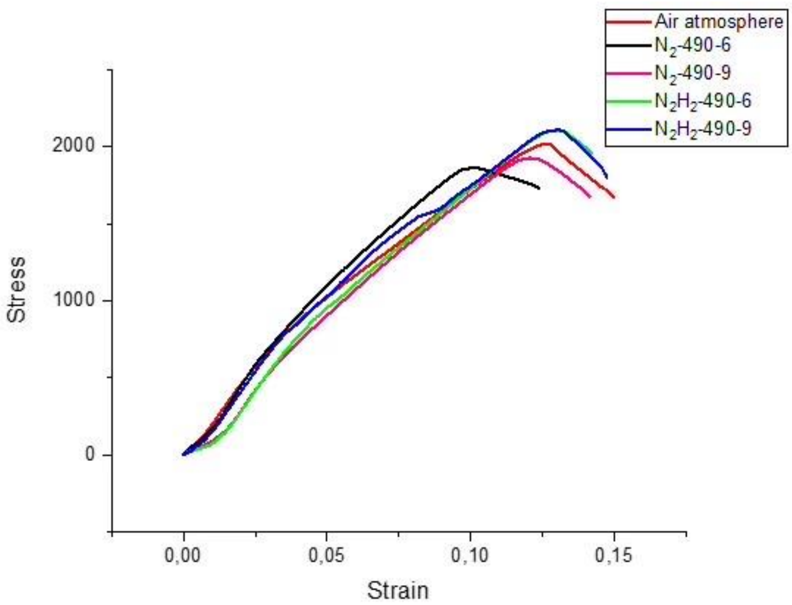
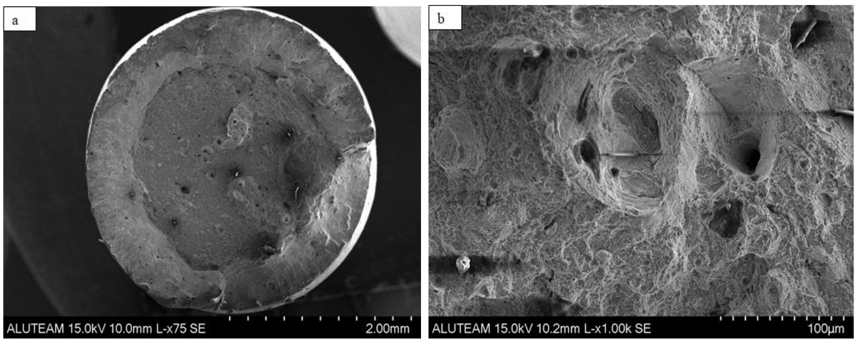


Figure 3.4: Representative tensile stress-strain curves of the heat-treated samples

The fracture surface SEM analysis result of maraging steel samples subjected to the tensile test after the test is as in Figure 3.5. When it can be examined the fracture surface SEM images of the Air-490-6 sample in Figure 3.5 (a-b), it exhibited a ductile diffraction appearance. The diffraction necking appearanced of this sample and its indented surface appearance indicate that it behaves ductilely. When the images compared it with the elongation results, it supported this result. Figure 3.5 (c-d) When it can be examined the N2-490-6 sample, it exhibited a spongy appearance.

It showed more ductile behavior compared to the Air-490-6 sample. Figure 3.5 (e-f) N_2-490-9 sample showed a similar image to N_2-490-6 sample. When it is examined at the tensile test elongation results, the closeness of the values supports that this behavior was similar. When it is observed at the sample in Figure 3.5 (g-h) N_2/H_2-490-6, although there are no spongy structures like the samples made in the N_2/H_2 atmosphere, its indented surface shows that it exhibits ductile behavior. Figure 3.5 (i-i) N_2/H_2-490-9 sample's fracture surface image showed that it exhibits a semi-ductile-semi-brittle behavior. While some of them exhibit an indented structure, some of them show a flatter structure. The reason for the decrease in elongation with increasing time in samples made in N_2/H_2 atmospheres can be attributed to this behavior. In a similar study by Zhu et al., they investigated the effect of aging heat treatment applied to maraging steel at 500°C at different durations. They examined the fracture surface SEM images of the heat-treated tensile-tested samples. Looking at the results, it was observed that the sample, which was heat treated for 6 hours at 500°C, exhibited a ductile behavior after plastic deformation. They commented that the reason for this is that during the tensile test process, the sample undergoes a large plastic deformation and voids occur in the precipitates and defects. It exhibited similar fracture surface behavior with our study [47].



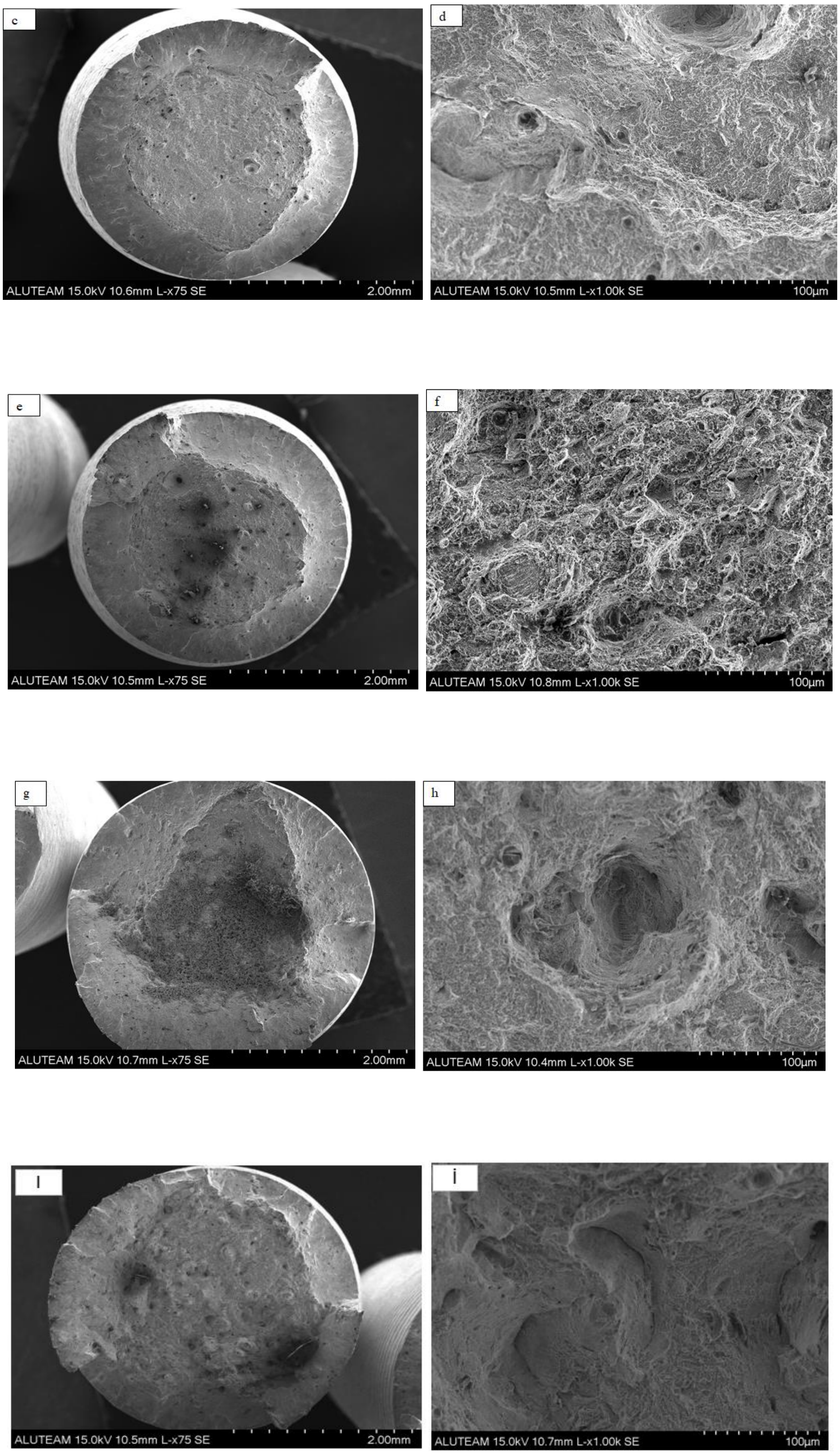


Figure 3.5: Fractured surface SEM images of tension fracture, (a-b) Air-490-6, (c-d) N_2-490-6 (e-f) N_2-490-9, (g-h) N_2/H_2-490-6, (ı-i)) N_2/H_2-490-9.

3.3.3 Wear Test Results

Wear is defined as the change that occurs by the separation of small parts from the surfaces of the material used for mechanical reasons. In a wear system, base material, counter material, intermediate material, load and movement are the basic elements of wear [48]. Figure 3.6 shows the variation of the friction coefficient between the alumina ball and the sample during the wear tests of the maraging steels produced by additive manufacturing, which were heat treated in different atmospheres and at different durations. Wear rate values are transferred to Table 3.3. The sample with the worst wear resistance is the Air-490-6 sample. We can say that the wear resistance is badly affected with increasing time. Figure 3.6 shows how deep these samples can go during the abrasion test. As seen in Figure 3.5, N_2/H_2-490-9 sample has the highest friction coefficient. From this, it can be said that the positive effect of the nitriding process on maraging steels cannot be determined as the processing time increases. When we examine Figure 3.6, it is seen that the abrasion loss of the Air-490-6 sample is higher than the other samples. The wear test results from the welding phenomenon that occurs especially in the metal-metal wear pair, which makes sliding friction with each other. The stresses on the sliding surfaces reach the yield stress limit even with small loads. Adhesive wear is directly proportional to the normal load affecting the surface, through sliding, and the surface hardness of the material being worn. Since the hardness test measurement we have done is made from the center, there is no relationship between them. Also friction occurs as a result of energy loss, and wear is a cause of material loss that cannot be recovered. It is not possible to establish a relationship between friction and wear. The frictional resistance between different material pairs may be the same. However, the difference in the amount of wear between them can be 100 times or more [48].

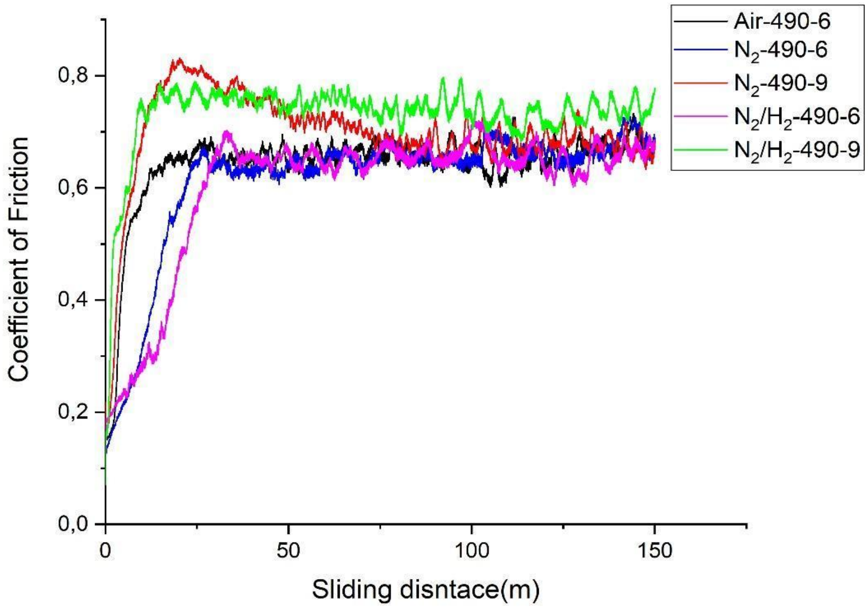


Figure 3.6: Friction coefficient with time.

Tablo 3.3: Wear rate values of samples aged at different durations and atmospheres

Sample Name	Wear Rate (mm^3/m)
Air-490-6	$8.762x10^{-5}$
N_2-490-6	$7.457\ x10^{-5}$
N_2-490-9	$8.821x10^{-5}$
N_2/H_2-490-6	$7.325x10^{-5}$
N_2/H_2-490-9	$8.436x10^{-5}$

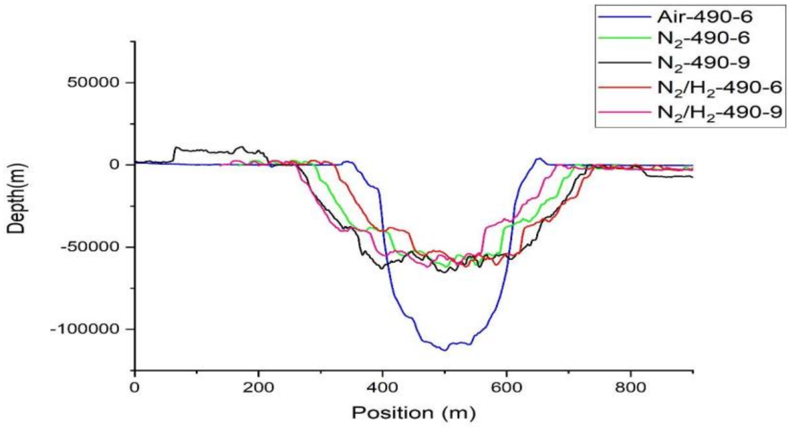
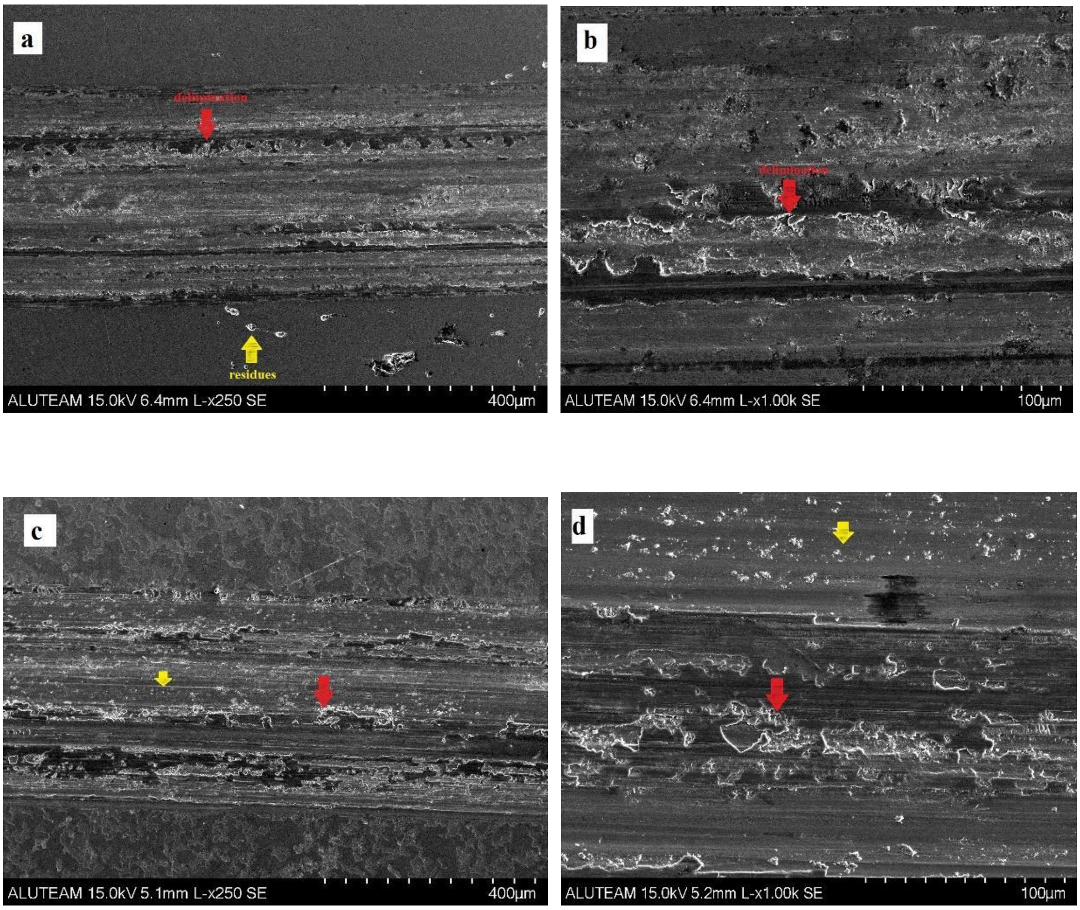


Figure 3.7: Profile image of wear tracks of samples aged at different durations and atmospheres

In a similar study, Hong et al. investigated the effect of plasma nitriding on the mechanical properties of maraging steel produced by SLM method. In this study, T6 heat treatment (solution at 900°C for 2 hours followed by aging at 480°C for 4 hours) was applied. In this study, they carried out the wear test with Si_3N_4 balls. When they analyzed their results, they interpreted that all nitrided samples exhibited lower coefficients of friction and less wear loss when compared to the unheat-treated SLM sample, indicating that the wear resistance of SLM 18Ni300 steel can be improved by nitriding. When we compare this study with our study, as the aging process time increases, the nitriding process affects the wear negatively, while in this study, the nitriding process shows that the wear resistance is affected positively. This can be interpreted as the fact that the Si3N4 alloy ball in their study performs less wear loss as a softer than the $Al2O_3$ ball in our study or the nitriding durations differ [49].

The post-wear SEM images were shown in Figure 3.8. When it examined at the images of the air sample, there were traces of wear and many small wear residues (Figure 3.8 (a-b)).Wear residues appear as light colored particles (shown by yellow arrows) . This shows that the material has adhesive wear behavior. Adhesive wear occurs in materials with ductile behavior. It is seen that there are delaminations around the deep abrasion seen in Figure 3.8b (shown by red arrows). Delaminations are formed from eroded fragments formed during wear. The presence of wear marks and the presence of inflated structures negatively affect the wear feature. Figure 3.8(c-d) and (e-f) images give information about the wear properties of N_2-490-6 and N_2-490-9 samples, respectively. It has been observed that the wear properties of this sample are more worn than the air sample and there are more wear residues. When we compare the samples heat-treated in N_2 atmosphere within themselves, the wear residues became rarer as the aging time increased. Figure 3.8 (g-h) and (i-i) images give information about the wear characteristics of N_2/H_2-490-6 and N_2/H_2-490-9 samples, respectively. When we examine the image, it is seen that there are declinations in the structure (indicated by the red arrows) in general. The wear marks appear brighter than the Air-490-6 sample. Materials with good wear resistance show brighter marks [50]. If we compare the samples heat-treated in N_2/H_2 atmosphere among themselves, we it can said that the wear resistance increases as the aging time increases.



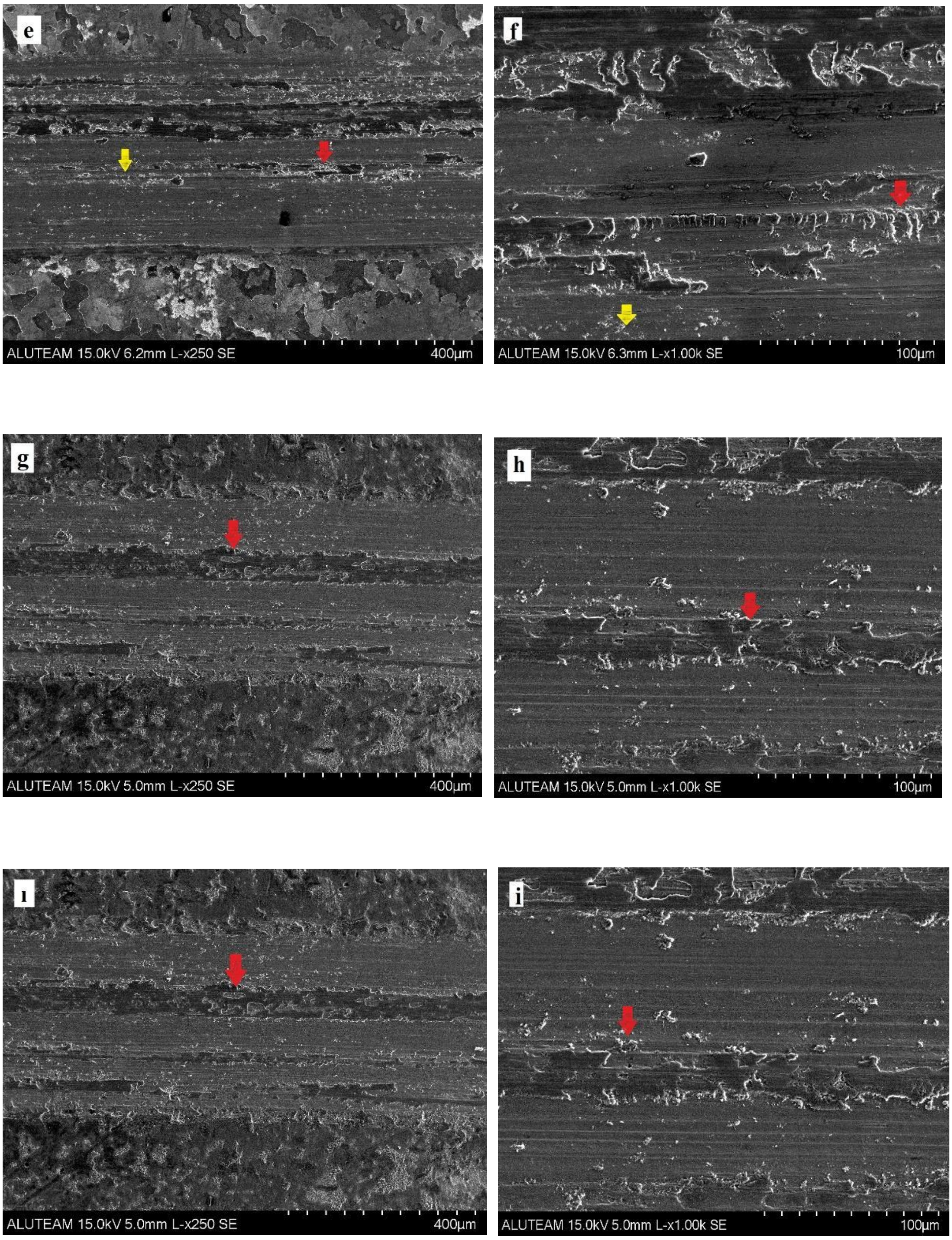


Figure 3.8: SEM images after wear test, (a-b) Air-490-6, (c-d) N_2-490-6 (e-f) N_2-490-9, (g-h) N_2/H_2-490-6, (ı-i)) N_2/H_2-490-9.

3.3.4 Corrosion Test Results

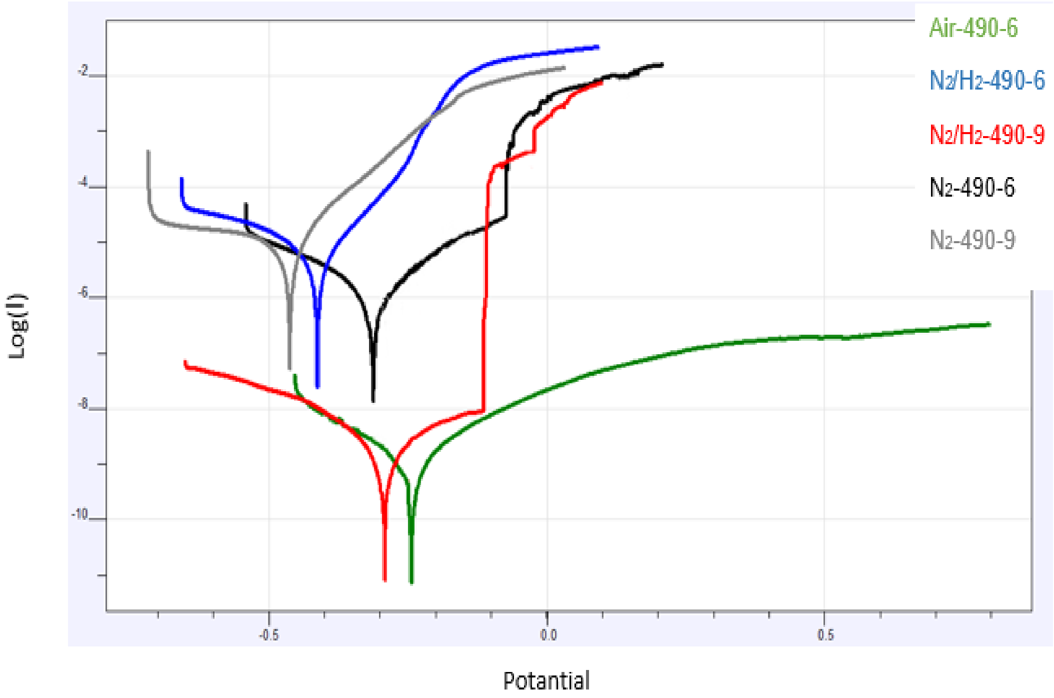


Figure 3.9: Tafel corrosion test curves of the heat-treated samples.

Tablo 3.4: Corrosion results after heat treatment samples

Sample Code	**E_{corr}(V)**	**I_{corr}(A/cm^2)**	**Corrosion Rate mm/y x 10^{-3}**
Air-490-6	-0,23662	2,05 x10^{-9}	2,62
N_2-490-6	-0,31472	9,02 x10^{-6}	0,29
N_2-490-9	-0,4617	4,80 x10^{-7}	1,50
N_2/H_2-490-6	-0,4125	5,93 x10^{-7}	1,93
N_2/H_2-490-9	-0,2910	3,25 x10^{-8}	0,97

The corrosion tests of the samples, which were subjected to aging heat treatment in different atmospheres and durations, were examined with results. Figure 3.9 showed the graph of the tafel corrosion test of the aging heat treatment of maraging steel at 490°C in different atmospheres (air, N_2 and N_2/H_2) and at different durations (6 and 9 hours). Corrosion potentials, corrosion current densities and corrosion rates were listed in Table 3.4. Figure 3.9 showed that the onset of corrosion was not the same in almost all samples. The reason why the starting points were not the same when we examined the corrosion results may be that the heat treatment at different durations at the same temperature changed the corrosion behavior in table 3.4.

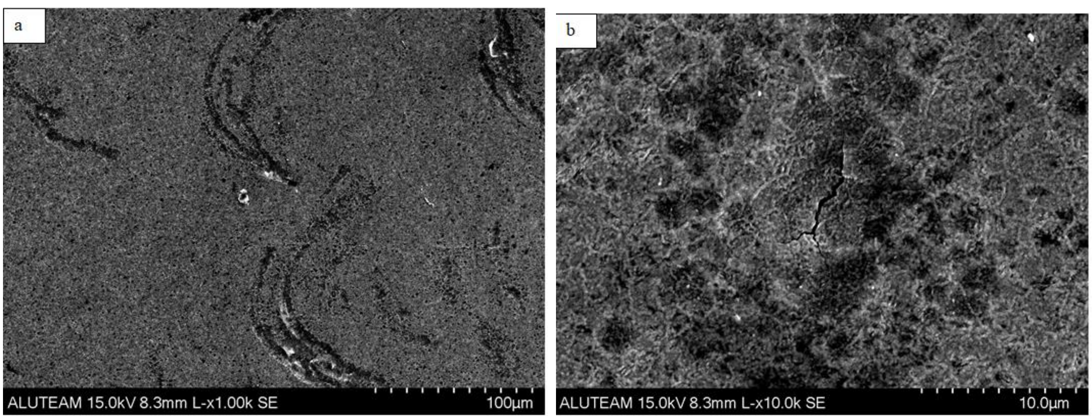
When we examined the corrosion results of the heat treatment applied to N_2/H_2 atmospheres, it has been observed that the icorr and vcorr values decrease as the treatment time increases. As the processing time increases, it is seen that passive film structure is formed in the N_2/H_2-490-9 sample. In a study by Almandoz et al., they investigated the effect of temperature by performing plasma nitriding on maraging steel at a constant time and at different temperatures. When they examined the results, they observed that passive film was formed in all nitrided samples [51]. They commented that this protects the material better regardless of the processing temperature.

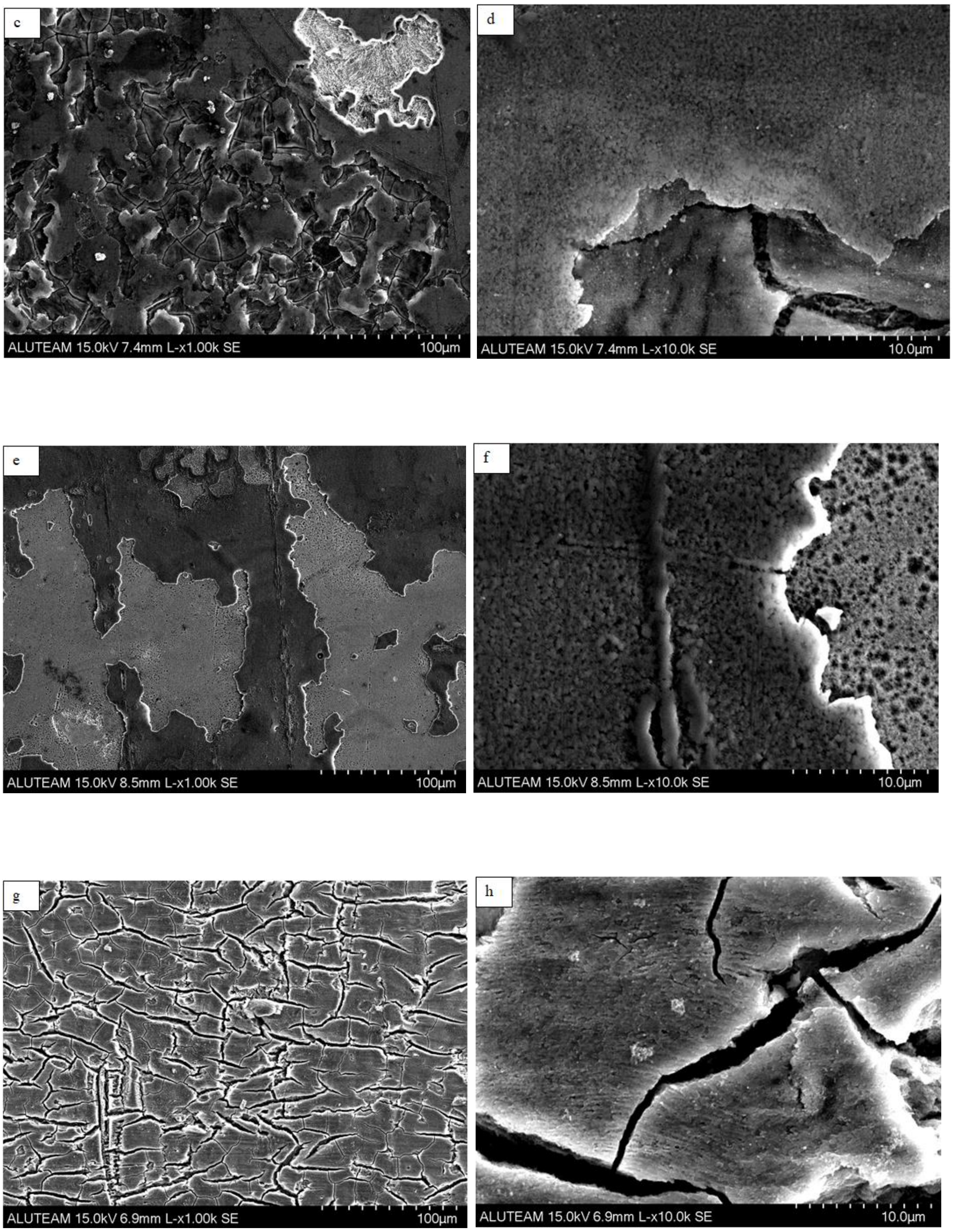
In the corrosion study of Leon et al., the following were mentioned about ikor; the lower the corrosion current, the higher the passivation tendency and the lower the corrosion rate. Therefore, they interpreted that surfaces with lower corrosion current perform better in aggressive environment [52]. When compared with our study, we can say that the N_2/H_2-490-9 sample exhibits a good behavior against corrosion.

In a similar study by Shen H et al., low alloy steels were plasma nitrided with NH_3 and N_2 gas mixture at different temperatures and at different durations. When they examined the results, they observed that the corrosion resistance increased by decreasing the icorr and vcorr values with increasing time at 560°C and a passive film was formed in the nitrided samples. They commented that the reason for this is that the white layer formed after the plasma nitriding process improves the corrosion resistance. In addition, when the SEM images of the nitrided samples after corrosion were examined, the corrosion pits and size tended to decrease as the white layer thickness increased with increasing time. They interpreted this trend as indicating that the thicker white layer can help improve the corrosion resistance of low alloy steel [53].

In a similar study by Özer et al., they compared the corrosion behavior of the construction sample with the aging heat treatment (490°C for 6 hours) applied to the maraging steel in air atmosphere. When they examined the results, they observed that the pore morphology of the aging heat-treated sample did not differ from the construction sample. Therefore, they interpreted that it exhibited the same corrosion behavior. The Air-490-6 sample that we compared with our study and the construction samples in their study show the same results. It can be said that the aging heat treatment of Burdan maraging steels in air atmosphere has no effect on the corrosion behavior [54].

Surface morphology and SEM images after electrochemical test were shown in Figure 3.9. In all samples, it was observed that the molten pools, grain boundaries, and crack areas were corroded. It can be said that there is a decrease in cracks with the increase of the processing time, which positively affects the corrosion behavior. When we compared the samples made in N_2 and N_2/H_2 atmospheres, it is observed that there are not many cracks in the N_2-490-6 sample, but there are cracks on the surface of the N_2/H_2-490-6 layer due to internal stresses.It was observed that the corrosion behavior improved as the aging process increased in both atmospheres.

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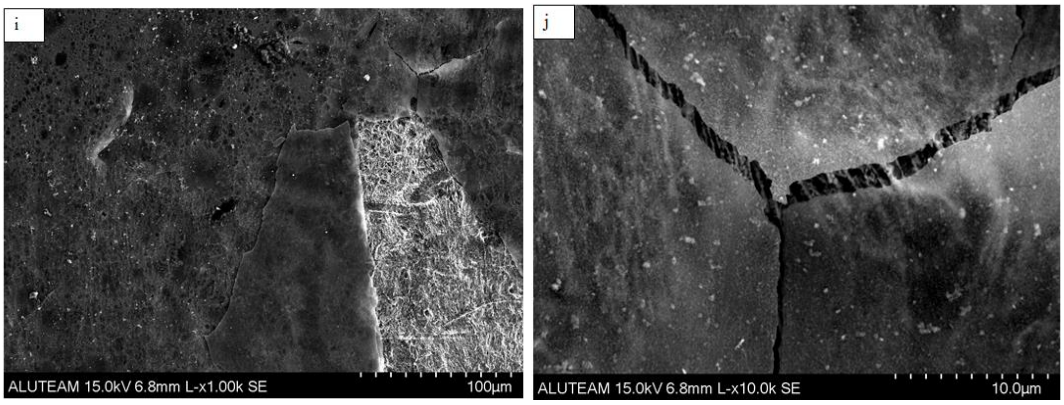


Figure 3.10: SEM images after corrosion, , (a-b) Air-490-6, (c-d) N2-490-6 (e-f) N2-490-9 , (g-h) N_2/H_2 -490-6, (ı-i)) N_2/H_2 -490-9.

3.3.5 EDX Analyzes of the Surfaces

Figure 3.11 shows the EDS analysis image made to the SEM image of the lateral surface of the N_2/H_2 -490-6 sample. The results of the analysis are presented in Table 3.5. Spectrum 5 was located on the outermost surface. When we look at the EDS results, it was observed that the spectrum 5 layer is rich in nitrogen, while it is observed that this situation decreases as we go down from the outer surface to the inner layers. The reason for the decreased of the N element towards the inner layers can be attributed to diffusion. The reason that Fe element appeared in small amounts in Spectrum 5 is the formation of Fe_3N_4 compound on the surface. When the element percentages are examined, it was observed that there are only changes in Fe and N elements, while there were no noticeable differences in the ratios of other elements.

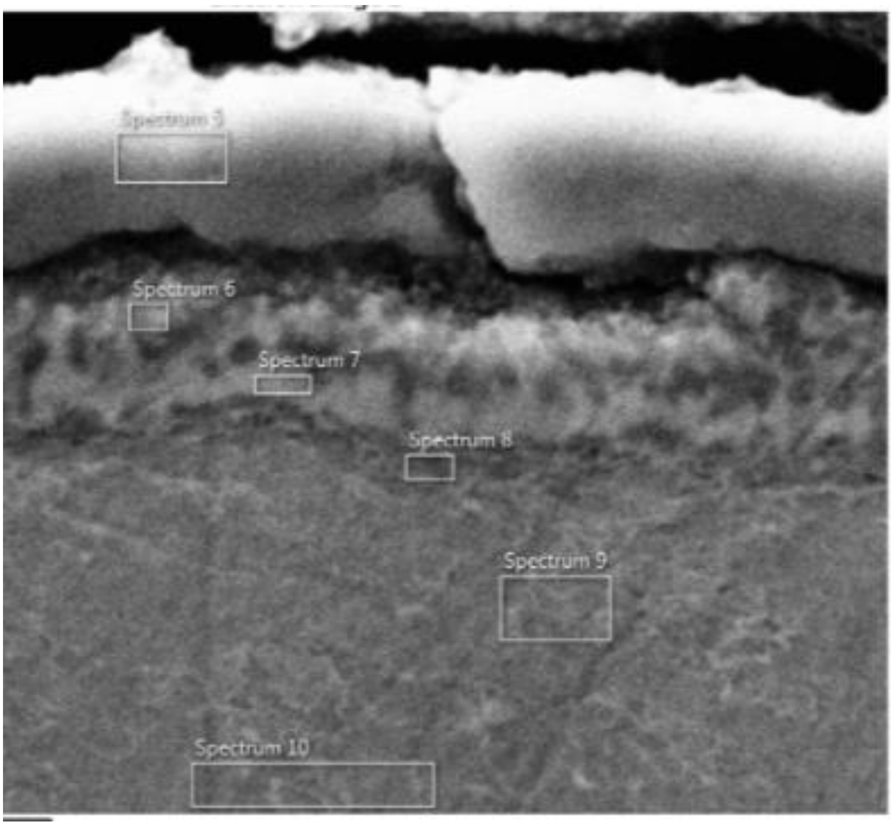


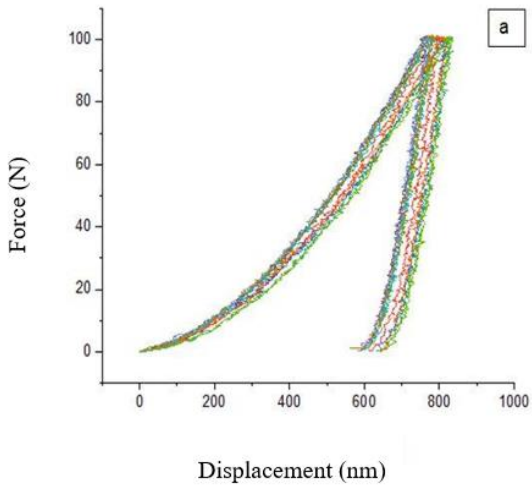
Figure 3.11: SEM images of N_2/H_2-490-6

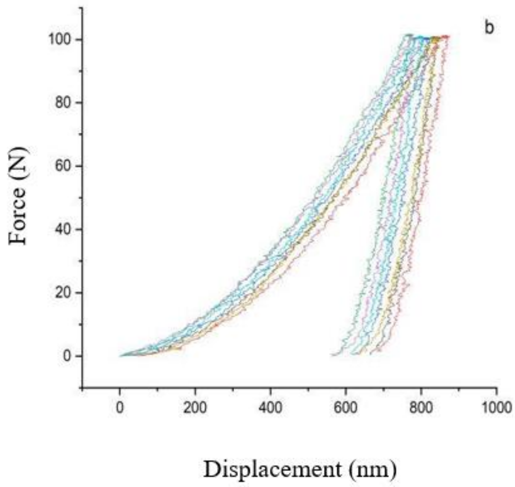
Tablo 3.5: EDS analysis resutls

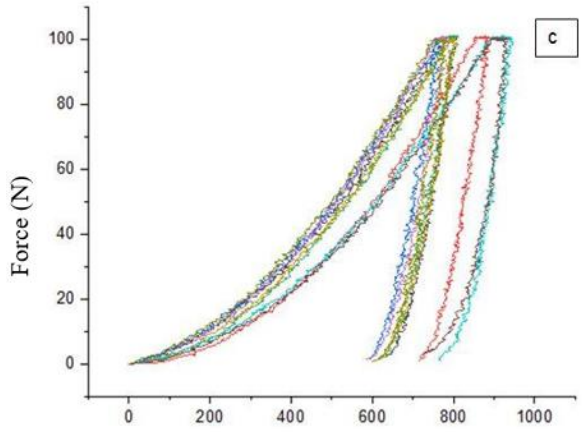
Element	Spectrum 5 Atomic Weight%	Spectrum 6 Atomic Weight %	Spectrum 7 Atomic Weight %	Spectrum 8 Atomic Weight %	Spectrum 9 Atomic Weight %	Spectrum 10 Atomic Weight %
Fe	36.88	49.75	60.94	60.54	60.15	59.84
Co	7.50	8.24	8.19	8.33	8.11	8.64
Ni	16.79	19.26	17.49	16.84	17.11	16.74
Mo	3.46	3.75	3.29	3.30	3.27	3.23
Ti	0.86	1.15	0.79	0.70	0.81	0.99
Al	1.15	0.63	0.63	0.84	0.83	0.89
N	32.80	17.22	8.67	9.46	9.72	9.67
Si	0.56	-	-	-	-	-

3.3.6 Nanoindentation Analysis

Figure 3.11 shows the graph of the nano-indentation test results of the aging heat treatment of maraging steel at 490°C in different atmospheres (air and N_2/H_2) and at different durations (6 and 9 hours). 10 tests were performed for each sample. The graph shows all of these tests. The results in the graph are transferred to Table 14. Considering the hardness results, the sample with the highest hardness is Air-490-6. When we compare the nano-indentation results of heat treatments in N_2/H_2 atmosphere compared to air atmosphere, it can be said that it affects the hardness negatively. An increase in hardness was observed with increasing time for heat treatment in N_2/H_2 atmosphere.







Displacement (nm)

Figure 3.12: Graphs of nano-indentation analysis results; (a) Air-490-6; (b) N_2/H_2 -490-6; (c) N_2/H_2-490-9.

Table 3.6: Nanoindentation test results

Sample	**HV**	**Hmax (nm)**
Air-490-6	810,66±3,62	768,81±7,29
N_2/H_2-490-6	734,40±21,4	814,50±9,50
N_2/H_2-490-9	784,96±19,45	785,48±13,30

Chapter 4

4. Conclusion

The results of the aging process applied to the maraging steels produced by the dmls method, which is one of the additive manufacturing methods, in different atmospheres and durations can be summarized as follows.

- To summarize the microstructure features in general, coaxial cellular structures and stripes are found in SEM images. It is seen that increasing temperature blurs the boundaries of the melt reservoir, but it is not enough to completely destroy it. In the XRD results, the same phases appear in all samples, but an additional Ɛ-F_3N phase was formed in the N_2-490-9 sample. The nitride layer was confirmed by EDS.

- We can interpret its mechanical properties in general as follows. Increasing time decreased hardness. In the tensile test results, the strength values of all samples were quite close to each other, the sample with the lowest strength is N_2-490-6. In the wear test, the sample with the worst wear resistance is Air-490-6. Increasing time had a negative effect on wear resistance.

- In the corrosion results, the nitrogen atmosphere gave more positive results than the air atmosphere. When we look at the Archimedean tests, we can say that the density values of the samples are very close to the values in the literature, and we can say that they were produced successfully by the additive manufacturing method.

- Considering the results of nano-indentation analysis, the sample with the highest hardness is Air-490-6. When we compare the nano-indentation results of heat treatments in N_2/H_2 atmosphere compared to air atmosphere, it can be said that it affects the hardness negatively. It was observed that the hardness increased with increasing time in the heat treatment carried out in N_2/H_2 atmosphere.

When interpreted in general; It was observed that protective atmospheres ($N_2$and N_2/H_2) improved their mechanical properties compared to air atmosphere, but increased time slightly reduced hardness, shrinkage and wear results. The best mechanical results were obtained in heat treatments applied for 6 hours. Therefore, we can be determined the 6-hour heat treatment as the optimum time.

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