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Effect of nitriding time and temperature on case depth in AISI H13 steel

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Abstract
In this study, the formation and behavior of the nitrided layer in AISI H13 tool steel were investigated through a controlled gas nitriding process. The effects of temperature and treatment duration on the development of this layer were analyzed. Prior to nitriding, the steel underwent a thermochemical treatment consisting of quenching followed by tempering to enhance its mechanical properties. Among the samples analyzed, the one with a nitrided layer thickness of 0.01 inches showed the best performance, reaching a surface hardness of 68 HRC and a core hardness of 39 HRC. Microhardness measurements were obtained using a Brinell hardness tester, while metallographic analysis was performed with a Vickers microhardness tester. These methods allowed for a direct correlation between the characteristics of the nitrided layer and mechanical behavior. The findings provide a basis for optimizing the gas nitriding process in AISI H13 steel to improve its durability and performance in demanding industrial applications.

Keywords*: Nitriding, hardness, AISI H13, heat treatment, nitrided layer.*

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I. Introduction

AISI AISI H13 steel is widely used in hot-working operations, especially in the manufacturing of injection molds and die-casting tools, due to its excellent resistance and toughness at high temperatures [1]. Its chemical composition grants it superior properties, such as high resistance to thermal fatigue, exceptional heat tolerance, remarkable toughness and ductility, and good tempering stability [2]. The gas nitriding process using ammonia involves three key phases:

Ammonia dissociation: At elevated temperatures, ammonia partially decomposes into atomic nitrogen and hydrogen, as shown in Equation 1:

$$2NH_3 \rightarrow 2N + 3H_2 \qquad (1)$$

The atomic nitrogen generated in this reaction is responsible for initiating the nitriding process [3].

Absorption of nitrogen in alpha ferrite (Feα): Atomic nitrogen diffuses into the surface of the steel, forming an interstitial solid solution. As nitrogen accumulates, it reacts with iron to form stable nitrides such as the ε-phase (Fe_4N) and the γ′-phase (Fe_2N and Fe_3N), as represented in Equation 2 [3]:

$$N + xFe \rightarrow Fe_xN \qquad (2)$$

Diffusion of nitrogen into the subsurface: After the formation of the compound layer on the surface, nitrogen continues migrating toward the substrate, generating a gradient that gives rise to two distinct regions: a compound layer (commonly known as the “white layer”) and a diffusion zone below it, where nitrogen dissolves into the steel’s crystal lattice. This structure significantly improves the material's resistance to wear and fatigue under contact stresses. Unabsorbed atomic nitrogen recombines into molecular nitrogen, thus ceasing its involvement in the nitriding process, as indicated in Equation 3 [3]:

$$2N \rightarrow N_2 \qquad (3)$$

In its untreated state, H13 steel already exhibits favorable mechanical and physical characteristics, such as high resistance at elevated temperatures, excellent wear resistance, and great robustness [4]. However, gas nitriding is widely recognized as an effective method to further enhance the surface properties of this steel, particularly its resistance to wear, corrosion, and thermo-mechanical fatigue [5].

After the nitriding process, AISI H13 exhibits improved mechanical performance, with a significant increase in surface hardness and greater wear resistance [6]. Its corrosion resistance is also enhanced, a crucial factor in aggressive operating environments [7]. Reports indicate that nitrided H13 steel typically achieves hardness levels between 50 and 60 HRC [8].

The nitriding process induces microstructural changes in H13, including the formation of nitrides, alterations in crystalline arrangement, localized increases in carbon content, and the appearance of carbides, all of which contribute to enhanced performance [9].

Thanks to its ability to maintain dimensional stability under thermal stresses and its high wear resistance, H13 is frequently used in plastic injection molding. It is also suitable for forging and stamping operations where components are exposed to high temperatures [10]. Gas nitriding further enhances its tribological properties by reducing the coefficient of friction and increasing wear resistance [11]. However, it should be noted that improper cooling during or after nitriding may reduce the steel's toughness and ductility. Therefore, careful control of the cooling phase is essential to avoid such adverse effects [12].

II. Methodology

2.1 Heat treatments

For the experimental phase of this study, H13 steel samples with dimensions of 4 cm × 1 cm × 1 cm were prepared. Prior to nitriding, the samples underwent a series of heat treatments aimed at improving their mechanical properties. The quenching process consisted of heating the specimens to 980 °C for two hours in a controlled-atmosphere furnace, followed by air cooling. Subsequently, tempering was performed at 600 °C for two hours to relieve internal stresses and stabilize the microstructure.

The gas nitriding process was conducted through five distinct experimental configurations, each defined by specific parameters of time, temperature, and atmosphere. In the first experiment (M1), the treatment cycle consisted of six hours at 510 °C under an ammonia atmosphere with an average pressure of 498 Pa, followed by a diffusion stage of five hours at 520 °C. In the second trial (M2), the nitriding duration was extended to 19 hours at 510 °C, maintaining the same ammonia concentration and including a four-hour diffusion stage at 520 °C.

The third (M3) and fourth (M4) experiments were conducted with longer exposure times 25 and 30 hours, respectively at a temperature of 520 °C under an ammonia atmosphere of 747 Pa. Unlike the previous trials, these tests did not include a diffusion stage. The fifth and final experiment (M5) involved a nitriding cycle of 25 hours at 520 °C under an ammonia atmosphere of 623 Pa, followed by a diffusion phase of six hours at an elevated temperature of 540 °C.

Throughout all experimental procedures, both temperature and atmospheric composition were systematically monitored every hour. This ensured strict adherence to the predetermined conditions for each trial and allowed for a reliable comparison of the effects of the various treatment parameters on the formation of the nitrided layer [13].

The specific parameters for each nitriding treatment are summarized in Table 1, which details the conditions of temperature, dwell time, atmospheric pressure, and the presence or absence of a diffusion stage for each sample (M1 to M5).

Table 1: Process Conditions for Gas Nitriding of AISI H13 Steel under Varying Temperature, Pressure, and Time Parameters

SPECIMEN	1	2	3	4	5
CYCLE (HRS)	6	19	25	30	25
AVERAGE TEMPERATURE (°C)	510	510	520	520	520
AVERAGE ATMOSPHERE (Pa)	498	498	747	747	623
AVERAGE DISSOCIATION	60-70	60-70	30-40	30-40	30-40
DIFFUSION	SI	SI	NO	NO	SI
HOURS OF DIFFUSION	5	4	0	0	6
DIFFUSION TEMPERATURE (°C)	520	520	0	0	540

2.2 Metallography

After completion of the nitriding process, the samples were cross-sectioned using a low-speed cutting technique with lubrication. This method was employed to minimize heat generation and prevent any thermal or mechanical alteration of the microstructure. Subsequently, the samples were mounted and subjected to a sequential grinding and polishing process. Initial grinding was performed using abrasive papers of progressively finer grit sizes typically 180, 240, 320, 400, and 600, until a flat and scratch free surface was obtained. Final polishing was carried out with a cloth disc in combination with alumina suspensions of 5 µm and then 1 µm, achieving a mirror-like finish [14].

To reveal the microstructure, the previously polished surfaces were chemically etched using a 5% nital solution, composed of 5% nitric acid and 95% ethanol or methanol. During microscopic observation, the etched face was oriented downward to ensure optimal visibility of the nitrided layer [14]. Afterwards, the surface was repolished to remove the effects of the chemical etching and to prepare the sample for hardness testing. These tests were conducted using a Vickers microhardness tester, whose technical specifications are detailed in Table 2 [14].

Table 2: Technical Specifications of the Vickers Microhardness Tester Akashi MVK-E

CHARACTERISTIC	DESCRIPTION
EQUIPMENT	VICKERS MICROHARDNESS TESTER
BRAND	AKASHI
MODEL	MVK-E
SCALES USED	HV 0.5 (500 GF), HV 1 (1000 GF)
LOAD RANGE	10 GF TO 1 KGF
LOAD APPLICATION	MOTORIZED, AUTOMATIC LOAD TIME CONTROL
DWELL TIME	ADJUSTABLE, TYPICALLY BETWEEN 5 AND 30 SECONDS
OPTICAL SYSTEM	MICROSCOPE WITH OBJECTIVES (10X, 40X, 100X) AND MICROMETRIC OCULAR
ILLUMINATION	ADJUSTABLE HALOGEN OR LED LIGHT
APPLICABLE STANDARDS	ASTM E384, ISO 6507
TYPICAL APPLICATIONS	MICROHARDNESS MEASUREMENT IN METALS, COATINGS, AND HEAT-TREATED SURFACES

2.3 Hardness

Initial hardness measurements were recorded before any heat treatment such as quenching, tempering, or nitriding, using a Brinell hardness tester. The Brinell method involves applying a load of 3000 kgf with a 10 mm diameter carbide ball indenter [15]. Additionally, microhardness profiles were obtained using a Vickers microhardness tester, which employs a 1000 gf load and a diamond pyramidal indenter with a 136° angle [16].

After heat treatment, hardness was re-evaluated to analyze the effects of quenching and tempering. The sample was placed on the anvil of the hardness tester, and a preload was applied followed by a main load of 150 kgf for 10 to 15 seconds [16]. For the analysis of the nitrided layer, microhardness measurements were performed using a 500 gf load. Three successive indentations were made from the surface toward the interior, spaced approximately 3 to 5 µm apart [17]. These indentations allowed for the determination of the nitrided layer depth profile by correlating hardness values with distance from the surface.

The depth of the nitrided layer is defined by an approximate 5 HRC difference between the outer layer and the core, ensuring a clearly defined boundary [18]. The results are typically expressed in both Vickers and Rockwell hardness scales.

III. Results

The alloying elements present in H13 tool steel significantly influence its mechanical behavior, particularly in terms of hardness, wear resistance, and toughness. Chromium, for instance, contributes to increased surface hardness and improves corrosion resistance by promoting the formation of stable chromium carbides. Molybdenum enhances wear resistance and helps withstand thermal fatigue, while also aiding in the retention of ductility at elevated temperatures. Vanadium, although it increases hardness and wear resistance through the formation of fine vanadium carbides, can lead to increased brittleness when present in high concentrations [19]. Table 3 presents the chemical composition of H13 steel.

Table 3: Chemical composition of H13 steel

CHEMICAL ELEMENT	COMPOSITION RANGE (%)
CARBON	0.39
CHROMIUM	10.25
MOLIYBDENUM	1.43
VANADIUM	1
MANGANESE	0.35
SILICON	1
PHOSPHORUS	≤ 0.030
SULFUR	≤ 0.030

The balance of alloying elements in H13 steel plays a crucial role in its response to heat treatment and in its final mechanical properties. Variations in the proportion of specific elements can significantly alter the surface characteristics and performance of the material. For example, a high carbon content may lead to excessive carbide formation at the surface, which could increase hardness but also reduce corrosion resistance due to the formation of a carbide network. Similarly, excessive chromium can promote the development of an oxide layer on the surface during thermal processing, which may enhance corrosion resistance under certain conditions but also affect hardness and surface integrity depending on the structure and adhesion of the oxide [20].

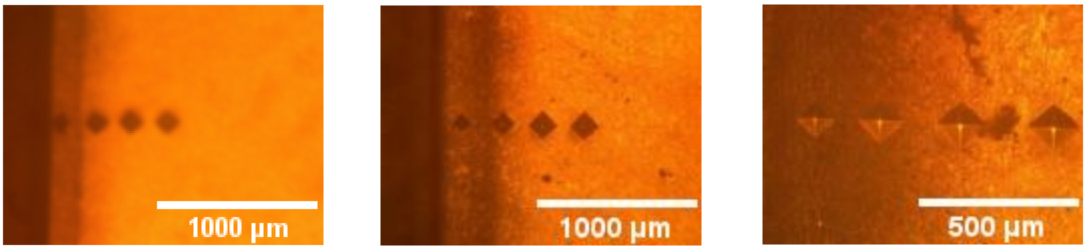
3.1 Metallography

As illustrated in Figure 1, M1, subjected to a gas nitriding process at 510 °C for 6 hours with a dissociation rate between 60% and 70%, did not exhibit the formation of a compound layer (white layer). This result is attributed to the relatively high dissociation percentage, which reduces the concentration of active ammonia in the atmosphere, thereby limiting the nitrogen potential necessary for the formation of the white layer, as discussed in "CAP13 Surface Heat Treatments" [21].

In contrast, M2, which underwent nitriding at the same temperature (510 °C) but for an extended duration of 19 hours under similar dissociation conditions (60–70%), also showed no visible evidence of white layer formation. In this case, the longer exposure time allowed for more effective diffusion of nitrogen into the substrate, favoring the development of a diffusion zone and minimizing the formation of brittle phases on the surface. This behavior is consistent with nitrogen diffusion kinetics, where sufficient time facilitates subsurface hardening without generating a defined white layer, which is commonly composed of ε (Fe_2N and Fe_3N) or γ' (Fe_4N) phases [22].

As for M3, M4, and M5, the nitriding treatments were carried out at a slightly higher temperature of 520 °C, with processing times ranging from 25 to 30 hours and a lower dissociation rate (30–40%). Under these conditions, the samples developed compound layers of varying thicknesses, accompanied by a noticeable decrease in core hardness. This behavior is influenced both by the higher nitrogen potential, resulting from the lower dissociation rate and the prolonged exposure to elevated temperatures, which favors the formation of nitride layers on the surface. Elements such as chromium and vanadium, present in H13 steel, are key factors in this effect, as they form stable nitrides that significantly increase surface hardness. However, these same elements also affect the overall mechanical response by contributing to internal stresses and to the depth and nature of the nitrided layer [23].

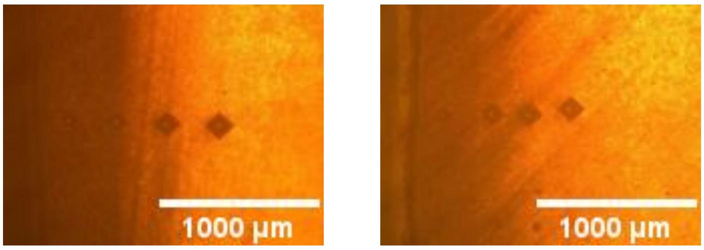
Figure 1: Metallographic Micrographs of H13 Steel Samples After the Nitriding Process



M1)
Without the presence
of a white layer

M2)
Without the presence
of a white layer

M3)
Presence of a thin
white layer



M4)
Presence of a thin
white layer

M5)
Considerable presence
of white layer

3.2 Hardness

The initial hardness measurements for the H13 steel samples were recorded at approximately 217 HB (Brinell hardness) and 240 HV (Vickers hardness), corresponding to an estimated hardness of around 20 on the Rockwell C (HRC) scale. These values reflect the typical condition of H13 steel in its supplied state, characterized by moderate hardness prior to any thermal or thermochemical treatment.

After quenching and tempering processes, the samples exhibited a significant increase in hardness, reaching average values between 40 and 54 HRC. These results are consistent with the established data for H13 tool steels. For example, SISA H13 steel, when subjected to similar heat treatments, typically reaches hardness values between 44 and 52 HRC, in line with the results obtained in this study [24].

To more accurately assess the hardness distribution, core hardness values were determined for each sample using a Vickers microhardness tester. These measurements provide relevant information about the effectiveness of the heat treatment and the steel's response to subsequent processes. Table 4 summarizes the keyprocess variables along with the corresponding hardness results for each sample.

Table 4: Variables and results obtained from H13 alloy samples during nitriding

SPECIMEN	1	2	3	4	5
CYCLE (HRS)	6	19	25	30	25
AVERAGE TEMPERATURE (°C)	510	510	520	520	520
AVERAGE ATMOSPHERE (Pa)	498	498	747	747	623
AVERAGE DISSOCIATION	60-70	60-70	30-40	30-40	30-40
DIFFUSION	SI	SI	NO	NO	SI
HOURS OF DIFFUSION	5	4	0	0	6
DIFFUSION TEMPERATURE (°C)	520	520	0	0	540
SURFACE HARDNESS (HRC)	70	70	68	67	65
CORE HARDNESS (HRC)	54	53	39	37	37
LAYER (IN)	0.005	0.007	0.01	0.012	0.015

A study conducted by the National Autonomous University of Mexico (UNAM) highlights the critical influence of both temperature and exposure time on the formation and evolution of the nitrided layer in alloy steels such as H13 [25]. The development of this layer is closely regulated by the diffusion kinetics of nitrogen atoms within the steel matrix.

In the early stages of nitriding, prolonged exposure facilitates the formation of a surface compound layer enriched with iron nitrides, which contributes to a significant increase in surface hardness. However, when the treatment duration becomes excessive, particularly at high temperatures, a phenomenon known as over-nitriding can occur. Under these conditions, the high nitrogen potential favors deep penetration, which in turn causes a redistribution of interstitial and substitutional elements such as carbon, chromium, and molybdenum towards the core of the material. This migration of elements can lead to surface decarburization and depletion of alloying elements, reducing the effectiveness of the nitrided layer. As a result, the surface hardness may begin to decrease, a behavior that is reflected in the downward trend observed in the final segments of Figure 2 [25].

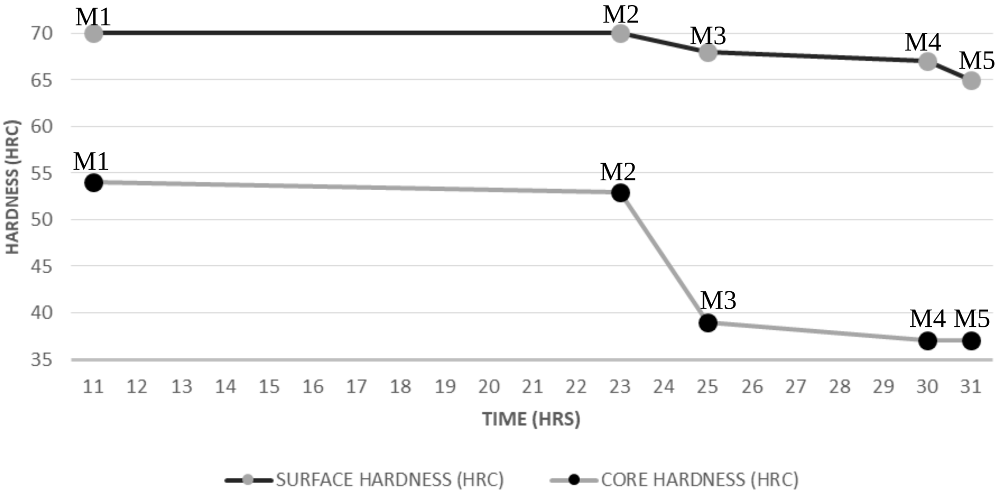


Figure 2: Comparison of Surface and Core Hardness as a Function of Nitriding Time in AISI H13 Steel (M1–M5)

Figure 3 illustrates the correlation between surface hardness and nitriding temperature. According to the findings reported in Moyano Cano's thesis (2008), increasing the process temperature during gas nitriding tends to decrease the surface hardness of H13 tool steel [26]. This reduction in hardness is primarily attributed to the higher diffusivity of nitrogen at elevated temperatures, which facilitates deeper penetration into the material but simultaneously reduces the concentrations of nitrogen and carbon near the surface. As a result, the formation of hard nitride phases becomes less favorable.

Additionally, high temperatures favor the stabilization of less desirable phases, such as γ′ (gamma prime, Fe_4 N), which are more brittle and less wear-resistant compared to the more stable and harder ε (epsilon, with chemical composition varying between Fe_2 N and Fe_3 N) phase. Furthermore, the accelerated diffusion reduces the nitrogen retention time on the surface, which may lead to the formation of a thinner and less coherent compound layer. These effects together reduce both the hardness and the structural integrity of the nitrided surface.

Therefore, identifying an optimal temperature range for the gas nitriding of H13 steel is essential. Within this range, an equilibrium can be achieved between the depth of nitrogen diffusion and nitrogen retention on the surface, allowing the formation of a nitrided layer that offers improved hardness, wear resistance, and thermal performance [26].

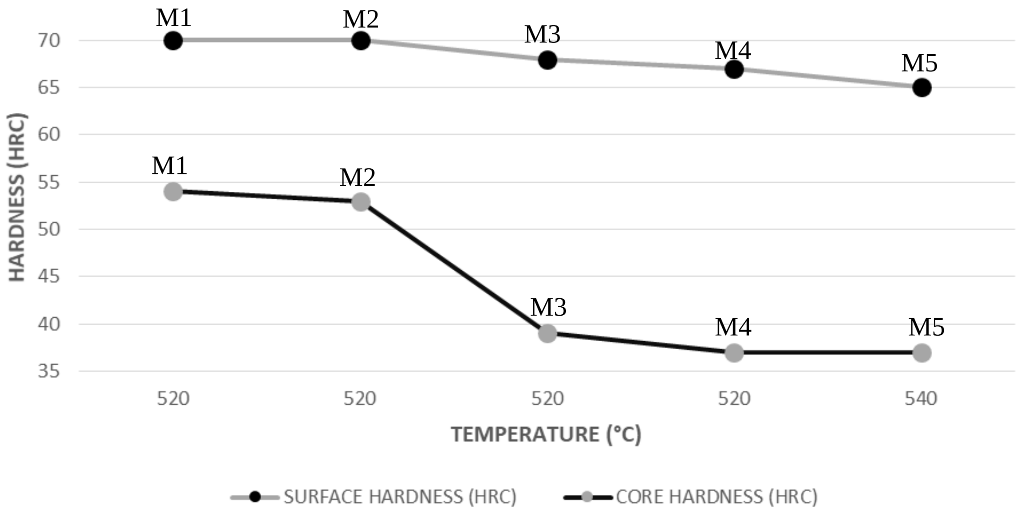


Figure 3: Comparison of Surface and Core Hardness as a Function of Nitriding Temperature in AISI H13 Steel (M1–M5)

Studies conducted by Cifuentes Aya (2012) on H13 tool steel have shown that an increase in the thickness of the nitrided layer is usually accompanied by a gradual decrease in both the surface hardness and core hardness [27]. This phenomenon is mainly attributed to the extended diffusion of nitrogen into the steel matrix, resulting in a reduction of the concentration of carbon and alloying elements such as chromium and molybdenum at the surface. The depletion of these elements reduces the formation of strengthening nitrides in the outermost region, which negatively impacts the overall hardness.

This behavior is clearly illustrated in Figure 4, which shows a downward trend in hardness as the nitrided layer becomes thicker. While moderate growth of the layer can improve surface resistance, beyond a certain threshold, the benefits start to reverse due to the dilution of the main hardening constituents near the surface.

Furthermore, Figure 5 provides a comparative view of the nitrided layer thickness in various samples subjected to different treatment conditions. These discrepancies in layer formation directly influence the mechanical performance, emphasizing the importance of precise process control. Parameters such as treatment time, temperature, and gas dissociation levels must be carefully optimized to achieve a uniform nitrided layer that maximizes surface hardness without compromising the core properties of the material [27].

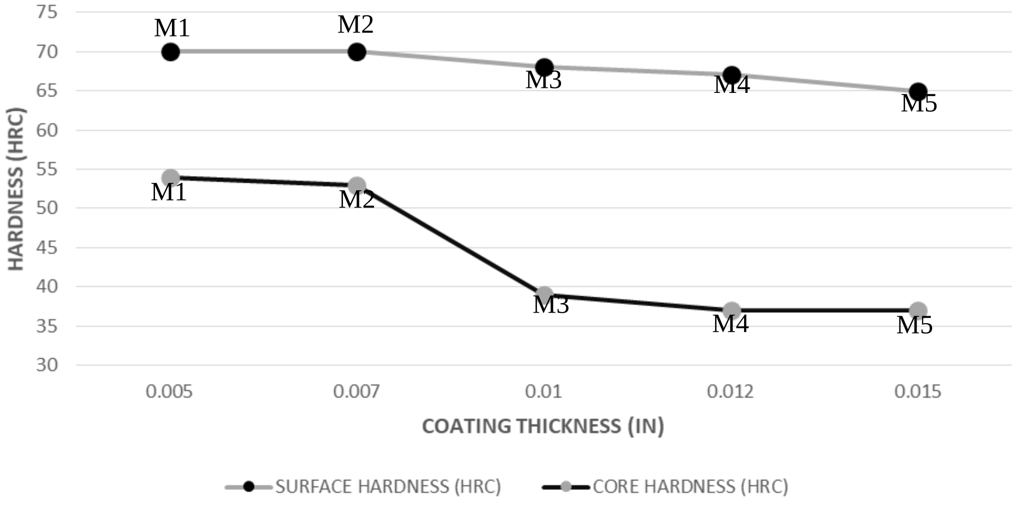


Figure 4: Comparison of Surface and Core Hardness in Nitrided AISI H13 Steel Samples (M1–M5)

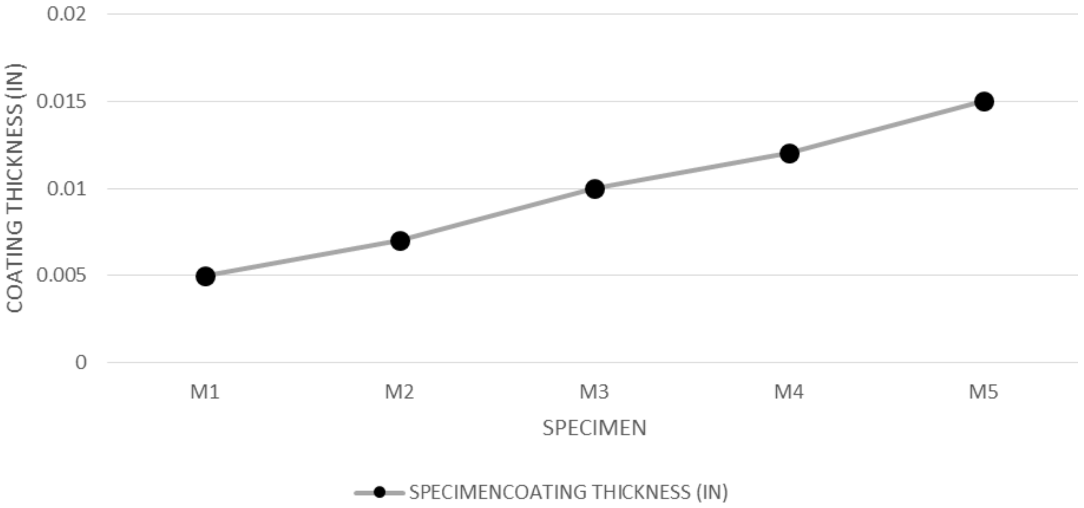


Figure 5: Comparison of the Nitrided Layer in AISI H13 Steel Samples (M1–M5)

IV. Conclusion

The evaluation of the gas nitriding process applied to H13 tool steel has allowed the identification of several critical parameters that govern the effectiveness of the treatment and its influence on the material's mechanical performance:

1. High nitriding temperatures significantly increase nitrogen diffusivity, which promotes greater penetration into the substrate, but at the same time reduces both surface hardness and core hardness due to the depletion of carbon and alloying elements in the outer layer.

2. Prolonged exposure times further contribute to the decrease in hardness, as extended diffusion periods intensify the redistribution of hardening elements, lowering their concentration in the nitrided zone.

3. Although the formation of nitrides improves surface hardness and wear resistance, an excessive thickness of the layer can negatively affect the overall mechanical properties, particularly when overnitriding leads to the migration of elements and fragility.

4. The presence of chromium, molybdenum, and vanadium in the alloy composition is essential for the formation of a stable, wear-resistant nitrided layer. These elements play a key role in improving both hardness and corrosion resistance.

5. Precise control of key process variables, including temperature, duration, and ammonia dissociation rate, is crucial to achieving an optimally thick, uniform nitrided layer with superior mechanical performance.

6. Despite possible reductions in core hardness, a well-optimized nitriding process results in substantial improvements in surface hardness and wear resistance, making H13 steel more suitable for demanding applications involving thermal and mechanical stress.

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