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Current Research Status on the Corrosion of B30 Copper-Nickel Alloy in Seawater

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Abstract
B30 copper-nickel alloy, also known as BFe30-1-1 or 70/30 Cu-Ni alloy, is a typical corrosion-resistant material widely used in marine and ocean engineering. Owing to its high thermal conductivity, good formability, and excellent resistance to seawater corrosion, it has been extensively applied in seawater cooling systems, condenser tubes, and heat-exchanger pipelines. Despite these advantages, B30 alloy still suffers from serious corrosion damage under complex marine service conditions. In deep-sea environments, high salinity, high hydrostatic pressure, low temperature, and low dissolved oxygen content may alter the corrosion kinetics and surface film stability of the alloy. In shallow and dynamic seawater environments, high flow velocity, suspended sand particles, and microbial attachment further intensify material degradation through the combined effects of electrochemical corrosion, erosion, and biofouling. As a result, B30 alloy may undergo uniform corrosion, pitting corrosion, erosion-corrosion, and even stress corrosion cracking, which significantly threaten the reliability and service life of marine piping systems. Field investigations have shown that corrosion-induced leakage and perforation of B30 seawater pipelines occur repeatedly in practical ship service, especially in sea areas with high sediment content, thereby reducing equipment availability and increasing operational risk. Therefore, a systematic understanding of the corrosion behavior and degradation mechanisms of B30 copper-nickel alloy in seawater environments is essential for both theoretical research and engineering practice. This paper reviews recent domestic and international studies on the seawater corrosion of B30 alloy, with emphasis on the main experimental approaches, key environmental and material factors affecting corrosion behavior, the evolution characteristics of corrosion product films, and the underlying degradation mechanisms. On this basis, current challenges in corrosion protection and performance evaluation are discussed, and future research directions are proposed to support the long-term safe service of B30 alloy in marine engineering equipment.

Keywords: *B30 copper-nickel alloy; seawater corrosion; erosion-corrosion; corrosion mechanism*

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I. INTRODUCTION

The B30 copper-nickel alloy (also referred to as BFe30-1-1 or 70/30 copper-nickel alloy) is a corrosion-resistant material composed of a copper matrix with approximately 30% nickel, along with appropriate additions of iron and manganese. This alloy is widely utilized in marine and ocean engineering applications, including seawater cooling systems, condenser tubes, and heat exchanger pipelines, owing to its excellent thermal conductivity, good workability, and outstanding resistance to seawater corrosion [1,2]. Statistics indicate that copper-nickel alloys account for approximately 2% to 3% of the total weight of commercial and military vessels [2]. Nevertheless, B30 alloy still faces severe corrosion challenges in harsh marine environments. Deep-sea environments are characterized by high salinity, high pressure, low temperature, and low dissolved oxygen content, whereas shallow dynamic environments involve complex factors such as high flow velocity, sand erosion, and microbial adhesion [3,4]. These conditions may lead to uniform corrosion, pitting corrosion, and even stress corrosion cracking of the B30 alloy. In particular, erosion-corrosion in seawater piping systems has become a significant threat to ship operational availability and equipment safety. According to Zhang's analysis, B30 copper-nickel alloy pipes used in ships have experienced corrosion-induced leakage incidents, especially in the East China Sea where sand content is high [5]. Shen et al. also pointed out that frequent corrosion perforation of seawater pipelines seriously affects the normal operation of equipment, reduces ship availability, and creates potential accident hazards [6]. Therefore, systematic investigation of the corrosion behavior and mechanisms of B30 copper-nickel alloy in seawater environments, along with the identification of effective protection strategies, holds substantial theoretical value and engineering significance for ensuring the long-term service safety of marine engineering equipment. This paper reviews relevant domestic and international research, summarizing the main experimental methods, influencing factors, surface film evolution, and future research directions concerning the corrosion of B30 alloy in seawater.

2 Research Methods for the Corrosion of B30 Alloy in Seawater

2.1 Static Immersion Testing

Static immersion testing is the most fundamental corrosion research method. Specimens of B30 alloy are fully immersed in natural or artificial seawater, and weight loss is measured periodically to calculate the corrosion rate. Simultaneously, microscopic characterization techniques such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and atomic force microscopy (AFM) are employed to analyze corrosion morphology and product composition [7]. Chi's study demonstrated that the corrosion rate of B30 alloy during static seawater immersion gradually decreases with increasing immersion time, which is attributed to the formation and growth of a protective oxide film on the surface [8]. Static immersion data from the Qingdao sea area showed that the corrosion rate of B30 alloy after 1200 hours of immersion was approximately 2.8 μm/year, indicating a relatively low uniform corrosion rate [8]. Pehkonen et al. investigated the effect of specific water quality parameters on copper corrosion and found that the composition of the immersion solution significantly influences the corrosion product film [9]. However, static immersion methods cannot account for the complex effects of fluid flow on corrosion behavior, and the resulting corrosion data tend to be overly idealized, failing to reflect the synergistic interaction between erosion and corrosion under actual service conditions [10]. Du's research also noted that static immersion tests often underestimate the actual corrosion damage that occurs under flowing conditions [11].

2.2 Rotating Disk/Cylinder Electrode

The rotating disk/cylinder electrode apparatus drives specimen rotation in a corrosive medium using a motor, achieving a relatively uniform flow velocity distribution on the specimen surface, thereby enabling the study of flow velocity effects on corrosion behavior [12]. The advantages of this apparatus include simple equipment structure, short testing periods, and small required solution volumes. Moreover, the shear stress on the specimen surface can be precisely controlled by adjusting the rotation speed [13]. Chi investigated the erosion-corrosion behavior of B30 copper-nickel alloy under different flow velocity conditions using a rotating cylinder erosion-corrosion tester, and the results indicated that B30 material exhibits high resistance to erosion-corrosion in seawater at flow velocities below 5 m/s [8]. Zheng et al. noted that rotating experiments impose stringent requirements on motor stability and shaft verticality, and vortex effects induced by rotation may compromise testing accuracy [14]. Furthermore, electrochemical signal acquisition and reference electrode placement under high-speed rotation conditions present technical difficulties [14,15]. Postlethwaite et al. studied erosion-corrosion in slurry pipelines using rotating cylinder electrodes and demonstrated that this method provides reliable data for comparative material evaluation [16]. Heitz et al. provided a detailed discussion on the hydrodynamic models of rotating disk and rotating cylinder systems, concluding that the rotating disk is most suitable under laboratory conditions [17]. Nevertheless, the rotating electrode method remains a primary laboratory technique for investigating velocity–corrosion relationships and is particularly suitable for rapid screening and comparative evaluation of material resistance to erosion-corrosion [18].

2.3 Pipe Flow Testing Apparatus

The pipe flow testing apparatus is the most accurate research method for simulating actual pipeline service conditions [19]. It consists of a storage tank, circulating pump, piping system, control valves, flow meter, and test section. This apparatus enables precise control of flow velocity, flow regime, and water quality parameters, possesses a well-defined hydrodynamic model, and yields results with strong engineering practical value [20]. Chi investigated the corrosion behavior of B30 alloy under different flow velocity conditions using a flowing seawater test bench, validating the corrosion resistance of this material in practical pipeline environments [8]. Lotz et al. conducted erosion-corrosion studies using pipe flow systems and emphasized the importance of mass transfer considerations in interpreting experimental results [21]. However, the pipe flow testing apparatus has several disadvantages, including high construction and operating costs, large space requirements, long experimental periods, and technical challenges related to pump reliability and leak prevention [14,22]. Postlethwaite et al. pointed out that the reliability of pumps and valves and the prevention of leakage are critical issues in long-term pipe flow experiments [16]. Wei et al. pointed out that numerical simulation methods (e.g., computational fluid dynamics, CFD) can be integrated with pipe flow testing to simulate flow fields and particle distributions in special pipeline sections such as elbows, thereby predicting areas susceptible to erosion-corrosion and providing guidance for experimental design and engineering protection [2]. Ferng and Lin demonstrated that CFD methodology can effectively predict wall thinning engendered by erosion-corrosion in pipeline systems [23].

2.4 Jet Impingement Testing Apparatus

The jet impingement testing apparatus delivers corrosive medium at high velocity onto the specimen surface through a nozzle, enabling precise control of impact velocity and impact angle, and is therefore suitable for studying erosion-corrosion under high-flow-velocity conditions [24]. The advantages of this apparatus include the ability to achieve significant erosion-corrosion effects within a short period, substantially reducing experimental duration, and the convenience of electrochemical measurements due to the stationary specimen [25]. Wei et al. reviewed that the main disadvantage of the jet apparatus is its inability to adequately simulate actual pipeline service conditions, as the erosion conditions tend to be more severe than those encountered in practice, potentially leading to measured critical flow velocities that are lower than those obtained from pipe flow tests [2]. Matsumura et al. compared different jet configurations and recommended the jet-in-slit test as a standard method for erosion-corrosion studies [26]. Furthermore, the impact angle influences the erosion mechanism: shear stress dominates at low impact angles (<45°), whereas normal stress dominates at high impact angles (>45°) [27,28]. Burstein and Sasaki investigated the effect of impact angle on the slurry erosion-corrosion of 304L stainless steel using a jet impingement system and found that impact angle significantly influences surface roughness development and pitting potential [29]. This apparatus is particularly suitable for investigating the effects of impact angle on the erosion-corrosion behavior of B30 alloy and for evaluating the corrosion resistance of materials under different hydrodynamic conditions [2,8].

3 Factors Influencing the Corrosion Behavior of B30 Alloy

3.1 Alloy Composition

The excellent corrosion resistance of B30 copper-nickel alloy is primarily attributed to its rational compositional design[30]. Nickel is the core element imparting corrosion resistance. Research by Crousier and Beccaria showed that the polarization curves of pure copper and Cu-Ni alloys exhibit a current plateau in the anodic polarization region, and the current plateau value decreases with increasing nickel content; nickel is the main cause of passivation in Cu-Ni alloys [31]. Iron is another critical alloying element. The addition of 0.5%–2% iron significantly improves the resistance of Cu-Ni alloys to erosion-corrosion in flowing seawater [32,33]. Two hypotheses exist regarding the mechanism of iron action: one suggests that solid-solution iron promotes the formation of a corrosion product film containing hydrous iron oxide, which acts as an anodic inhibitor [32]; the other proposes that iron, like nickel, can be incorporated into the defective Cu_2O lattice, increasing both the anodic and cathodic resistance of the corrosion product film [34]. Efird conducted comparative studies on copper-nickel alloys with different Ni and Fe contents and found that alloys without iron addition formed corrosion products with high oxygen content, whereas iron-containing alloys formed corrosion products with high nickel content [35]. Manganese in B30 alloy primarily functions as a deoxidizer, significantly enhancing the alloy’s resistance to impact corrosion. When the iron content is low, manganese can partially substitute for iron. Additionally, manganese eliminates the adverse effects of excess carbon [11]. Wang et al. investigated the effect of trace boron on the microstructure and properties of 70Cu-30Ni alloy and found that microalloying with boron can improve the erosion-corrosion resistance of Cu-Ni alloys [36]. It should be noted, however, that when iron precipitates out of solid solution, the resulting corrosion products lack nickel enrichment and exhibit a darkened color, which instead reduces the alloy’s corrosion resistance [37].

3.2 Temperature

The effect of temperature on the corrosion behavior of B30 alloy is complex, involving multiple factors such as the kinetic parameters of corrosion reactions, the diffusion coefficient of oxygen, and the dissolved oxygen concentration[38]. Generally, increasing temperature accelerates electrochemical reaction kinetics and oxygen diffusion, but simultaneously reduces oxygen solubility. Moreover, the characteristics of the surface film and the repassivation ability of the alloy also change with temperature[39]. Yin et al. employed response surface methodology to investigate the effects of temperature on the corrosion behavior of B30 alloy in deep-sea environments, finding that temperature is the second most influential factor after dissolved oxygen, and that there exists a significant interaction effect between temperature and pressure[3]. Chi’s research also confirmed that the corrosion resistance of B30 alloy decreases with increasing temperature[8]. Melchers studied the temperature effect on seawater immersion corrosion of 90:10 copper-nickel alloy and found that corrosion rates vary significantly with temperature due to changes in biofouling and oxygen diffusion [40]. Gat et al. classified materials into two categories based on the trend of erosion-corrosion performance with increasing temperature:

the performance of the first category decreases with rising temperature, whereas that of the second category increases, depending on the transition of the dominant mechanism[41]. Therefore, apparently contradictory conclusions from different studies can be attributed to differences in experimental conditions (flow, pH, dissolved oxygen, etc.) leading to different dominant mechanisms [2,14].

3.3 Oxygen Content

Dissolved oxygen is a key environmental factor influencing the corrosion behavior of B30 alloy. In neutral seawater environments, oxygen participates in the reduction reaction as a cathodic depolarizer, and its concentration directly affects the corrosion rate[42]. Yin et al. demonstrated that among the various environmental factors in deep-sea environments, dissolved oxygen exerts the greatest influence on the corrosion of B30 alloy, with the order of effect being dissolved oxygen > temperature > flow velocity > pressure [3]. For B30 alloy, which exhibits passivation characteristics, a sufficient supply of oxygen is necessary to maintain the passive state. When oxygen content is adequate, a dense Cu_2O protective film forms on the alloy surface, effectively retarding the corrosion process. Conversely, under low-oxygen or anoxic conditions, the formation of the protective film is suppressed, potentially leading to an increased corrosion rate [8,11]. Macdonald et al. studied the corrosion of Cu-Ni alloys 706 and 715 in flowing seawater and found that even in the presence of sulfides, the corrosion rate was not extremely high under certain conditions, suggesting that oxygen availability plays a crucial role [43]. Notably, the role of oxygen interacts with other factors; for example, increasing temperature reduces oxygen solubility, whereas increasing flow velocity enhances oxygen mass transfer to the metal surface [39]. These complex coupling relationships result in diverse corrosion behavior of B30 alloy under actual seawater conditions [2,14].

3.4 Flow Velocity

Flow velocity is the most important hydrodynamic factor affecting the erosion-corrosion behavior of B30 alloy [44]. It is generally accepted that B30 alloy exhibits a critical flow velocity in seawater, beyond which the erosion-corrosion rate increases significantly [8,11]. Chi's research indicated that B30 material possesses high erosion-corrosion resistance in seawater at flow velocities below 5m/s [8]. Efird explained this phenomenon from the perspective of shear stress, proposing that flowing seawater generates shear stress on the alloy surface. When the shear force exceeds the adhesion strength between the corrosion product film and the substrate, the protective film is mechanically detached, leading to accelerated corrosion. The critical shear stress for B10 copper-nickel alloy was calculated to be approximately $43.1 N/m^2$ [35]. Tuthill tested the critical shear stress values of Cu-Ni alloys in seawater under different pipe diameters and found that larger pipe diameters allow higher allowable seawater flow velocities [45]. Syrett and Wing proposed from an electrochemical perspective that Cu-Ni alloys exhibit a critical breakdown potential (Eb) in flowing seawater. When the free corrosion potential (Ec) exceeds Eb, high-rate localized corrosion occurs; conversely, when Ec is below Eb, low-rate uniform corrosion predominates [46]. The influence of flow velocity is also manifested through accelerated mass transfer: high flow velocities enhance the supply of depolarizers to the metal surface and the diffusion of corrosion products away from it, thereby increasing the rate of electrochemical reactions [14,47]. Bianchi et al. proposed that in flowing seawater, if bubble size exceeds the thickness of the interfacial layer, bubbles exert a mechanical effect on the protective layer, promoting further corrosion development [48].

3.5 Sand Content

In sand-containing seawater environments, the presence of solid particles significantly aggravates the erosion-corrosion damage of B30 alloy [2,49]. The effect of sand content is primarily manifested through alterations in the shear stress on the material surface. The hardness, particle size, angularity, and concentration of sand particles all influence the magnitude of shear stress [50]. It is generally accepted that higher sand particle hardness and greater angularity lead to stronger cutting action on the alloy surface and, consequently, higher corrosion rates [51]. Zheng et al. demonstrated that as sand concentration increases, the frequency of collisions between sand particles and the alloy surface increases, leading to an increased corrosion rate. However, when the concentration becomes excessively high, a shielding effect among sand particles reduces the impact on the material surface, causing the corrosion rate to decrease [52]. Lu et al. and Pang et al. also confirmed that sand concentration has a threshold effect on erosion-corrosion rates [53]. Furthermore, the presence of sand intensifies agitation of the diffusion layer, promoting more frequent contact between ions in seawater and the alloy surface, thereby accelerating corrosion reactions [2，54]. Yin's research found that under sand-containing conditions, as the impact angle increases, the morphology of impact craters gradually transitions from horseshoe-shaped to dot-shaped. The stable and dense film provides protection for B30 alloy only during erosion by clean seawater; the presence of sand significantly weakens the protective effect of the film[55].

4 Effect of Pre-Immersion Film Formation on the Corrosion Behavior of B30 Alloy

When B30 copper-nickel alloy is immersed in seawater, a corrosion product film gradually forms on the surface. The structure and properties of this film directly influence the subsequent corrosion behavior of the alloy [56]. Numerous studies have shown that the excellent seawater corrosion resistance of B30 alloy relies precisely on the formation of this surface film [8,11,57]. The film typically exhibits a bilayer structure: the inner layer consists of dense Cu_2O, into which Ni and Fe are incorporated, reducing the defect density of the Cu_2O lattice and modifying its semiconducting properties; the outer layer consists of relatively loose Cu^{2+} products (such as CuO and $Cu_2(OH)_3Cl$) and amorphous γ-FeOOH mixtures [58,59]. North and Pryor proposed that the incorporation of Fe into the Cu_2O lattice increases both anodic and cathodic polarization resistance, thereby reducing the corrosion rate [34]. The protective function of this bilayer structure on the underlying metal is twofold: the dense inner layer effectively blocks direct contact between the corrosive medium and the metal substrate, while the outer layer stabilizes the thermodynamic conditions of the inner layer [60].

The duration of immersion plays a decisive role in film evolution [61]. Chi's research demonstrated that the average corrosion rate of B30 alloy gradually decreases with increasing immersion time, which is precisely the result of continuous growth and perfection of the surface protective film [8]. In the early stage of immersion (the "juvenile" stage), the alloy surface has not yet formed a complete protective film, and the corrosion rate is relatively high. After the immersion time exceeds a certain critical value (e.g., approximately 20 days), the film tends to become complete and stable, and the corrosion resistance of the alloy is significantly enhanced [8,62]. Research has shown that under optimized pre-immersion conditions (50°C, 1.5 m/s flow velocity, 0.15 mol/L Cl^-), a layered amorphous pre-immersion film forms on the B30 alloy surface, and the protective performance of all surface states reaches its peak [4]. XPS analysis results indicate that the deposition of the pre-immersion film follows the sequence $Fe_2O_3 \rightarrow NiO \rightarrow Cu_2O \rightarrow CuO \rightarrow Cu_2(OH)_3Cl \rightarrow \gamma\text{-}FeOOH$, wherein the nucleation and growth driving force of Ni-based species is significantly higher than that of Cu-based species, making it the core of dense protective film formation [4,63].

Surface state has a significant effect on the formation and quality of the film [64]. Recent studies have shown that polished surfaces (PT), characterized by low defect density and low roughness, most readily form a continuous protective film, exhibiting the best corrosion resistance among all surface states. In contrast, sandblasted surfaces (SBT) exhibit substantially reduced corrosion resistance due to increased roughness and sand contamination. Surfaces with residual carbon film (DT) induce severe galvanic corrosion, with corrosion products consisting mainly of loose Cu-based products that offer almost no protective capability [4]. The Cu^{2+}/Cu^{+} ratio in the corrosion products is a key indicator of film protective performance—the higher the ratio, the stronger the protective ability. Under static conditions, the Cu^{2+}/Cu^{+} ratios for PT, BT (bright surface), SBT, ST (scratched surface), and DT surfaces are 4.05, 3.82, 1.77, 1.72, and 1.26, respectively, which perfectly align with the order of corrosion resistance [4,65].

The effect of the film on the subsequent corrosion behavior of B30 alloy is mainly manifested in the following aspects [66]. First, the intact film can act as a physical barrier, impeding the diffusion of aggressive ions such as Cl^- toward the substrate and reducing the probability of pitting corrosion [67]. Second, the incorporation of Ni and Fe into the film modifies the semiconducting properties of Cu_2O, increasing the film resistance and reducing the rate of electrochemical reactions. Third, the film can mitigate mechanical damage during erosion, delaying the mechanical detachment of the substrate. However, the protective effect of the film is limited. When environmental conditions change dramatically (e.g., sudden increase in flow velocity, temperature rise, or sand content increase) or when the film is locally damaged, the damaged area forms a "large cathode–small anode" corrosion cell, leading to severe localized corrosion. Furthermore, the presence of microorganisms may also compromise the integrity of the film, accelerating the occurrence of pitting. Syrett and Wing found that exposure time also influences film stability, with longer exposure times making localized corrosion more likely to occur [46].

5 Outlook

Considering the progress of existing research, several key scientific questions regarding the corrosion of B30 copper-nickel alloy in seawater remain to be addressed [2,14]. Future research may focus on the following aspects.

First, quantitative investigation of corrosion mechanisms under multi-factor coupling conditions. In actual marine environments, multiple factors including temperature, pressure, dissolved oxygen, flow velocity, and microorganisms coexist and interact [75]. Most current studies remain limited to single-factor controlled experiments, which cannot adequately reflect the complexity of real service conditions [2]. Yin et al. have made an attempt to establish a mathematical model relating the corrosion behavior of B30 alloy to environmental factors using response surface methodology, an approach worthy of extension [3]. Future efforts should strengthen quantitative studies of multi-factor interactions, develop corrosion prediction models based on machine learning or numerical simulation, and provide scientific bases for engineering design and life prediction.

Second, investigation of the kinetic mechanisms of surface film formation and evolution.Although existing studies have clarified the bilayer structure and basic composition of the film, the kinetic processes of film nucleation, growth, and failure remain incompletely understood [4,34]. In particular, the mechanisms of Ni and Fe incorporation into the film and their regulation of the semiconducting properties of Cu_2O require further in-depth study using high-resolution characterization techniques (such as TEM, ToF-SIMS, and XPS depth profiling) and first-principles calculations. Furthermore, pre-immersion treatment, as an effective surface modification method, warrants systematic optimization of the relationship between process parameters and film protective performance [4].

Third, study of the corrosion behavior of B30 alloy under extreme environments.With the advancement of deep-sea resource exploitation, the corrosion behavior of B30 alloy under extreme deep-sea conditions such as high pressure, low temperature, and low oxygen has attracted increasing attention [3]. Existing studies have preliminarily revealed the order of effects of various environmental factors, but understanding remains insufficient regarding corrosion mechanisms under high-pressure conditions and the influence of deep-sea microorganisms on corrosion processes. Additionally, how the differences between deep-sea and shallow dynamic environments affect the long-term service performance of B30 alloy is an engineering question requiring urgent answers [2].

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