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Research status of marine Microbiologically Influenced Corrosion (MIC) Resistant Alloys

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Abstract

This paper focuses on microbiologically influenced corrosion (MIC) resistant alloys, systematically reviewing their current research status and future development directions. It first elucidates the biochemical–electrochemical mechanisms of marine MIC, covering the metabolism of typical microorganisms such as sulfate-reducing bacteria (SRB), the evolution of the biofilm microenvironment, and core mechanisms including cathodic depolarization, extracellular electron transfer (EET), metabolite acid attack/sulfide-induced pitting corrosion, and synergistic damage with chloride ions. The key challenges of multi-factor coupled synergistic corrosion models are also identified. Regarding corrosion-resistant alloying strategies, the microscopic mechanisms of Cu (contact killing and sustained ion release), Cr (passive film self-repair), and rare earth elements (interface purification and inclusion modification) are detailed, along with multi-element synergistic alloy design principles. The effects of heat treatment processes such as solution treatment and aging are analyzed, focusing on how they regulate precipitate phase size and distribution to reduce grain boundary corrosion susceptibility and micro-galvanic corrosion.

Keywords: Marine Microbiologically Influenced Corrosion; Corrosion Mechanism; Multi-Element Synergy; Heat Treatment

1. Introduction

With the progressive expansion of marine resource development into deep-sea and open-ocean regions, large-scale engineering equipment such as ships, offshore platforms, and submarine oil and gas pipelines are exposed to increasingly complex and harsh service environments. The combined effects of high-concentration chloride ions, dissolved oxygen, temperature gradients, and complex microbial communities in seawater place metallic materials under long-term multi-factor coupled corrosion conditions. Among these, microbiologically influenced corrosion (MIC)—a typical bio-chemo-electrochemical coupling failure mode—has become a critical factor affecting the safe service of marine engineering equipment. Studies have shown that MIC accounts for a significant proportion of industrial corrosion failures, causing severe economic losses in oil and gas transportation, marine energy equipment, and water treatment systems, with global annual economic losses reaching hundreds of billions of dollars[1-3]. Unlike conventional uniform corrosion or localized electrochemical corrosion, MIC involves the attachment, proliferation, and secretion of extracellular polymeric substances (EPS) by microorganisms, forming complex biofilm structures on the metal surface that are both protective and destructive. This alters the mass transport, charge transfer, and local chemical environment at the material/solution interface, leading to failure behaviors such as pitting corrosion, crevice corrosion, and stress corrosion cracking[4,5]. The synergistic effect between Cl^- and microbial metabolites accelerates passive film breakdown and amplifies crevice corrosion, rendering the corrosion process a multi-factor coupled complex phenomenon. Establishing an accurate synergistic corrosion model has thus become a major challenge.

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Among the various microorganisms involved in MIC, sulfate-reducing bacteria (SRB), iron-oxidizing bacteria (IOB), and sulfur-oxidizing bacteria (SOB) are considered the key functional groups affecting the corrosion behavior of marine metals. SRB can utilize sulfate (SO_4^{2-}) as an electron acceptor to produce sulfides and promote anodic metal dissolution through the cathodic depolarization theory. Their metabolic product, H_2S, is not only highly corrosive but also alters the structure of the corrosion product film, accelerating the development of localized corrosion[6]. In recent years, advances in microbial electrochemistry have further revealed that some microorganisms can directly participate in electron exchange at the metal surface via extracellular electron transfer (EET), forming a novel mechanism distinct from traditional electrochemical corrosion[7]. These mechanisms interact with the abundant Cl^- in seawater, constituting a complex corrosion system influenced by multiple cross-cutting factors. Understanding this from a bio-chemo-electrochemical coupling perspective is now of critical importance.

In response to the problem of MIC in marine environments, the design and development of MIC-resistant alloy steels have attracted widespread attention in recent years. Research has focused primarily on alloying element regulation, various heat treatment processes, and surface protection technologies. For example, the addition of Cu, Cr, and rare earth elements can modify the composition of the passive film on the steel surface, enhancing the material's resistance to microbial attachment and corrosive media ingress. Through the control of grain size, second-phase distribution, and inclusion morphology, corrosion-sensitive regions within the material can be further optimized[8,9]. In terms of processing, heat treatment methods such as solution treatment and aging effectively reduce grain boundary corrosion susceptibility and micro-galvanic corrosion tendencies by controlling the size and distribution of precipitates. Meanwhile, surface strengthening technologies such as laser shock peening and thermal spray coatings impart excellent resistance to microbial adhesion and corrosion while preserving the high strength of the substrate, offering an important pathway for achieving a balance between mechanical properties and corrosion resistance. Additionally, surface alloying strategies such as bioinspired superhydrophobic coatings and graphene-based nanocomposite coatings provide new approaches for blocking microbial adhesion and reducing corrosion rates[10,11].

However, current research on MIC-resistant materials still has certain limitations. On one hand, traditional “trial-and-error” alloy design and process optimization struggle to reveal the intrinsic mechanisms of material–microorganism interactions under multi-factor coupling. On the other hand, a systematic design framework for synergistically regulating alloy composition, microstructure, and surface state to simultaneously enhance MIC resistance and mechanical properties is still lacking.

This paper systematically reviews the research progress on MIC-resistant alloy steels in marine environments, following the logical thread of “corrosion mechanism and multi-factor synergistic effects—corrosion-resistant alloying strategies—surface alloying strategies—mechanism-guided synergistic design”. From the perspectives of microbial metabolism, biofilm evolution, cathodic depolarization, EET, and their synergistic interaction with Cl^-, the bio-chemo-electrochemical mechanisms of corrosion induced by typical microbial groups are analyzed. The multi-factor coupled synergistic corrosion model is also discussed. On this basis, the microscopic anti-corrosion mechanisms of alloying elements such as Cu, Cr, and rare earths are emphasized, along with the regulatory effects of multi-element synergistic alloy design and heat treatment processes on MIC resistance. Finally, surface treatment technologies—including bioinspired superhydrophobic coatings, nanostructured coatings, laser shock peening, and thermal spray coatings—are summarized, focusing on their mechanisms for achieving anti-adhesion and corrosion protection while maintaining high substrate strength. The paper concludes by exploring pathways for the synergistic optimization of MIC resistance and mechanical properties in alloy steels through cross-scale design strategies such as microstructure refinement, precipitate phase control, and surface strengthening, and offers perspectives on future development directions to provide a theoretical basis for the development of next-generation MIC-resistant materials for marine engineering.

2. Biochemical–Electrochemical Mechanisms and Multi-Factor Synergistic Effects of Marine Microbiologically Influenced Corrosion

The occurrence of marine microbiologically influenced corrosion (MIC) is not solely due to the presence of microorganisms, but is the result of the combined action of mechanisms such as microbial metabolic activity, biofilm formation, and electrochemical reactions at the metal/seawater interface. Microorganisms alter the interfacial chemical environment, electron transfer processes, and corrosion product composition, establishing a bio-chemo-electrochemical coupling system distinct from traditional electrochemical corrosion. Therefore, MIC exhibits pronounced localized, complex, and dynamically evolving characteristics [1,12,13].

2.1. Typical Corrosive Microorganisms and Their Metabolic Characteristics

The microorganisms closely associated with corrosion in marine environments mainly include sulfate-reducing bacteria (SRB), iron-oxidizing bacteria (IOB), sulfur-oxidizing bacteria (SOB), and various facultative heterotrophic bacteria[14,15]. Different microbial groups form complex biofilm ecosystems through metabolic interactions[16,17], collectively influencing the corrosion behavior of metals.

Sulfate-reducing bacteria are obligate anaerobes, commonly found in the depths of biofilms beneath oxic seawater or in anoxic sediments. They utilize sulfate (SO_4^{2-}) as the terminal electron acceptor for respiratory metabolism, producing hydrogen sulfide (H_2S) and other metabolites[14]. Hydrogen sulfide is not only corrosive to steel itself[18], but more importantly, it alters the entire cathodic reaction pathway, acting as an "engine" for anaerobic corrosion. In the corrosion of 304 stainless steel in SRB-containing simulated seawater[19], the iron in the passive film is sulfidized to FeS and FeS_2, while chromium exists in the form of CrO_3 and Cr_2S_3, leading to a decline in the protective performance of the passive film. This study was the first to use X-ray photoelectron spectroscopy (XPS) to quantitatively analyze the sulfide composition, but it did not consider the effect of the dynamic biofilm growth process on the sulfidation reaction.

Iron-oxidizing bacteria[20] inhabit regions with relatively abundant oxygen and can oxidize dissolved ferrous ions to ferric iron, producing voluminous and loose iron oxide nodules. Once these nodules cover the material surface, they create an oxygen-depleted zone beneath them, establishing an oxygen concentration cell and inducing severe crevice corrosion. Furthermore, the deposition layer formed by iron-oxidizing bacteria can provide a suitable growth environment for other anaerobic microorganisms, further promoting synergistic interactions among different functional microbial groups.

Sulfur-oxidizing bacteria[21] can oxidize sulfur, thiosulfate, or even sulfides to sulfuric acid, causing a sharp drop in the pH of the surrounding environment, thereby corroding the metal substrate.

These functional microbial groups rarely exist in isolation; they are distributed in layers on the same metal surface in response to micro-environmental changes, with their metabolites mutually utilized, forming a complex "corrosive symbiotic network".

2.2. Biofilm Formation and Microenvironment Evolution

Microbiologically influenced corrosion is not directly caused by free-floating bacteria in seawater, but is the result of the continuous evolution of the microenvironment within the biofilm attached to the metal surface. Biofilm formation generally undergoes four stages: reversible attachment, irreversible adhesion, microcolony maturation, and detachment/dispersal. Once bacteria adhere irreversibly, they secrete large amounts of extracellular polymeric substances (EPS), which contain polysaccharides, proteins, nucleic acids, and even lipids, constructing a three-dimensional hydrogel-like matrix[22]. This EPS layer protects the bacterial cells from external disturbances and biocide damage, and also acts as a barrier for mass transport.

Perpendicular to the metal surface, this biofilm creates strong chemical gradients. The respiration of aerobic bacteria in the outer layer continuously consumes oxygen, while EPS hinders the inward diffusion of dissolved oxygen, resulting in a nearly zero dissolved oxygen concentration at the biofilm/metal interface. Meanwhile, metabolic activities such as sulfate reduction cause organic acids and hydrogen sulfide to accumulate beneath the biofilm, leading to a sharp drop in pH, with local acidity becoming even higher. In addition, aggressive ions such as chloride ions are also enriched at the interface due to the barrier effect of the biofilm.

EPS not only determines the mechanical stability of the biofilm but can also adsorb Fe^{2+}, Cl^-, and various organic metabolites, altering local ion transport and diffusion behavior, serving as an important basis for the formation of a localized corrosive environment[7,15,23].

Thus, a micro-galvanic corrosion cell driven by the oxygen concentration cell is formed: the oxygen-depleted zone becomes the anode, where iron dissolution occurs; the oxygen-rich zone or biofilm defect area becomes the cathode, where oxygen reduction takes place.

2.3. Detailed Explanation of Core Corrosion Mechanisms

2.3.1. Cathodic Depolarization—The Classic Acceleration Pathway of SRB

The Cathodic Depolarization Theory (CDP) is the earliest classical model proposed to explain SRB-induced corrosion. This theory posits that hydrogenase produced by SRB[18] can promote the consumption of adsorbed hydrogen on the cathode, thereby reducing the degree of cathodic polarization and accelerating the anodic dissolution of the iron matrix. However, an increasing number of studies in recent years have shown that CDP struggles to explain the phenomenon where some SRB can still induce rapid corrosion in the absence of hydrogen, and thus its applicability is somewhat limited.

Under anoxic conditions, the cathodic process of metal corrosion is typically the reduction of hydrogen ions, producing adsorbed hydrogen atoms on the metal surface. These hydrogen atoms may recombine to form hydrogen gas molecules that evolve. Once the surface coverage increases, the cathodic reaction rate is retarded due to the "hydrogen overpotential". The presence of SRB completely breaks this limitation. As shown in Figure 1, the hydrogenase they contain can efficiently convert adsorbed hydrogen atoms into hydrogen molecules[24] and further react hydrogen with sulfate ions through the sulfate respiration pathway to produce hydrogen sulfide and water. Consequently, the hydrogen produced by the cathodic reaction is continuously removed, and the cathode potential is forced to be "depolarized" to a more negative value, allowing anodic dissolution to proceed unimpeded.

The hydrogen sulfide thus generated combines with ferrous ions to form an iron sulfide precipitate that covers the surface. However, its structure is loose and electronically conductive, which not only fails to form a protective layer but further accelerates galvanic corrosion[23].

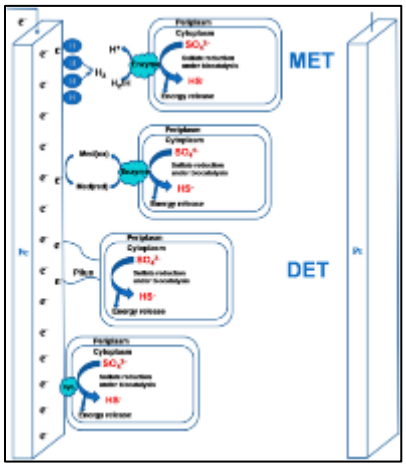

Figure 1 Schematic representation of the interaction between cathodic protection and activity of sulfate reducing bacteria.

2.3.2. Extracellular Electron Transfer—Directly "Stealing" Electrons from the Metal

Recent studies have revealed a more direct corrosion mode: certain SRB can directly extract electrons from zero-valent iron without the need for hydrogen as an electron carrier. This process is considered a representative mechanism of Electrical MIC (EMIC) [15]. These bacteria establish physical–electrical connections with the iron matrix either through extended conductive pili (nanowires) or via c-type cytochrome proteins on the outer membrane, directly transferring electrons released from metal oxidation into the cell for respiratory processes such as sulfate reduction.

This mode of electron transfer significantly enhances electron transfer efficiency, with corrosion current densities several times higher than those achieved by the depolarization mechanism relying solely on hydrogenase. In essence, the bacteria act as a living "electron sink," coupling the oxidation of the metal with their own metabolic activities, thereby removing the general limitations of passivation or diffusion control on corrosion.

2.3.3. Metabolite Acid Attack and Sulfide-Induced Pitting Corrosion

In addition to depolarization and electron transfer, Metabolite MIC (M-MIC) caused by microbial metabolites cannot be ignored. Organic acids and sulfuric acid produced by SRB, SOB, and others can directly dissolve metals, causing uniform

thinning or local acid attack. Among these, ferrous sulfide (FeS) is particularly destructive. The FeS layer covering the steel surface is loose and porous, and its potential is typically much more positive than that of the underlying iron substrate. In a humid environment, this forms numerous micro-galvanic couples: iron acts as the anode and is preferentially dissolved, while FeS serves as an efficient cathode providing a large-area reaction site, promoting local anodic dissolution of the steel matrix[25]. This micro-galvanic action gives rise to pitting nuclei in localized regions. Once formed, the pit enters a self-catalytic process: hydrolysis of iron ions further lowers the pH inside the pit; to maintain charge neutrality, chloride ions migrate in from the outside, creating a microenvironment of concentrated hydrochloric acid that makes repassivation at the pit bottom nearly impossible, allowing corrosion to propagate rapidly in depth[26].

This is entirely consistent with the classical autocatalytic acidification model of pitting corrosion, except that the presence of the biofilm makes this process more concealed and sustained. Furthermore, the FeS deposit layer produced by SRB exhibits semiconducting or semi-conductive properties and can act as an electron transfer mediator, further promoting localized corrosion.

2.3.4. Synergistic Damage with Chloride Ions—Breakdown of the Passive Film and Amplification of Crevice Corrosion

The key to the corrosion resistance of alloy steels lies in the formation of a nanoscale passive film on the surface. However, this film becomes exceptionally vulnerable in the presence of microbial activity. Certain components of EPS can complex with cations such as chromium and iron in the film, causing film thinning; metabolic acids directly dissolve the film; and sulfides can alter the structure and composition of the film[27]. Once the passive film becomes locally weakened, the abundant chloride ions in seawater penetrate the film, adsorb onto the bare metal surface, and catalyze the initiation of pitting. More critically, the biofilm itself acts as a natural “crevice”: the narrow gap between the biofilm and the metal severely hinders mass transport, creating an occluded region, which is precisely the condition that fosters crevice corrosion.

Within these occluded regions, dissolved oxygen is depleted, acidity rises, and chloride ions become enriched—all the factors that promote corrosion are amplified[1], while inhibitive factors cannot enter. The entire process can be described as: microbial metabolism → degradation of passive film integrity → chloride ion adsorption and breakdown → establishment of an occluded cell → severe localized corrosion.

This process explains why, even in high-alloy steels, microbially induced localized corrosion is difficult to completely avoid in real seawater environments. There is a significant synergistic effect between microbial metabolism and chloride ion attack[28]. EPS can alter interfacial ion transport behavior and promote the enrichment of aggressive ions in the region beneath the biofilm, accelerating the destabilization of the passive film and the initiation of pitting.

2.4. Key Challenge: Synergistic Corrosion Model under Multi-Factor Coupling

The various mechanisms described above do not operate in isolation. In real marine environments, microbial communities are diverse and dynamically changing, while factors such as temperature, dissolved oxygen, flow rate, and applied stress are also intertwined. For example, SRB dominate corrosion in anaerobic zones, but the sulfides they produce can be oxidized by upstream SOB into strong acids, and the respiration of aerobic heterotrophs pre-establishes oxygen gradients on the surface. The various mechanisms alternate in space and relay in time, forming a complex coupled network. Currently, the understanding of this multi-factor synergistic effect is very limited. Most laboratory studies are conducted with single bacterial strains or in simplified media, making it difficult to reproduce the degree of interaction in real environments. Future efforts need to develop in situ, high-spatial-resolution multi-parameter characterization techniques, as well as advances in high-throughput sequencing, metagenomics, in situ Raman spectroscopy, scanning vibrating electrode technique (SVET), scanning electrochemical microscopy (SECM), and synchrotron radiation X-ray techniques, to provide new means for revealing the dynamic evolution process of MIC.

3. Microscopic Mechanisms of Alloying Elements Against Microbiologically Influenced Corrosion and Corrosion-Resistant Alloying Strategies

Elements such as Cu, Cr, and rare earths are not simply “additives” in steel; each intervenes in the microorganism–metal interface interaction through unique chemical and physical pathways, either by directly killing at the cellular level, building barriers at the material level, or enhancing the permeability of bacterial cell walls to potentiate Cu ion bactericidal effects and inhibiting biofilm formation.

3.1. Contact Killing and Sustained Ion Release Mechanism of Cu

Copper has been used as an antimicrobial material for thousands of years. In the complex service environment of marine alloy steels, its inhibitory mechanism is far more sophisticated than simply “copper is toxic”. The mechanisms widely accepted by the academic community can be categorized into three levels: contact killing, ion release killing, and destruction of the biofilm matrix.

Contact killing is one of the most distinctive inhibition modes of Cu. When bacteria approach and adhere to the steel surface via flagella or EPS, if the surface contains dispersedly distributed Cu-rich phases or Cu-containing nanoprecipitates, the bacterial cell membrane comes into direct contact with copper. This solid–solid interfacial interaction destabilizes the phospholipid bilayer structure of the cell membrane, sharply increasing permeability, leading to massive leakage of intracellular ions such as potassium and small molecules like nucleic acids, an irreversible collapse of membrane potential, and ultimately cell lysis[29].

In essence, this process is a physico-chemical coupled damage, rather than a purely chemical toxic killing. Its advantage is that it is difficult for bacteria to develop classical resistance through efflux pumps or enzymatic detoxification systems. In the microstructure of alloy steels, Cu is often precipitated as ε-Cu phases during aging treatment[30]. These nanoscale Cu-rich particles form a “killing site array” across the surface, posing a risk of membrane damage to any bacteria attempting to colonize.

Ion release killing represents a sustained chemical defense. Even if bacteria do not directly contact the Cu-rich phase, trace amounts of dissolved Cu^{2+} can exert toxic effects in the surrounding microenvironment. Once Cu^{2+} enters bacterial cells, it can catalyze the decomposition of hydrogen peroxide via a Fenton-like reaction[31], generating highly reactive hydroxyl radicals. These reactive oxygen species cause DNA strand breaks, oxidize thiol groups and iron–sulfur clusters in proteins, disrupt electron transport in the respiratory chain, and trigger a multi-target oxidative damage storm. Cu^{2+} can also competitively bind with intracellular reducing molecules such as glutathione, depleting the cell's antioxidant defenses and plunging the bacteria into an irreparable state of oxidative stress.

This ion release mechanism exhibits sustained-release characteristics. As long as the corrosive medium persists, the steel surface maintains a low-concentration but long-lasting gradient of Cu^{2+}, constituting a chemical interception barrier against planktonic and non-adherent bacteria.

The third line of defense of Cu is the destruction of EPS. EPS serves as the “skeleton” and “shield” of the biofilm, but Cu^{2+} can coordinate with the hydroxyl groups of polysaccharides, carboxyl groups, and thiol groups of proteins in the EPS, causing the collapse of the originally ordered cross-linked network structure. The matrix becomes loose, hydrophilicity changes, and adhesion strength decreases significantly[32]. Deprived of the protection of EPS, the bacterial cells embedded in the biofilm are exposed to the oxygen-containing environment and bactericidal ions, disrupting the community's synergistic metabolism and thus the biofilm's ability to construct a stable corrosive microenvironment.

3.2. Passivation and Film Self-Repair Mechanism of Cr

Unlike Cu's “active offense” strategy, Cr plays a “passive defense” role in resisting MIC. It does not directly kill bacteria, but fundamentally cuts off the electrochemical pathways for microbial participation in the corrosion reaction by reshaping the electrochemical state of the metal surface.

Superior passivation is the most core function of Cr. When the Cr content in steel exceeds a certain threshold (typically about 12% or more), in an oxygen-containing environment, Cr preferentially oxidizes and forms a dense, extremely thin passive film of $Cr_2O_3/Cr(OH)_3$ on the surface[33]. This film differs from ordinary rust in key aspects: it is amorphous or nanocrystalline, has low electronic conductivity, and an extremely low diffusion coefficient for cation vacancies. Electrochemically, this means the pitting potential is significantly increased, metastable pitting nuclei struggle to reach a critical size, and even a small amount of Cl^- attack is difficult to penetrate the film[34]. For microbial communities that rely on pitting as the starting point of corrosion, the integrity of the film makes it difficult for them to find “weak points” on the surface to initiate localized attack.

Inhibiting extracellular electron transfer is another key contribution of the Cr passive film. As a p-type semiconductor[35], the valence band and conduction band structure of Cr_2O_3 film greatly increases the energy barrier for electrons to cross the interface from the substrate. The conductive pili or outer membrane proteins of bacteria face not bare iron atoms, but a nearly insulating oxide layer, and the efficiency of electron tunneling decays exponentially.This means that on the surface of Cr-containing alloy steels, the efficient corrosion pathway of

"bioelectrical corrosion" is physically cut off. Even if SRB and other bacteria survive, they cannot maintain a high corrosion rate through direct electron uptake.

The functional logic of Cr can be summarized as: constructing a highly stable inert barrier both electrochemically and physically, simultaneously blocking the dual pathways of microbial electron harvesting and corrosive medium attack on the substrate from the source. It is this dual blocking that makes the passivity stability of Cr-containing alloy steels in bacteria-containing seawater far superior to that of ordinary carbon steels.

3.3. Interface Purification and Inclusion Modification by Rare Earth Elements

Rare earth elements (Ce, La, Y, etc.) are typically present in very low concentrations in steel, but their inhibitory effect on MIC is attracting increasing attention. Unlike Cu and Cr, rare earths do not primarily rely on bactericidal action or solely on passivation; instead, they eliminate the inherent defects where corrosion is prone to initiate through "purification" and "reconstruction" of the microscopic interfaces in the steel.

Inclusion modification is the most prominent contribution of rare earths to MIC resistance[36]. In ordinary alloy steels, sulfide inclusions (most typically MnS) are almost inevitable. MnS forms a micro-galvanic couple with a significant potential difference relative to the surrounding iron matrix, and its boundaries are often the weakest points of the passive film—in Cl^--containing environments, pitting almost always preferentially initiates at these locations.

More critically, bacteria exhibit a strong attachment preference for MnS inclusions: SRB and other bacteria often aggregate at the MnS/matrix interface, utilizing the electrochemical activity and local acidity of the sulfide boundary to accelerate colonization and corrosion. However, the addition of rare earth elements completely changes this situation.

The chemical affinity of rare earths for sulfur is much higher than that of other elements. Sulfur in steel preferentially combines with rare earths to form fine, dispersed, and thermodynamically stable rare earth oxides (RE_2O_3) or oxysulfides (RE_2O_2S). As shown in Figure 2 and Table 1, after adding Ce to 2101 duplex stainless steel, the inclusion type changed from irregular Al_2O_3 to spherical rare earth composite inclusions such as $CeAlO_3$ and Ce_2O_2S[37], with the size decreasing from 3–5 μm to 1–3 μm. In the steel without Ce, the inclusions were irregular Al_2O_3 and Al_2O_3-MnS composite inclusions (a, b), while after Ce addition, they transformed into ellipsoidal $CeAlO_3$ and Ce_2O_2S (c, d, e, f).

Table 1 Chemical compositions of experimental steels/%(Mass fraction)

NO.	C	Si	Mn	P	S	Cr	Ni	Mo	Al	O	N	Ce
a,b	0.035	0.40	4.83	0.0067	0.0045	21.97	1.48	0.42	0.009	0.0033	0.25	0
c,d	0.031	0.39	4.90	0.011	0.0019	21.95	1.53	0.36	0.020	0.0023	0.22	0.004
e	0.032	0.42	4.88	0.012	0.0039	21.78	1.55	0.36	0.024	0.0017	0.21	0.010
f	0.030	0.40	4.85	0.008	0.0035	22.00	1.50	0.36	0.014	0.0017	0.20	0.026

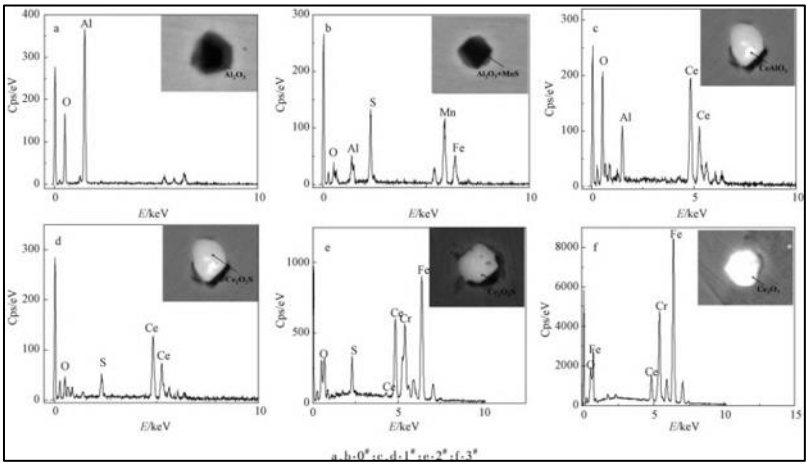

Figure 2 Composition and morphology of inclusions in each group of steel samples

Similarly, after adding rare earth Y to DH36 ship plate steel[38], the MnS + SiO_2 composite inclusions were transformed into spherical Y_2S_3 + MnS inclusions, and the stress around the inclusions decreased by approximately 40%. This modification reduced microcracks at the inclusion/matrix interface, thereby inhibiting localized corrosion triggered by microbial attachment through these cracks. Furthermore, rare earth inclusions possess a higher electron work function (e.g., $LaCrO_3$ > Fe), allowing them to function as cathodes in micro-galvanic corrosion and preventing their own anodic dissolution[39]. In Q420 high-strength steel, the addition of Ce reduced the content of active γ-FeOOH in the corrosion products, increased the proportion of stable phases (α-FeOOH and Fe_3O_4), and enhanced the rust layer resistance by 50%[40]. Additionally, RE^{3+} ions released from the dissolution of rare earth elements can adsorb onto the microbial surface, interfering with their electron transport chain and indirectly inhibiting metabolic activity [41].

Moreover, rare earth elements promote the formation of a dense rust layer enriched in α-FeOOH and Fe_3O_4, which suppresses the oxygen-depleted microenvironment required by microorganisms. In GCr15-RE steel, the α-FeOOH content in the rust layer was 21.57% higher than that in the unmodified steel, and the increased compactness of the rust layer led to a reduction in Cl^- permeability[42]. In rare earth microalloyed steels, the synergistic effect of Nb and Ce increases the α-FeOOH/γ-FeOOH ratio in the rust layer, significantly enhancing its protective properties. This structural change reduces the available attachment sites and nutrient diffusion pathways for microorganisms.

3.4. Multi-Element Synergy: From Single Bactericidal Action to Multi-Mechanism Coupled Corrosion Inhibition

The mechanisms of the three elements described above each have their own focus, but also their respective shortcomings: excessive Cu severely deteriorates the hot workability and toughness of steel, and relying solely on the bactericidal effect of Cu is insufficient to completely prevent corrosion beneath an already formed biofilm; Cr does not kill bacteria, and in the face of stubborn microbial communities capable of attaching to and breaching the passive film, auxiliary means are required; rare earth elements solve the problem of pitting initiation and film layer stability, but they themselves have no inhibitory effect on planktonic bacteria. Therefore, the true technological breakthrough lies in multi-element synergy.

Taking the combination of Cu and Cr as an example, the two form a “active sterilization—passive passivation” spatiotemporal complementary mechanism. Cu exerts its antibacterial effect through the release of Cu^{2+} and direct contact between Cu-rich phases and bacteria, thereby reducing the possibility of bacterial attachment and biofilm formation[43]. The Cu-rich phases precipitated during aging treatment[44] can further eliminate bacteria that manage to escape the Cu^{2+} diffusion layer through contact killing at the initial stage of attachment.

The synergy of copper with elements such as chromium and nickel can enhance the antibacterial performance of the material through a dual mechanism of “physical barrier + chemical sterilization”, while also improving corrosion resistance by regulating the phase composition of the rust layer (e.g., the proportion of α-FeOOH), microstructure (grain size, compactness), and electrochemical properties (ion selectivity). In Cu-Cr-bearing pipeline steel[45], Cr forms a dense Cr_2O_3 oxide layer, constructing a physical barrier on the material surface that hinders microbial attachment; meanwhile, the sustained release of Cu^{2+} achieves chemical sterilization by disrupting bacterial cell membrane permeability and DNA structure. The synergy of these two elements improves the resistance to microbiologically influenced corrosion (MIC) by 40%. In dry-wet cyclic immersion tests, it was found that the corrosion rate of a novel Cu-Mo weathering steel was significantly lower than that of Cr-bearing weathering steel and Q355C carbon steel in the later stage of corrosion (>480 h)[46]. Rust layer characterization revealed that Cu and Mo elements were significantly enriched at the substrate interface in the Cu-Mo steel, forming a dense inner rust layer rich in (Cu, Mo). Cu promotes the formation of α-FeOOH, while Mo segregates at defects in the rust layer. The synergy of these two elements enhances the cation selectivity of the rust layer, hindering the penetration of aggressive ions such as Cl^-.

In addition, rare earth elements (such as Ce, La) promote the formation of a dense Cr- and Fe-rich oxide or passive film, constructing a long-lasting antibacterial barrier. After adding 0.0025% Ce to Q370qENH bridge steel[47], the α-FeOOH content in the rust layer increased by 35%. This phase achieves dual inhibition of microbiologically influenced corrosion by hindering the penetration of aggressive ions such as Cl^- and suppressing the transport of nutrients required by bacteria (e.g., iron ions). Furthermore, the segregation of rare earth elements at grain boundaries can inhibit intergranular corrosion, preventing the formation of micro-oxygen-depleted microenvironments at grain boundaries that favor bacterial growth. These studies reveal that rare earth elements synergistically regulate the material surface microenvironment through “macroscopic film densification + microscopic grain boundary optimization”, providing a new dimension for antibacterial mechanisms. By precisely controlling the relative contents of elements such as Cu, Cr, and rare earths, along with the heat treatment regime, synergistic coupling of mechanisms in time and space can be achieved, ultimately realizing a comprehensive anti-MIC effect of “1+1>2”.

3.5. Regulation of Precipitate Phases and Micro-Galvanic Corrosion by Heat Treatment Processes

3.5.1. Solution Treatment

Solution treatment lays the microstructural foundation for controlling the size, quantity, and distribution of precipitate phases by regulating the dissolution and segregation state of alloying elements, thereby influencing grain boundary corrosion susceptibility. In austenitic stainless steel, adequate solution treatment can eliminate the high-strain layer and non-equilibrium phases introduced by processing, reducing preferential sites for subsequent corrosion. For example, after sufficient solution treatment of 304L stainless steel at 1066°C, the surface deformation-induced martensite content (approximately 1.95%) was significantly reduced, and the crack density decreased by more than 50% compared to the insufficiently solution-treated condition, effectively inhibiting the penetration of corrosive media along grain boundaries[48]. Further studies on 316N weldments demonstrated that solution annealing at 1065°C eliminated δ-ferrite and microsegregation, shifting the grain boundary corrosion potential in the positive direction and reducing the pitting density by 67% compared to untreated specimens[49]. At this stage, carbides and Cu-rich phases have not yet precipitated in large quantities, the matrix composition is uniform, and the tendency for Cr depletion at grain boundaries is minimal.

The solution treatment process also directly determines the morphology and distribution of carbides. In nickel-based Alloy 690, after adequate solution treatment at 1100°C for 240 min, the $M_{23}C_6$ carbides precipitated at grain boundaries exhibited a dendritic three-dimensional structure [50]. This discontinuous morphology effectively hindered the continuous propagation of corrosion channels, maintaining the intergranular corrosion susceptibility index (IGCI) at a low level. In contrast, under insufficient solution treatment conditions (e.g., 1100°C for 10 min), carbides precipitated continuously along grain boundaries in a rod-like morphology, forming interconnected Cr-depleted zones, causing the IGCI to sharply increase from 0.8 to 2.3. This indicates that optimizing the solution treatment regime can control the precursor state of carbide precipitation, avoiding the formation of a continuous Cr-depleted network. For Cu-containing alloys, a reasonable solution treatment or double solution treatment process can promote the uniform precipitation of Cu-rich phases. For instance, in Cu-containing aluminum alloys, a double solution treatment at 474°C for 6 h + 2.5 h promoted the uniform nucleation of the Cu-rich $Mg(Zn,Cu)_2$ phase[51], reducing the width of the precipitate-free zone (PFZ) along grain boundaries from 120 nm to 50 nm and decreasing the corrosion depth from 148 μm to 15 μm. The same principle applies to Cu-bearing antibacterial stainless steels: adequate solution treatment allows Cu atoms to be uniformly dissolved in the solid solution matrix, providing the conditions for the precipitation of fine, dispersed Cu-rich phases during subsequent aging treatment, thereby avoiding local micro-galvanic coupling caused by excessive Cu segregation near grain boundaries.

3.5.2. Aging Treatment

Aging treatment is a key step in controlling the size, quantity, and distribution of precipitate phases such as Cu-rich phases and carbides, directly determining the degree of Cr depletion at grain boundaries and the driving force for micro-galvanic corrosion. An optimized aging regime allows precipitate phases to form in a favorable morphology and size, reducing grain boundary corrosion susceptibility. In cold-worked 316L stainless steel, short-term aging at 1075°C for 20 min promoted the reverse transformation of strain-induced martensite to austenite, increasing the Cr content at grain boundaries from 12.1% to 16.8%, while simultaneously promoting the diffusion of Cu to grain boundaries and the formation of nanoscale Cu-rich precipitates[52]. These Cu-rich phases significantly reduced the corrosion potential difference between the grain boundary and the matrix from 0.22 V to 0.08 V, effectively lowering the driving force for micro-galvanic corrosion and extending the stress corrosion cracking initiation time from 96 h to 170 h. This process demonstrates that controlling the size and distribution of Cu-rich phases through aging can reduce the micro-galvanic potential difference and inhibit the development of localized corrosion.

Conversely, inappropriate aging treatment can lead to the continuous precipitation of $M_{23}C_6$ carbides along grain boundaries, causing severe Cr depletion. For example, after aging 316N weldments at 550°C for 4 h[49], the substantial precipitation of $M_{23}C_6$ resulted in a sharp decline in Cr content near grain boundaries, and the corrosion depth increased by a factor of three compared to the solution-treated condition. Therefore, in Cu-bearing antibacterial alloy steels, appropriate aging temperature and time (e.g., medium-temperature, long-duration aging) should be selected to obtain fine, dispersed Cu-rich phases. On one hand, the fine Cu-rich phases can provide sustained release of Cu^{2+}, endowing the material with anti-biofouling capability. On the other hand, the small potential difference between these phases and the matrix will not induce a significant micro-galvanic effect. Simultaneously, it is necessary to avoid the continuous precipitation of carbides at grain boundaries. By controlling aging parameters (e.g., employing double aging or moderately reducing the aging temperature), the morphology of carbides can be adjusted to fine intragranular precipitates or discontinuous grain boundary particles, maintaining sufficient Cr content at grain boundaries and mitigating the degree of Cr depletion.

3.5.3. Comprehensive Mechanism for Inhibiting Localized Corrosion Under Microbial Attachment

The ultimate effect of heat treatment regulation is concentrated in the inhibition of intergranular corrosion and localized corrosion under conditions of microbial attachment. In the marine environment, after the formation of a biofilm, the local pH within the biofilm decreases and Cl^- becomes enriched, preferentially attacking Cr-depleted zones at grain boundaries and regions with high potential differences. Through aging treatments, Cu-rich phases (such as ε-Cu) can be precipitated and dispersed, which facilitates the sustained release of Cu ions, thereby significantly enhancing the antibacterial and microbiologically influenced corrosion resistance. Consequently, even if the biofilm creates a locally acidic microenvironment, the grain boundaries, lacking a continuous Cr-depleted layer, are less prone to preferential dissolution. The micro-galvanic effect is suppressed, and the tendencies for intergranular corrosion and pitting are substantially reduced. For example, additively manufactured 316L subjected to solution treatment at 1066°C followed by severe shot peening achieved a surface residual compressive stress of −750 MPa, accompanied by microstructural refinement, which delayed crack initiation time by 40% and reduced the retention of corrosive media[53]. If further supplemented by appropriate aging treatment to precipitate additional antibacterial Cu-rich phases and passivate grain boundaries, even better corrosion resistance can be achieved in environments with microbial attachment.

It is worth noting that existing studies are mostly conducted in single corrosive media, and there is a lack of analysis on the effects of heat treatment under multi-factor coupled conditions such as temperature, flow rate, and biofilm. Future efforts should establish a multi-factor synergistic evaluation system to provide a more reliable basis for the design of heat treatment processes for MIC-resistant alloy steels in actual marine environments.

4. Conclusion

Research on marine MIC-resistant alloys has evolved from single-element modification to a multi-dimensional synergistic regulation stage. Current research has elucidated the corrosion mechanisms of functional microbial groups such as SRB and iron-cycling bacteria in marine MIC, as well as the synergistic effects of chloride ions, dissolved oxygen, and microbial metabolism in the seawater environment. Through the synergistic design of alloying elements such as Cu, Cr, and rare earths, combined with solution and aging heat treatments and surface engineering technologies (e.g., bioinspired superhydrophobic coatings, graphene-based nanostructures), a balance between the corrosion resistance and mechanical properties of alloy steels has been achieved.

References

[1] Beech IB, Sunner J. (2004). Biocorrosion: towards understanding interactions between biofilms and metals. Current Opinion in Biotechnology, 15(3), 181-186.

[2] Lee JS, Little BJ. (2025). Microbiologically Influenced Corrosion. Journal of Pipeline Integrity, 2, 946-965.

[3] Liu, P., Zhang, H., Fan, Y., & Xu, D. (2023). Microbially influenced corrosion of steel in marine environments: a review from mechanisms to prevention. Microorganisms, 11(9), 2299.

[4] Lewandowski Z. (2013). Fundamentals of biofilm research. CRC Press.

[5] Videla HA, Herrera LK. (2005). Microbiologically influenced corrosion: looking to the future. International Microbiology, 8(3), 169-180.

[6] Hamilton WA. (1998). Bioenergetics of sulphate-reducing bacteria in relation to their environmental impact. Biofouling, 9(3), 201-212.

[7] Venzlaff H, Enning D, Srinivasan J, et al. (2013). Accelerated cathodic reaction in microbial corrosion of iron due to direct electron uptake by sulfate-reducing bacteria. Corrosion Science, 66, 88-96.

[8] Wei FI. (1995). Influence of Alloying Elements on Corrosion Resistance of Low Alloy Steels in Marine Environment. In: CORROSION 1995. Association for Materials Protection and Performance, pp.1-12.

[9] Melchers RE. (2009). Long-term corrosion of steels exposed to marine environments. European Journal of Environmental and Civil Engineering, 13(5), 527-546.

[10] Vazirinasab E, Jafari R, Momen G. (2018). Application of superhydrophobic coatings as a corrosion barrier: A review. Surface and Coatings Technology, 341, 40-56.

[11] Srimaneepong V, Skallevold HE, Khurshid Z, et al. (2022). Graphene for antimicrobial and coating application. International Journal of Molecular Sciences, 23(1), 499.

[12] Little BJ, Lee JS. (2000). Microbiologically influenced corrosion. Kirk-Othmer Encyclopedia of Chemical Technology, pp.1-42.

[13] Videla HA, Herrera LK. (2009). Understanding microbial inhibition of corrosion. A comprehensive overview. International Biodeterioration & Biodegradation, 63(7), 896-900.

[14] Hamilton, W. A. (1985). Sulphate-reducing bacteria and anaerobic corrosion.

[15] Enning D, Garrelfs JJ. (2014). Corrosion of iron by sulfate-reducing bacteria: new views of an old problem. Applied and Environmental Microbiology, 80(4), 1226-1236.

[16] Flemming HC, Wingender J. (2010). The biofilm matrix. Nature Reviews Microbiology, 8(9), 623-633.

[17] Flemming HC, Neu TR, Wozniak DJ. (2007). The EPS matrix: the "house of biofilm cells". Journal of Bacteriology, 189(22), 7945-7947.

[18] Gu T, Jia R, Unsal T, et al. (2019). Toward a better understanding of microbiologically influenced corrosion caused by sulfate reducing bacteria. Corrosion, 35(4), 631-636.

[19] Yuan S, Liang B, Zhao Y, et al. (2013). Surface chemistry and corrosion behaviour of 304 stainless steel in simulated seawater containing inorganic sulphide and sulphate-reducing bacteria. Corrosion Science, 74, 353-366.

[20] Lee W, Lewandowski Z, Nielsen PH, et al. (1995). Role of sulfate-reducing bacteria in corrosion of mild steel: a review. Biofouling, 8(3), 165-194.

[21] Kaksonen, A. H., Dopson, M., Karnachuk, O., Tuovinen, O. H., & Puhakka, J. A. (2008). Biological iron oxidation and sulfate reduction in the treatment of acid mine drainage at low temperatures. Psychrophiles: from biodiversity to biotechnology. Springer, Berlin, 429-454.

[22] Wang Y, Zhang R, Duan J, et al. (2022). Extracellular polymeric substances and biocorrosion/biofouling: recent advances and future perspectives. International Journal of Molecular Sciences, 23(10), 5566.

[23] Xu D, Gu T, Lovley DR. (2023). Microbially mediated metal corrosion. Nature Reviews Microbiology, 21(11), 705-718.

[24] Guan F, Zhai X, Duan J, et al. (2016). Influence of sulfate-reducing bacteria on the corrosion behavior of high strength steel EQ70 under cathodic polarization. PLoS ONE, 11(9), e0162315.

[25] Shinozaki J, Muto I, Omura T, et al. (2011). Local dissolution of MnS inclusion and microstructural distribution of absorbed hydrogen in carbon steel. Journal of the Electrochemical Society, 158(9), C302-C309.

[26] Frankel GS. (1998). Pitting corrosion of metals: a review of the critical factors. Journal of the Electrochemical Society, 145(6), 2186-2198.

[27] Little BJ, Lee JS. (2014). Microbiologically influenced corrosion: an update. International Materials Reviews, 59(7), 384-393.

[28] Jia R, Unsal T, Xu D, et al. (2019). Microbiologically influenced corrosion and current mitigation strategies: a state of the art review. Corrosion Science, 137, 42-58.

[29] Grass G, Rensing C, Solioz M. (2011). Metallic copper as an antimicrobial surface. Applied and Environmental Microbiology, 77(5), 1541-1547.

[30] Nan, L., Yang, W. C., Liu, Y. Q., Xu, H., Li, Y., Lu, M. Q., & Yang, K. (2008). Antibacterial mechanism of copper-bearing antibacterial stainless steel against E. coli.

[31] Warnes S, Caves V, Keevil CW. (2012). Mechanism of copper surface toxicity in Escherichia coli O157: H7 and Salmonella involves immediate membrane depolarization followed by slower rate of DNA destruction which differs from that observed for Gram-positive bacteria. Environmental Microbiology, 14(7), 1730-1743.

[32] Harrison JJ, Ceri H, Turner RJ. (2007). Multimetal resistance and tolerance in microbial biofilms. Nature Reviews Microbiology, 5(12), 928-938.

[33] Olsson CO, Landolt D. (2003). Passive films on stainless steels—chemistry, structure and growth. Electrochimica Acta, 48(9), 1093-1104.

[34] Wang Z, Seyeux A, Zanna S, et al. (2020). Chloride-induced alterations of the passive film on 316L stainless steel and blocking effect of pre-passivation. Corrosion Science, 329, 135159.

[35] Duret-Thual C. (2014). Understanding corrosion: basic principles. In: Understanding Biocorrosion: Fundamentals and Applications, pp.3-32.

[36] Huang F, Li J, Geng R, et al. (2023). Effect of rare earth on inclusion evolution and corrosion resistance of HRB400E steel. Materials and Corrosion, 74(1), 53-67.

[37] Yang S, Gong W, Wang PF, et al. (2024). Effect of Ce on precipitates and corrosion resistance of 2101 duplex stainless steel. Materials Protection, 57(5)

[38] Meng XC, Liu ZF, Yang Y. (2024). Effect of rare earth Y on corrosion resistance of low alloy steel. Materials Protection, 57(8), 47-57.

[39] Liu, X., Ju, D., & Chen, L. (2024). Effect of rare earth metals on passivation behavior of UNS S31803 duplex stainless steel in sulfuric acid solution. Construction and Building Materials, 421, 135644.

[40] Gong W, Yang B, Chen H, et al. (2023). Effects of Ce-La rare earth microalloying on the microstructure and corrosion characteristics of Q420 high-strength steel. Journal of Materials Research and Technology, 18(9), 100242.

[41] Zhang X, Hu, Gong, Wang, Peng, Zhu, Wei, Wu. (2021). Corrosion behavior of rare earth and niobium microalloyed steel in marine atmospheric environment. Materials Protection, 54(6), 7-15.

[42] Qiao C, Zhang H, Wu F, et al. (2024). Rare earth addition powered corrosion resistance of the surface oxide film on GCr15 bearing steel substrate. Corrosion Science, 240, 112490.

[43] Liu S, Guo HJ. (2024). A short review of antibacterial Cu-bearing stainless steel: antibacterial mechanisms, corrosion resistance, and novel preparation techniques. Journal of Iron and Steel Research International, 31(1), 24-45.

[44] Zhang Z, Zhang XR, Jin T, et al. (2022). Antibacterial mechanism of Cu-bearing 430 ferritic stainless steel. Journal of Materials Science, 41(2), 559-569.

[45] Fan L, Sun Y, Wang D, et al. (2023). Microbiologically influenced corrosion of a novel pipeline steel containing Cu and Cr elements in the presence of Desulfovibrio vulgaris Hildenborough. Corrosion Science, 223, 111421.

[46] Wang HM, Huang F, Yuan W, et al. (2023). Corrosion behavior of novel Cu-Mo weathering steel in simulated marine atmospheric environment. Journal of Chinese Society for Corrosion and Protection, 43(3), 507-515.

[47] Chen Y, Yang J, Liu X. (2025). Effect of rare earth Ce on microstructure and properties of Q370qENHY bridge steel. Materials, 18(5), 1048.

[48] Ghosh S, Kain V. (2010). Effect of surface machining and cold working on the ambient temperature chloride stress corrosion cracking susceptibility of AISI 304L stainless steel. Materials Science and Engineering: A, 527(3), 679-683.

[49] Toppo A, Pujar M, Sreevidya N, et al. (2018). Pitting and stress corrosion cracking studies on AISI type 316N stainless steel weldments. International Journal of Pressure Vessels and Piping, 14(3), 226-237.

[50] Zhao X, Wang M, Hao XC, et al. (2021). Effects of solution annealing on the precipitation of dendrite-like carbides during continuous cooling in Alloy 690. Journal of Materials Research and Technology, 15, 3296-3309.

[51] Gao XP, Sun YZ, Cao SP, Niu BY, Li BL, Wang P. (2024). Effect of heat treatment process on microstructure and intergranular corrosion performance of 7075 aluminum alloy. Heat Treatment of Metals, 49(2), 159-165.

[52] Pak S, Ju H. (2020). Stress Corrosion Cracking Behavior of Cold Worked 316L Stainless Steel in Chloride Environment. Journal of Korean Foundry Society, 40, 129-133.

[53] Que Z, Riipinen T, Goel S, et al. (2023). SCC behaviour of laser powder bed fused 316L stainless steel in high-temperature water at 288°C. Corrosion Science, 214, 111022.