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SUSCEPTIBILITY OF IRON-BASED ALLOYS TO LOCALIZED (PITTING) CORROSION

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Abstract

Localized corrosion, particularly pitting corrosion, represents one of the most critical degradation mechanisms affecting iron-based alloys. Unlike uniform corrosion, pitting leads to the formation of small, deep cavities that can cause catastrophic failure with minimal overall material loss. This paper investigates the susceptibility of iron-based alloys—including carbon steels, low-alloy steels, and stainless steels—to pitting corrosion. The study explores the influence of environmental factors such as chloride concentration, pH, and temperature, as well as metallurgical parameters including microstructure, alloying composition, and surface condition.

Experimental electrochemical testing methods, including potentiodynamic polarization and electrochemical impedance spectroscopy (EIS), are analyzed alongside microscopic characterization techniques such as scanning electron microscopy (SEM). The results demonstrate that alloying elements such as chromium, molybdenum, and nickel significantly improve resistance to pitting by stabilizing passive films. However, defects in the passive layer, inclusions, and aggressive ions can initiate pit formation.

The study concludes with recommendations for improving corrosion resistance through alloy design, surface treatment, and environmental control strategies [1].

Keywords

Iron-based alloys, pitting corrosion, localized corrosion, passive films, chloride ions, electrochemical behavior, microstructure, corrosion resistance, stainless steel, alloying elements

Introduction. Iron-based alloys are widely used in engineering applications due to their excellent mechanical properties, availability, and cost-effectiveness. However, their susceptibility to corrosion, particularly localized forms such as pitting corrosion, poses significant challenges in industries such as oil and gas, marine engineering, chemical processing, and construction.

Pitting corrosion is a highly localized form of corrosion that leads to the formation of small cavities or “pits” on the metal surface. These pits can penetrate deeply into the material, often without significant visible signs on the surface. As a result, pitting corrosion is considered more dangerous than uniform corrosion because it can lead to sudden and unexpected failure.

The primary cause of pitting corrosion in iron-based alloys is the breakdown of the protective passive film on the metal surface. This breakdown is often triggered by aggressive anions such as chloride ions (Cl^-), which are commonly found in marine environments, de-icing salts, and industrial solutions [2].

This study aims to:
1. Analyze the mechanisms of pitting corrosion in iron-based alloys
2. Evaluate the influence of microstructure and alloy composition
3. Investigate environmental factors affecting pitting susceptibility
4. Provide strategies for mitigating localized corrosion [3].

Materials and Methods.

Table 1.

The following iron-based alloys were considered in this study.

	Material Type	Composition Characteristics	Application Areas
1	Carbon Steel	Low alloy content	Construction, pipelines
2	Low-Alloy Steel	Mn, Cr, Mo additions	Pressure vessels
3	Stainless Steel	≥10.5% Cr, Ni, Mo	Chemical and marine equipment

Experimental methods: Electrochemical testing and surface analysis.

In this study, a comprehensive set of electrochemical and surface characterization techniques was employed to evaluate the susceptibility of iron-based alloys to localized corrosion, particularly pitting corrosion, as well as to investigate the stability and integrity of the passive film formed on the material surface. The experimental methodology was divided into two major parts: electrochemical testing and surface analysis. Each method was carefully selected to provide complementary insights into corrosion mechanisms, passive film behavior, and microstructural degradation at the material surface [4].

Electrochemical testing. Potentiodynamic polarization. Potentiodynamic polarization testing was conducted to determine the pitting potential (E_pit) and to evaluate the general corrosion behavior of the studied alloys in a chloride-containing environment. This technique is widely recognized as a reliable and effective method for assessing the susceptibility of metallic materials to localized corrosion.

The experiments were carried out using a conventional three-electrode electrochemical cell configuration. The working electrode consisted of the prepared alloy sample, which was mechanically polished to obtain a smooth and reproducible surface. Prior to testing, the samples were cleaned using distilled water and ethanol to remove contaminants and ensure consistent surface conditions. A saturated silver/silver chloride (Ag/AgCl) electrode was used as the reference electrode, while a platinum electrode served as the counter (auxiliary) electrode [5].

The electrolyte solution typically contained sodium chloride (NaCl), as chloride ions are known to play a critical role in the initiation and propagation of pitting corrosion. The solution was prepared with analytical-grade reagents and deionized water to maintain high purity and reproducibility. All measurements were performed at room temperature under naturally aerated conditions unless otherwise specified.

During the potentiodynamic polarization test, the potential of the working electrode was swept at a constant scan rate, usually in the range of 0.5 to 1 mV/s, starting from a value below the open circuit potential (OCP) and progressing toward more positive potentials. The resulting current response was recorded continuously to generate polarization curves.

From these curves, several important electrochemical parameters were extracted. The corrosion potential (E_corr) and corrosion current density (I_corr) were determined using Tafel extrapolation methods. Most importantly, the pitting potential (E_pit) was identified as the potential at which a sharp and irreversible increase in current density occurred, indicating the breakdown of the passive film and the onset of stable pit formation.

In many cases, a hysteresis loop was observed when the potential scan was reversed. This phenomenon is indicative of the persistence of pits even after the potential is reduced, suggesting that once initiated, pitting corrosion can continue to propagate under less aggressive conditions. The magnitude of the hysteresis loop provides additional information about the repassivation ability of the material.

A higher E_pit value corresponds to greater resistance to pitting corrosion, as it indicates that the passive film can withstand more aggressive electrochemical conditions before breakdown. Therefore, potentiodynamic polarization serves as a critical tool for comparing the corrosion resistance of different materials and assessing the effectiveness of alloying elements or surface treatments [6].

Electrochemical impedance spectroscopy (EIS). Electrochemical impedance spectroscopy (EIS) was employed to assess the stability and protective properties of the passive film formed on the alloy surface. Unlike potentiodynamic polarization, which involves perturbing the system over a wide potential range, EIS is a non-destructive technique that applies a small-amplitude alternating current (AC) signal to probe the electrochemical interface.

EIS measurements were conducted at the open circuit potential after allowing the system to stabilize for a sufficient period, typically 30 to 60 minutes. A sinusoidal voltage perturbation with a small amplitude (commonly 5–10 mV) was applied over a wide frequency range, usually from 10^5 Hz down to 10^{-2} Hz. The resulting current response was measured, and the impedance of the system was calculated as a function of frequency.

The impedance data were presented in the form of Nyquist and Bode plots. The Nyquist plot, which displays the imaginary component of impedance versus the real component, typically exhibited one or more semicircular arcs. The diameter of these arcs is directly related to the charge transfer resistance (R_ct), which is a key parameter reflecting the resistance to corrosion processes. A larger semicircle indicates higher corrosion resistance and a more stable passive film.

The Bode plot, on the other hand, represents the logarithm of impedance magnitude and phase angle as functions of frequency. High impedance values at low frequencies suggest strong barrier properties of the passive film, while high phase angles approaching −90 degrees indicate capacitive behavior characteristic of an intact and homogeneous oxide layer.

To quantitatively interpret the EIS data, equivalent electrical circuit models were used. These models typically included elements such as solution resistance (R_s), charge transfer resistance (R_ct), and constant phase elements (CPE) to account for non-ideal capacitive behavior. In some cases, additional elements were incorporated to represent diffusion processes or multiple layers within the passive film.

The stability of the passive film was primarily evaluated based on the magnitude of R_ct and the characteristics of the capacitive response. A higher R_ct value and more pronounced capacitive behavior indicate a more protective and stable passive layer, which effectively inhibits corrosion processes. Conversely, a decrease in R_ct or deviation from ideal capacitive behavior may suggest film degradation, increased porosity, or localized breakdown.

EIS is particularly valuable because it allows for the monitoring of passive film evolution over time without significantly altering the surface condition. This makes it an essential tool for studying long-term corrosion behavior and the effects of environmental factors on material performance [7].

Surface analysis. Scanning electron microscopy (SEM). Scanning electron microscopy (SEM) was utilized to examine the surface morphology of the alloy samples after electrochemical testing, with a specific focus on the characterization of pitting corrosion features. SEM provides high-resolution imaging capabilities, enabling detailed observation of surface topography and microstructural changes.

Following electrochemical exposure, the samples were carefully rinsed and dried to remove residual electrolyte without disturbing the corrosion features. The SEM analysis was performed under appropriate vacuum conditions, and both secondary electron (SE) and backscattered electron (BSE) imaging modes were used to obtain comprehensive information about the surface.

SEM images revealed the presence, size, shape, and distribution of corrosion pits. Pits typically appeared as localized cavities with varying geometries, ranging from nearly circular openings to irregular and elongated shapes. The depth and density of pits were also assessed, providing insight into the severity of localized corrosion.

In addition to pit morphology, SEM allowed for the identification of surface defects, inclusions, and microstructural heterogeneities that may act as initiation sites for pitting corrosion. Grain boundaries, second-phase particles, and inclusions were often observed to play a significant role in pit nucleation.

The technique also enabled the examination of passive film damage, such as cracking, delamination, or localized thinning. These features are critical for understanding the mechanisms of passive film breakdown and the subsequent initiation of pitting corrosion [8].

Energy dispersive X-ray spectroscopy (EDS). Energy dispersive X-ray spectroscopy (EDS), integrated with the SEM system, was used to perform elemental analysis of the sample surfaces, particularly within and around corrosion pits. This technique is based on the detection of characteristic X-rays emitted from the material when it is bombarded with a focused electron beam.

***Table 2. Corrosive environment*.**

	Parameter	**Range Tested**
1	Chloride (Cl^-)	0.01 – 1.0 M
2	pH	2 – 10
3	Temperature	25°C – 80°C

Results.

Mechanism of Pitting Corrosion.

Pitting corrosion occurs in three main stages:

1. Initiation:
- Breakdown of passive film
- Localized dissolution begins
2. Propagation:
- Formation of anodic pit region
- Acidification inside pit
3. Stabilization.
- Pit grows autocatalytically

Figure 1. *Schematic of pitting corrosion mechanism.*

Observation: Stainless steels with higher Mo content showed superior resistance to pitting corrosion.

Effect of Chloride Ions. Chloride ions penetrate the passive film and destabilize it by forming soluble metal chlorides. The pitting potential decreases significantly with increasing chloride concentration.

Microstructural effects:

1). Grain boundaries act as preferential sites for pit initiation
2). Inclusions (e.g., MnS) accelerate localized corrosion
3). Fine-grained structures improve corrosion resistance

Discussion. The susceptibility of iron-based alloys to pitting corrosion is strongly influenced by both intrinsic material properties and external environmental conditions.

Passive film stability. The formation of a passive oxide layer is crucial for corrosion resistance. In stainless steels, chromium forms a Cr_2O_3 film that protects the surface. However, chloride ions can locally destroy this film, leading to pit initiation.

Role of alloying elements. Molybdenum plays a significant role in enhancing pitting resistance by promoting repassivation. Nickel stabilizes the austenitic structure, improving corrosion resistance.

Pitting corrosion growth mechanism. Once a pit initiates on a metal surface, it develops into a localized electrochemical cell that can sustain itself independently of the surrounding environment. Within the pit, the anodic reaction occurs, where metal atoms lose electrons and dissolve into the electrolyte, producing metal ions. This dissolution process is highly localized, meaning that the corrosion is concentrated in a very small area rather than being spread uniformly across the metal surface. On the surface surrounding the pit, the cathodic reaction takes place, usually involving the reduction of oxygen or hydrogen ions present in the solution.

The separation of anodic and cathodic regions creates an internal electrochemical gradient that further drives the corrosion process within the pit.

As the pit deepens, the environment inside it changes significantly. The concentration of metal cations increases, and chloride or other aggressive ions from the solution accumulate, leading to a significant drop in local pH. This local acidity accelerates the dissolution of the metal inside the pit, creating a feedback loop where deeper pits promote even faster corrosion. The pit essentially becomes self-sustaining because the electrochemical reactions inside continue independently, while the surrounding metal surface remains relatively passive. Over time, this mechanism can result in rapid penetration of the metal, potentially causing structural failure even if the total metal loss appears minimal. Understanding this pit growth mechanism is crucial for designing corrosion-resistant alloys and applying protective coatings that can prevent initiation and propagation of localized corrosion [9].

Industrial implications of pitting corrosion. Pitting corrosion poses serious challenges to industrial infrastructure because it is highly localized and often difficult to detect before significant damage occurs. One of the primary consequences is the development of leaks in pipelines. Even small pits can penetrate the metal wall over time, allowing fluids or gases to escape, which may lead to operational shutdowns or environmental hazards. In addition to leaks, pitting can compromise the structural integrity of equipment and components. Localized metal loss may lead to cracks or sudden failures, which are particularly dangerous in high-pressure systems or load-bearing structures. This not only threatens safety but also increases maintenance costs, as frequent inspections, repairs, and replacements become necessary to prevent catastrophic failures.

Industries that are most affected by pitting corrosion include marine engineering, where saltwater exposure accelerates pit formation; oil and gas pipelines, which transport corrosive fluids under high pressure; and chemical plants, where aggressive chemicals can initiate and propagate pits. Understanding the industrial implications of pitting corrosion is essential for developing effective corrosion management strategies, selecting resistant materials, and implementing protective coatings or inhibitors to prolong the lifespan of critical assets.

Prevention strategies for pitting corrosion. Preventing pitting corrosion requires a combination of careful material selection, surface treatment, and environmental control. One of the most effective strategies is choosing materials that are inherently resistant to localized corrosion. Stainless steels containing molybdenum, such as 316 grade, exhibit enhanced resistance to pitting due to the stabilizing effect of Mo on the passive film. It is also advisable to avoid alloys with high sulfur content, as sulfur can promote pit initiation and accelerate corrosion. Surface treatment plays a critical role in reducing susceptibility to pitting. Polishing the metal surface smooths out microscopic irregularities that often serve as initiation sites for pits. Additionally, protective coatings such as epoxy paints or polymer films create a barrier between the metal and the corrosive environment, significantly slowing down or preventing pit formation.

Environmental control is another essential approach. Reducing exposure to aggressive ions like chlorides is crucial, especially in marine or industrial settings. The use of corrosion inhibitors in solutions or process fluids can further limit the electrochemical reactions that drive pit growth. By combining these strategies, industries can effectively minimize the risk of pitting corrosion, extending the service life of critical components and reducing maintenance costs [10].

Table 4. Comparison of prevention methods.

	Method	**Effectiveness**	**Cost**	**Application**
1	Alloying	High	High	Long-term
2	Coatings	Medium	Medium	Surface protection
3	Inhibitors	Variable	Low	Temporary

Conclusion. Pitting corrosion is a critical failure mechanism in iron-based alloys, particularly in chloride-containing environments. The susceptibility of these materials depends on a combination of metallurgical and environmental factors.

Key findings include:

1. Passive film breakdown is the primary cause of pitting.
2. Alloying elements such as Cr and Mo significantly enhance resistance.
3. Chloride ions are the most aggressive contributors to pit formation.
4. Microstructure and inclusions play a crucial role in pit initiation.

Future research should focus on:

1. Advanced coatings.
2. Nanostructured alloys.
3. Smart corrosion monitoring systems.

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