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Influence of Etchants and factors affecting etching duration on microscopic observation of steels

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Abstract

Metallurgy explores metal properties, production, and purification. Alloys, like steels consist of multiple elements, with at least one metal. The etching approaches is important for the proper visualization of microstructure of steels under optical microscope. The research aims to enhance clarity and visibility of images under an optical microscope and to determine the duration for immersion of sample under etchant. The research utilized various etchants, including Nital etchant and Marble's reagent, to enhance the etching approaches for different types of steels. Etchants react with different phases of metals, such as pearlite, ferrite and austenite at varying rates. This reaction causes changes in the color of the phases, which in turn makes it easier to distinguish and observe them under a microscope.In conclusion, etching highlights grain boundaries and phase distribution. Optimal etching time results in a cloudy pattern on the metal surface. This paper also emphasizes on factors affecting etching duration such as heat treatment, material composition, concentration of etchants and rate of cooling alters etching time, affecting pattern formation. Notably, the immersion time in etchants for annealing samples was observed to be higher, opposing with the shorter duration for ice quenching. Efficient etching aids in microstructural analysis, crucial for understanding material properties and optimizing heat treatment processes.

Keywords

Metallurgy, Microstructure, Etching, Heat treatment

1. Introduction

Metals are generally solid materials that are typically hard, shiny, malleable, fusible, and ductile, with good electrical and thermal conductivity. Among various metals, steels have been a foundational material in shaping the modern world which has influenced in industrial revolution, technological advancements and infrastructure development. These steels contain micro-structures which are the arrangement and distribution of the various constituents and phases within steels [1]. The micro-structure of steels is crucial for predicting their mechanical properties, performance, and response to various processing and treatment methods. Therefore, achieving this requires the use of an optical microscope, which necessitates the application of etchants to facilitate observation [2].

Etching is a controlled chemical process used to selectively remove material from the surface of a sample in order to reveal its internal structure. The differential reactivity of different phase contributes to the visual contrast[3]. This helps in revealing the micro-structural features when the sample is examined under microscope. Thus, the crystalline structure (grains, grain boundaries and phase distribution) of the polished surface is revealed by etching with a proper etchant which are the chemical substances. They work by attacking certain components of the material, such as specific phases, while leaving other areas unaffected. This selective dissolution helps to enhance visual contrast between different micro-structural features, making them easier to observe under optical microscope. The choice of etchant depends on the type of material being studied and the specific micro-structural features of interest.For instance, ferrite and pearlite in steels are higlighted using Nital etchant[4].

2. Method and Methodology

In this research, samples of TMT rebar, mild steel rod, and stainless-steel rod, each with a diameter of 1.6cm and a length of 2.5cm, were prepared using a lathe machine to ensure proper handling and secure gripping for the investigation.

2.1 Grinding and Polishing

The machine used for grinding and polishing of sample pieces are[5]:

2.1.1 HandiMet 2 Roll Grinder

The HandiMet 2 Roll Grinder is a convenient and economical instrument for manual grinding applications[6]. It provides a four-step grinding station with controlled water flow. Water activated clamping holds abrasive papers firmly in position during the grinding process. Its excellent flush system removes grilling residue from the grits when the operation is finished.

2.1.2 Lab-pol duo twin Grinder

Lab-pol Duo twin Grinder include grinding and polishing of various material. This machine operates at variable speeds ranging from 50-500 rpm used in laboratories for micro-structure analysis and sample preparation. This machine helps to provide mirror like finish to the sample surface to be observed under optical microscope.

2.2 Etchants Preparation

For the grain structure analysis of steels that were taken into consideration their respective etchant agent was prepared in chemical laboratory with precaution.

2.2.1 Nital etchant

Nital is the etching agent with chemical composition of 90% ethanol and 10% nitric acid (Conc. HNO_3+C_2H_5OH)[7]. The alcohol serves as a diluent to control the etching rate. Nital is used as a etching agent for mild carbon steel.

2.2.2 Marble's Reagent

Marble's Reagent is the etching agent with chemical composition of hydrochloric acid, nitric acid and water (100ml water, 15ml concentrated hydrochloric acid, 5ml concentrated nitric acid)[8]. It is used for revealing the microstructure of stainless steels.

2.3 Optical Microscope

Optical Microscope is used to study grain structure and boundary of different steels. In this research eye piece of 12.5x was used along with objective lens of 40x which in total created 500 times magnification and diameter under observation was obtained mathematically[9].

$$\text{Diameter} = \text{Slide Division} \times \text{Scale} \tag{1}$$

where,
Microscope Slide Division= 36
Scale in Microscope Slide, 1 division= 0.001mm

2.4 Work flow

The initial stage involves gathering TMT rebar, MS rod and stainless steel samples for examination. Following this, the samples undergo preparation, which includes careful handling and gripping to ensure their suitability for testing. Subsequently, sorting and indexing are carried out using techniques like punching or scraping to facilitate organization for further analysis. Nital etchant and Marble's reagent are created within laboratory as per the type of material being studied. Additionally, a range of heat treatment processes such as Normalizing, Annealing, and Quenching are performed to modify sample properties[10]. Moreover, observations and records of the grain structure and boundaries of polished samples under an optical microscope are conducted. The optimal etching duration for different samples is determined through experimentation and iterative testing. Finally, the results regarding etching duration were documented based on the clarity of visibility observed under the optical microscope throughout the entire procedure.

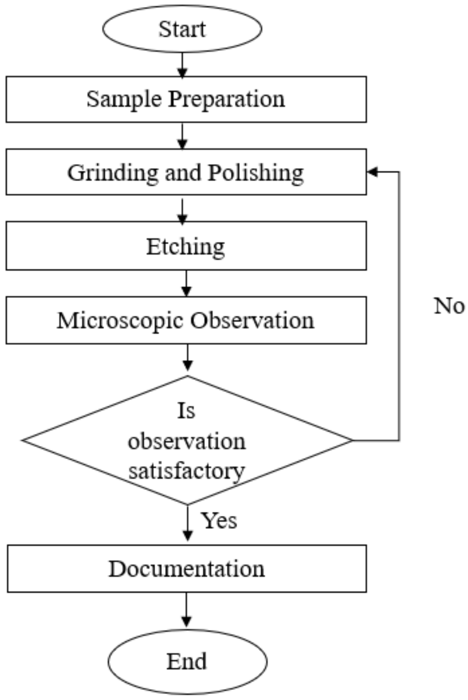


Figure 1: Work flow diagram

2.5 Working of etchants:

2.5.1 Nital Etchant

For ferrous alloys, which are primarily iron-based, the etching reaction involves the formation of iron nitrate:

$$2Fe + 6HNO_3 \rightarrow 2Fe(NO_3)_3 + 3H_2$$

The hydrogen gas evolves as bubbles during the reaction, and the iron nitrate remains on the metal surface[11]. The iron nitrate is typically dark in color and tends to accumulate along the grain boundaries as a result, grain boundaries appear darker than the rest of the grains, providing a clear contrast in the micro-structure[12]. The differential reactivity of ferrite and pearlite to nitric acid contributes to the visual contrast between these phases[13]. This helps in revealing the micro-structural features when the sample is examined under a microscope.

2.5.2 Marble's reagent

The etching reaction involves the formation:
Dissolution of Iron (Fe):

$$Fe + 6HCl \rightarrow FeCl_2 + 3H_2$$

Formation of Iron Chloride ($FeCl_2$):

$$FeCl_2 + 2HNO_3 \rightarrow Fe(NO_3)_2 + 2HCl$$

Formation of Iron Nitrate ($Fe(NO_3)_2$):

$$Fe(NO_3)_2 + 6HCl \rightarrow FeCl_3 + 3HNO_3$$

Iron chloride is often dark in color and accumulate along the grain boundaries as a result, grain boundaries appear darker than the rest of the grains, providing a clear contrast in the microstructure[14]. Ferrite is a phase in stainless steel that is more susceptible to chemical attack by acids like Hydrochloric acid hence appears darker whereas on the other hand, Austenite being more corrosion-resistant, its reactivity towards acids is typically lower than that of ferrite and hence appears brighter[15]. This aids in exposing the microscopic characteristics when the sample is observed through a microscope.

3. Result and Discussion

3.1 Etching Duration:

The etching time for sample pieces were found by performing hit and trial.

3.1.1 TMT Rebar

The etching time for the untreated TMT rebar sample was recorded as 10 seconds using Nital etchant. Table 1 displays the etching durations for TMT rebar following different heat treatment.

Table 1: Etching time obtained after heat treatment from various temperature range

Process	800°C	900°C	1000°C
Annealing	20 sec	20 sec	20 sec
Normalizing	10 sec	10 sec	5 sec
Oil Quenching	5 sec	5 sec	5 sec
Water Quenching	10 sec	10 sec	5 sec
Ice Quenching	5 sec	5 sec	1 sec

3.1.2 Mild steel

The etching time for the untreated mild steel sample using Nital etchant was measured to be 20 seconds. Table 2 illustrates the etching durations for mild steel following various heat treatment procedures.

Table 2: Etching time obtained after heat treatment from various temperature range

Process	800°C	900°C	1000°C
Annealing	20 sec	20 sec	20 sec
Normalizing	10 sec	10 sec	5 sec
Oil Quenching	5 sec	5 sec	3 sec
Water Quenching	8 sec	5 sec	3 sec
Ice Quenching	5 sec	2 sec	1 sec

3.1.3 Stainless steel

The etching duration for the untreated 304 grade stainless steel standard sample was recorded as 10 minutes using Marble's reagent. Table 3 presents the etching times for stainless steel following different heat treatment procedures.

3.2 Factors affecting etching time

The factor affecting etching time were found as follows:

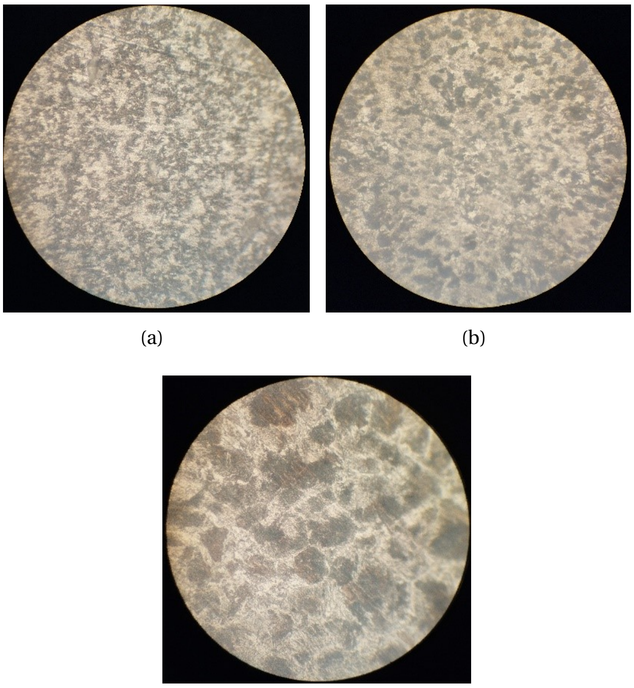
Table 3: Etching time obtained after heat treatment

S.N.	Process	1015°C
1	Annealing	60 sec
2	Normalizing	300 sec
3	Water Quenching	300sec
4	Ice Quenching	60 sec

Rate of cooling:
To ensure the consistent heat transfer with in the sample, different holding time at various temperature were considered which resulted in varying etching time for a same heat-treated sample. The Figure 2 shows clear image obtained through etching of water quenched Ms steel rod where white grains represent ferrite phase and black grains represent perlite. The needle shape structure represent martensite.

Table 4: Holding time for different temperatures

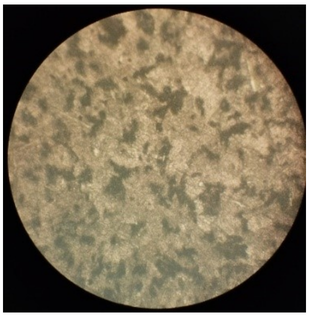
Temperature(°C)	Holding time (min)
800	10
900	30
1000	60



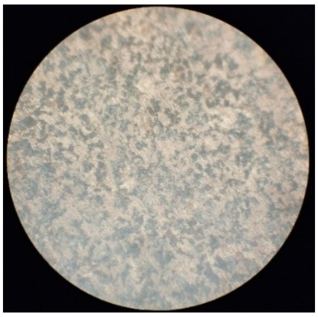
(a) (b) (c)

Figure 2: Microstructure of water quenched Ms steel when cooled from a) 800°C b) 900°C and c) 1000°C

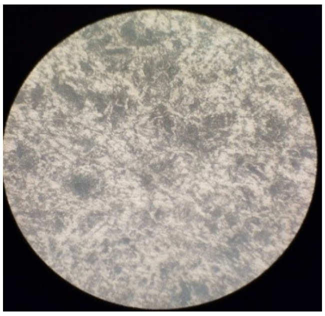
Heat treatment process:
For different heat-treated sample at same temperature and holding time etching time were found different. Following image were obtained through variation in etching time for TMT rebar for different heat-treated sample. Figure 3 shows clear image of heat treated TMT samples at various etching time mentioned at Table 1.



(a)



(b)



(c)

Figure 3: Microstructure of different heat-treated TMT steel at 900°C a) Annealed, b) Normalized and c)Oil quenched

Concentration of etchant

1. Attempt One (Dilute10% HNO_3+90%C_2H_5OH)
   The diluted etching solution lacked the sufficient etching rate to successfully show the microstructure. It is challenging to detect grain boundaries, phases, and other microstructural features when the etching is done too slowly. The diluted etching solution is advantageous than a concentrated one when a slower etching rate is required.

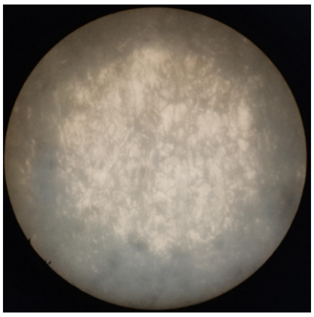


Figure 4: Microscopic view of sample piece in Dilute Etchant

2. Attempt Two (Conc.10% HNO_3+90%C_2H_5OH)
   Concentrated etchants took short time to show the microstructure than diluted solutions. It increased contrast between various microstructural traits, which made them simpler to distinguish and study under a microscope. Larger characteristics including grain boundaries, phase boundaries, and inclusions were readily revealed.

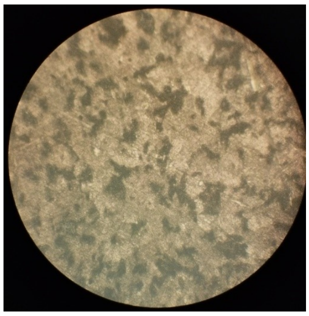
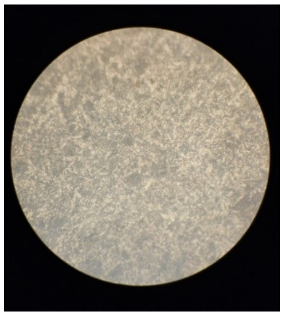
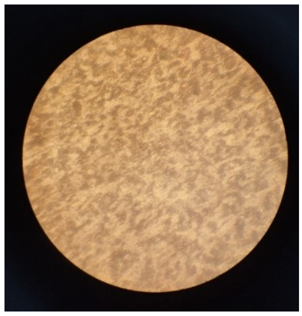


Figure 5: Microscopic view of sample piece in Conc. Etchant

Material composition: Differences in etching time were observed between TMT (Thermo-Mechanically Treated) rebar and mild steel rods, considering that both materials belong to the category of low carbon steel. Figure 6 (a) and (b) shows clear microstructure of TMT rebar and MS steel respectively. Figure 6 (c) shows clear microstructure of stainless steel where white structure represents austenite phase and black stucture represents Ferrite phase which are due to difference in reactivity of phases to etchants.



(a)



(b)

(c)

Figure 6: Microscopic view of a) TMT rebar and b) MS steel using Nital's etchant c)Stainless steel using marble's reagent.

4. Conclusion

Etching, a fundamental process in material analysis, selectively removes material from the specimen's surface to reveal its microstructure. Recognition of the optimal etching duration occurs as the mirror-like finish transitions to a cloudy surface. Inadequate etching result in unclear grain boundaries, while over-etching can dissolve grains, blurring boundaries and complicating grain differentiation. Variation in etching time is influenced by different factors such as cooling rate, material composition, heat treatment process, and etchant concentration. Nital etchant and Marbles reagent emerged as vital tools in uncovering the grain structure and phase composition of sample pieces, selectively corroding the material's surface to expose its internal microstructure. At the obtained etching duration, nital etchant clearly revealed the presence of ferrite, pearlite, and martensite phases in TMT and mild steel rods, while marbles reagent indicated the presence of austenitic phase and ferrite in stainless steel rods for both heat treated and untreated sample pieces. Observations showed that annealed samples typically display a refined and uniform microstructure, requiring longer etching durations, while quenched samples demand shorter times due to rapid cooling. Normalized samples fall in between these extremes. Understanding and adjusting etching durations to each heat treatment method is crucial for accurately assessing microstructural features. The study also explored different etching durations for untreated and heat-treated samples of TMT rebar, MS rod and stainless-steel rod, employing a trial-and-error approach. It helps in standardizing the etching process, reducing variability, and enabling meaningful comparisons between different materials. Overall, determining the optimum etching duration is essential for obtaining accurate, reliable, and meaningful results when studying the grain structure of materials.

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