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Review

Stress Corrosion Cracking of Copper–Nickel Alloys: A Review

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Abstract: Under the combination of certain corrosive ions and stress, Cu-Ni alloys may experience severe stress corrosion cracking (SCC), which causes premature failure and hinders their further applications as crucial construction materials in various engineering fields. To reveal the origin of such failure, minimize the related negative impacts, and achieve economic and social benefits, this review summarizes all SCC-related issues by making a brief introduction to Cu-Ni alloys, reporting the SCC behavior in various environments, identifying the effects of different factors during SCC, and revealing the SCC degradation mechanisms. S^{2-} and NH_4^+ are the prominent SCC initiators since the former can combine with Cu^+ to form Cu_2S as a non-protective corrosion product, while the latter has a great tendency to react with Cu_2O/Cu and accelerate the general or local dissolution. Their combination has the most detrimental effect. The SCC mechanisms of Cu-Ni alloys are summarized as film rupture theory and dealloying theory. The related SCC mitigation strategies, including using inhibitors, tailoring alloying elements, and removing/reducing the stress are also discussed. In addition, future directions are made at the end of this paper.

Keywords: stress corrosion cracking; Cu-Ni alloys; corrosion; sulfide; ammonia

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1. Introduction

Cu-Ni alloys (Cupronickel) are the important branch of Cu alloys with several outstanding properties, such as good mechanical properties at both low and elevated temperatures, high thermal/electric conductivity, wear resistance, high corrosion resistance, biofouling resistance, tarnish resistance, weldability, and good processing characteristics. Because of these attractive features, Cu-Ni alloys were developed and widely used in marine, electrical, chemical, and petroleum fields as heat changers, shipbuilding materials, electrical resistors, pumps, valves, frames, fittings, lines/tubes, coinage, and so on. Typical Cu-Ni alloys include Cu-10Ni (B10, C70600) and Cu-30Ni (B30, C71500) ones. Ni has unlimited solubility in Cu, and it is added as the major alloying element to improve corrosion resistance and mechanical strength. Additionally, small amounts of Fe and Mn are also introduced in Cu-Ni alloys for the optimization of microstructures and the improvement in properties such as mechanical strength and corrosion resistance. Table 1 presents the typical chemical compositions of Cu-10Ni and Cu-30Ni alloys. Given that Cu and Ni are adjacent to each other in the periodic table, they share a lot of similarities in atomic properties. Therefore, Cu and Ni are completely miscible in both liquid and solid conditions, and the formed Cu-Ni alloys have an FCC structure with no heterogeneous structure over the whole concentration range.

Table 1. Chemical compositions of Cu-10Ni and Cu-30Ni alloys based on ASTM B-111 standard (in wt.%) [1].

	Cu	**Ni**	**Fe**	**Mn**	**Sn**	**C**	**Pb**	**S**	**Zn**
Cu-10Ni	Bal.	9.0–11.0	1.2–2.0	0.5–1.0	<0.02	<0.05	<0.03	<0.05	<0.5
Cu-90Ni	Bal.	29.0–32.0	0.4–1.0	0.5–1.5	<0.02	<0.06	<0.03	<0.06	<0.5

During their industrial service, Cu-Ni alloys inevitably experience environment-induced degradation. Previous studies systemically investigated the corrosion behaviors in various environments [2]. For instance, the effect of Cl^- content on the corrosion behavior of Cu-10Ni in H_2SO_4 solution was investigated by several electrochemical techniques [3]. In another study, the corrosion performance of Cu-10Ni in natural seawater was investigated in a one-year field exposure test in the North Atlantic Ocean [4]. In general, Cu-Ni alloys show acceptable performance in industrial environments, and they are believed to be Cl-resistant, especially when compared with other commonly used Cu alloys such as Cu-Sn and Cu-Zn alloys [5]. However, when serving as structural components, Cu-Ni alloys may experience stress corrosion cracking (SCC) when subject to the synergistic effects of stress and corrosion [6,7]. When served as heat exchangers, valves, compressor blades, etc., or other load-bearing components in corrosive environments, Cu-Ni alloys are prone to the gradual growth of cracks [8]. They become especially susceptible to corrosion in ammonia-, sulfide-, and nitrate-containing environments. For example, in the simultaneous presence of NH_4^+, S^{2-}, and seawater, SCC cracks were found on Cu-Ni alloys within a short testing period [9]. These SCC issues will cause irreparable losses and sudden failure of Cu-Ni alloys as structural components, thus making them a threat to facility operation, fortune, or even human safety. Therefore, more attention should be paid to the SCC of Cu-Ni alloys, and it is of great importance to elucidate how the SCC of Cu-Ni alloys takes place and how it is affected by different factors.

As schematically shown in Figure 1, SCC is a combination of three factors, namely stress, corrosive environment, and susceptible material. To elucidate the SCC behavior of Cu-Ni alloys, the specific effects of different factors should be thoroughly screened. Unfortunately, the related review articles reporting SCC of Cu-Ni alloys are still insufficient. Some previous works try to make a summarization, yet they fail to cover all the crucial factors [8]. How different factors affect the SCC of Cu-Ni needs further clarification. It should be confirmed in which environment the SCC becomes more pronounced. The related corrosion mechanisms in different environments are still unclear, which makes the setting up a corrosion mitigation strategy difficult. Therefore, this article tries to conduct a comprehensive literature survey and make a systematic summarization. First, basic information on Cu-Ni alloys is provided. Second, the general corrosion behaviors of Cu-Ni alloys are summarized based on corrosion products and the effects of different corrosive ions. Then, the research progress on the SCC of Cu-Ni alloys is reviewed regarding the corrosion features of various environments and SCC mitigation strategies. More importantly, future research directions regarding the SCC of Cu-Ni alloys are proposed at the end of this article. It is anticipated to provide a summary of how different factors affect the SCC performance of Cu-Ni alloys, to make a theoretical guideline of SCC mitigation, and finally, to bring an economic benefit by reducing the maintenance cost and increasing the service life of these Cu-Ni components during their industrial applications.

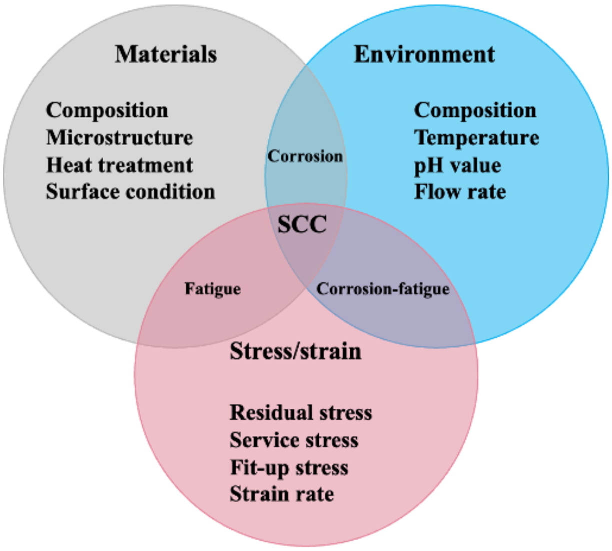

Figure 1. The relationship between materials, environment, and stress/strain.

2. Corrosion of Cu-Ni Alloys

2.1. Basic Corrosion Mechanisms

Once exposed to aqueous environments, the Cu-Ni alloys spontaneously form a corrosion layer mainly composed of Cu/Ni oxides/hydroxides. It is generally accepted that the Cu-Ni alloys tend to develop a double-layer oxide layer, which largely decides the following corrosion performance. The inner layer is dominantly a compact and protective Cu_2O, while the outer one can be a porous layer consisting of Cu compounds ($Cu(OH)_2$, CuO, $Cu_2(OH)_3Cl$, $CuCl_2$ or $CuCO_3$ $Cu(OH)_2$) [10]. The corrosion resistance is mainly contributed by the inner Cu_2O. NiO and $Ni(OH)_2$ may also be found within the double layer and assist in improving the corrosion resistance. The formation routes of these corrosion products are depicted below.

In an aqueous environment, Cu_2O is formed via the direct oxidation of substrate Cu.

$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \tag{1}$$

In the presence of Cl^-, an alternative pathway is that the substrate Cu first dissolves as $CuCl_2$, then is turned into Cu_2O. The specific cathodic and anodic reactions are shown below [11–13].

Cathodic

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2}$$

Anodic

$$Cu + 2Cl^- \rightarrow CuCl_2^- + e^- \tag{3}$$

$$2CuCl_2^- + H_2O \rightarrow Cu_2O + 2H^+ + 4Cl^- \tag{4}$$

The addition of Ni significantly improves the passivity of the surface film, thus enhancing the corrosion resistance. It is said that the doping of Ni^{2+} can reduce the vacancy number of Cu^+, thus improving the resistance of Cu_2O. At the same time, the microstructure of Cu_2O is unchanged. How Ni participates in the formation of Cu_2O and reduces the concentration of Cu^+ is shown below.

$$Ni + V'_{Cu} \rightarrow Ni^{\cdot}_{Cu} + 2e^- \tag{5}$$

Additionally, Ni may also form NiO and incorporate it into the surface oxide layer, thus helping to improve the corrosion resistance [13].

$$NiCl_2 + 2OH^- \rightarrow NiO + H_2O + 2Cl^- \tag{6}$$

Increasing Ni content helps to improve corrosion resistance. So, Cu-30Ni generally has a higher corrosion resistance than Cu-10Ni. However, if the value is higher than 40%, the further addition of Ni will deteriorate the corrosion resistance.

Fe also plays a similar role. The moderate content of Fe at 0.5–2.0% helps to refine the crystal structure and improve the corrosion resistance. It reduces the defect concentration and increases the compactness of the Cu_2O layer. However, once beyond the value, higher Fe content brings about the precipitation of Ni-Fe in the substrate, leading to the formation of loose and porous oxide layers.

2.2. *Effect of Environments*

Although the Cu-Ni alloys have high corrosion resistance in the water, the introduction of certain ions will arouse severe corrosion. This section summarizes the detrimental effects of several anions and cations on the corrosion performance of Cu-Ni alloys.

Chlorine

Chlorine (Cl^-) is commonly found in marine environments and industrial manufacturing processes, and its negative effect on corrosion cannot be ignored. Cu has a higher tendency to react with Cl^- over OH^-. In the early stage of corrosion, Cl^- will attack the atomic Cu in the substrate, as shown in reaction 3. In addition, Cl^- can destroy the integrity of the surface Cu-O layer (Cu_2O and CuO) and arouse pitting corrosion [14].

$$Cu_2O + Cl^- + 2H_2O \rightarrow Cu_2(OH)_3Cl + 2e^- + H^+ \tag{7}$$

$$2CuO + Cl^- + H^+ + H_2O \leftrightarrow Cu_2(OH)_3Cl \tag{8}$$

Furthermore, increasing Cl^- content will induce the general dissolution of Cu_2O at a high rate.

$$Cu_2O + 4Cl^- + H_2O \rightarrow 2CuCl_2^- + 2OH^- \tag{9}$$

Cl^- can also turn metallic Ni into $Ni(OH)_2$ in a similar way, namely the first soluble chlorides and then oxide/hydroxide via hydrolysis [15].

The specific corrosion mechanisms of Cl^- are summarized from the following aspects:

- the adsorption of Cl^- in the oxide layer will destroy its structure and integrity;
- Cl^- may inhibit the formation or passivation of the surface oxide layer;
- Cl^--induced electric field will accelerate the dissolution of the substrate.

Sulfide

Sulfur can be found from different sources such as industrial wastewater pollution, biodegradation, and the reducing product by sulfate-reducing bacteria. Sulfide (S^{2-}) can increase the corrosion sensitivity of copper. It combines with Cu^+ as Cu_2S, which is hard, brittle, and porous. These features make it a non-protective corrosion product layer, especially in the flow of seawater. S^{2-} can also react with Ni to form non-protective Ni_2S. The specific formation processes of Cu-S and Ni-S compounds are presented as follows [16]:

$$Cu + HS^- \rightarrow Cu(HS^-)_{ads} \tag{10}$$

$$Cu(HS^-)_{ads} \rightarrow Cu(HS) + e^- \tag{11}$$

$$\mathrm{Cu(HS)} \rightarrow \mathrm{Cu}^{+} + \mathrm{HS}^{-} \tag{12}$$

$$2\mathrm{Cu}^{+} + \mathrm{HS}^{-} + \mathrm{OH}^{-} \rightarrow \mathrm{Cu_2S} \downarrow + \mathrm{H_2O} \tag{13}$$

$$2\mathrm{Cu}^{+} + \mathrm{S}^{2-} \rightarrow \mathrm{Cu_2S} \downarrow \tag{14}$$

$$\mathrm{Ni} + \mathrm{HS}^{-} \rightarrow \mathrm{Ni}\left(\mathrm{HS}^{-}\right)_{\mathrm{ads}} \tag{15}$$

$$\mathrm{Ni}\left(\mathrm{HS}^{-}\right)_{\mathrm{ads}} \rightarrow \mathrm{Ni(HS)}^{+} + 2\mathrm{e}^{-} \tag{16}$$

$$\mathrm{Ni(HS)}^{+} \rightarrow \mathrm{Ni}^{2+} + \mathrm{HS}^{-} \tag{17}$$

$$\mathrm{Ni}^{2+} + \mathrm{HS}^{-} + \mathrm{OH}^{-} \rightarrow \mathrm{NiS} \downarrow + \mathrm{H_2O} \tag{18}$$

$$\mathrm{Ni}^{2+} + \mathrm{S}^{2-} \rightarrow \mathrm{NiS} \downarrow \tag{19}$$

Ammonium

Ammonium (NH_4^+) can enhance the corrosion of Cu-Ni alloys by destroying the surface copper oxide layer and inhibiting the following repassivation. Under the continuous attack, the Cu_2O may be dissolved via the following reactions [13]

$$\mathrm{Cu_2O} + 4\mathrm{NH_3{\cdot}H_2O} \rightarrow 2\mathrm{Cu(NH_3)}_2^{+} + 2\mathrm{OH}^{-} + 3\mathrm{H_2O} \tag{20}$$

$$1/2\mathrm{Cu_2O} + 2\mathrm{NH_3} + \mathrm{H}^{+} \rightarrow \mathrm{Cu(NH_3)}_2^{+} + 1/2\mathrm{H_2O} \tag{21}$$

$$2\mathrm{Cu(NH_3)}_2^{+} + 4\mathrm{NH_3{\cdot}H_2O} + 1/2\mathrm{O_2} \rightarrow 2\mathrm{Cu(NH_3)}_4^{2+} + 2\mathrm{OH}^{-} + 3\mathrm{H_2O} \tag{22}$$

In addition, NH_3 can also attack Cu as the oxidizing agent

$$\mathrm{Cu} + 2\mathrm{NH_3} \leftrightarrow \mathrm{Cu(NH_3)}_2^{+} + \mathrm{e}^{-} \tag{23}$$

The formed copper–ammonia complex is quite stable. The equilibrium constant of $Cu(NH_3)_2^+$ (5.5×10^8) is actually much higher than that of $CuCl_2^-$ (3.2×10^5) [5]. This makes NH_4^+ quite a corrosive ion.

3. SCC Studies of Cu-Ni Alloys

The study of stress corrosion cracking (SCC) is significant for Cu-Ni alloys. In practical applications, the stress applied on Cu-Ni alloys includes residual stress during machining, sudden opening and closing of the valve, fluid pressure, and so on [17]. As for the SCC resistance, it is widely recognized that Cu-Ni alloys are typically SCC-resistant in seawater or related marine environments [18,19]. Nonetheless, in Cl^- environments containing ammonia and/or sulfide, the SCC of Cu-Ni alloys becomes notably apparent. This section will discuss and analyze the SCC performance of Cu-Ni alloys in these situations by describing the commonly used SCC testing methods, revealing the effects of solution components, ion concentrations, and temperatures on SCC, and summarizing the SCC mechanisms.

3.1. SCC Testing Methods

3.1.1. Slow Strain Rate Test

Slows strain rate test (SSRT), as one can tell from its name, is an SCC testing method that makes the sample subjected to a constant yet slow strain rate (usually at 10^{-5}~10^{-7}/s). Once the fracture takes place, the SCC susceptibility of samples can be evaluated by the fracture time/elongation, yield/ultimate tensile strength, and fracture morphology. The specific sample size can be referred to as per ASTM G129 standard [20]. It is one of the most commonly used methods for SCC sensitivity evaluation.

3.1.2. Constant Loading Method

This method carries out SCC tests by machining the material into a cylinder or rectangular bar, fixing one end, and then applying a constant static load (via springs or weights) on the other end when the whole bar is immersed in the testing solution. Analyses of the time to failure as a function of applied stress will help to evaluate the SCC susceptibility.

3.1.3. Constant Strain Method

In this method, the tested sample is pre-deformed by stretching or bending to a certain strain value and then exposed to testing environments. The commonly strained samples include three/four-point bending ones, U-bended ones, and C-ring ones. The surface corrosion products and cracking conditions will be examined after certain periods. This method is greatly popular for the advantages of simpleness, low cost, and good adaptability for experiments in isolated containers.

3.2. SCC Performance

3.2.1. Sulfide

As mentioned in Section 2.2, S^{2-} can react with Cu and Ni to form non-protective corrosion products. With the assistance of external force, S^{2-} can also increase the SCC-susceptibility of Cu-Ni alloys, especially at higher concentrations. A. El Domiaty and J. N. Alhajji reported the SCC behavior of Cu-10Ni alloy in sulfide-polluted seawater by slow strain rate tests (SSRT) at 20 °C [16]. It was found that the severity of SCC increases with the increasing concentration of sulfide S^{2-} (from 0 to 1000 ppm) in the seawater. The selective dissolution of copper resulted in the accelerated degradation of Cu-10Ni alloys in low (<100 ppm) and high (>1000 ppm) sulfide solutions. Two SCC mechanisms were proposed according to the damaging effect of stress on the protective layer, namely sulfide stress cracking associated with the anodic dissolution and hydrogen embrittlement due to the synergism of sulfide and stress in the low and high sulfide concentration ranges, respectively. With the sulfide concentration rising to 3120 ppm, both the Cu-10Ni and Cu-30Ni alloys exhibited susceptibility to SCC. The most severe SCC was observed in Cu-30Ni alloys at 25 °C, which also reflects the influence of Ni content [21]. With sulfide concentrations reaching up to 3120 ppm, both the Cu-10Ni and Cu-30Ni alloys are susceptible to SCC. The most severe SCC was observed in the Cu-30Ni alloys at 25 °C, which also highlights the Ni content. With the sulfide concentration diluted to 0.002–0.03 M, the Cu-Ni alloys were no longer sensitive to SCC [22,23].

3.2.2. Ammonium

NH_4^+ is a well-known SCC inducer on Cu alloys. T. R. Pinchback et al. [24] documented the intergranular SCC of Cu-40Ni alloys, which was induced by exposing stressed C-ring specimens to ammoniacal vapor [24]. Results show that increasing ammonia concentration enhanced the corrosion rates of vapor-exposed specimens, reducing the strength of SCC samples and thus causing more severe SCC failure. The SCC mechanism was attributed to the depletion of copper from the material at the crack tip. Furthermore, the exposure time governed the depth of corrosion penetration, which was independent of the ammonia concentration [25]. Upon sufficient exposure, the crack walls developed as a corrosion layer consisting of two phases, namely an inner nickel-rich phase adjacent to the alloy substrate and an outer copper-rich phase. M. H. Johar et al. [26] observed the intergranular brittle SCC of Cu-27Ni alloy in Mattsson's solution (containing 1M NH_4^+ and 0.05 M Cu^{2+}). Figure 2 presents the fracture morphology, with Figure 2a,b,d,e from the top view and Figure 2c,f from the side view. Intergranular fracture presented in Figure 2b illustrates the crack propagation features. It indicates that intergranular corrosion is the failure mechanism in such an NH_4^+-containing environment.

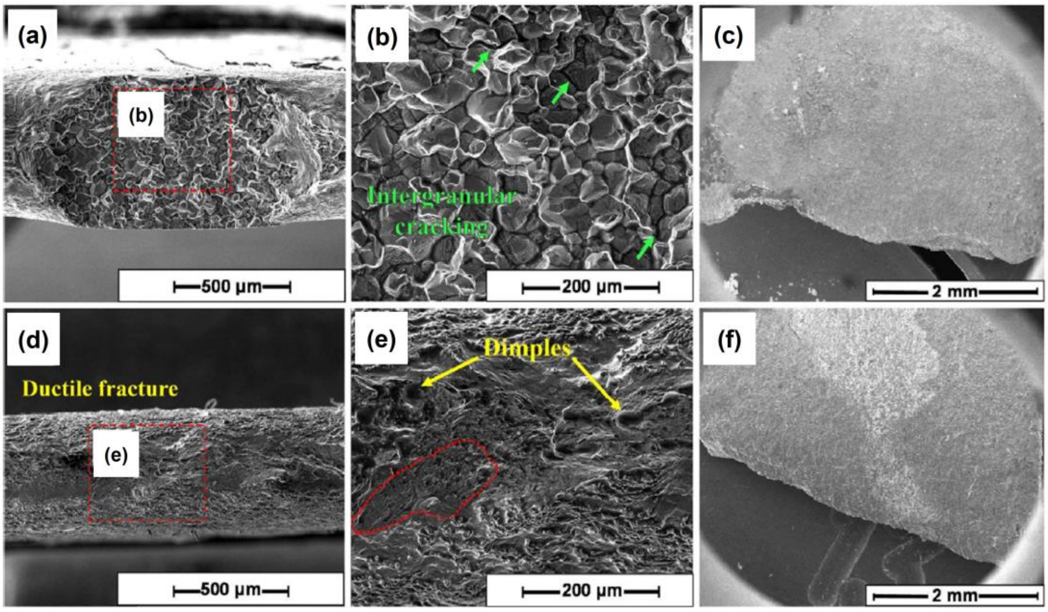

Figure 2. SEM fracture images of both front and side views of Cu-27Ni after SSRT tests in different environments: (**a**–**c**) Mattsson's solution; (**d**–**f**) Mattsson's solution with 500 ppm of Benzotriazole [26]. (**a**,**b**,**d**,**e**): top view; (**c**,**f**): side view.

SCC typically occurs beyond the elastic limit, namely in the plastic region. However, it was observed to occur below the elastic limit on the Cu-5.37Ni alloy when subjected to superimposed cyclic stress. During the cyclic stress test, a static load of 180 MN/m^2 was loaded, followed by a periodic cyclic load of 18 MN/m^2 with a low frequency (15–30 Hz) [25]. The accelerative influence of superimposed cyclic stresses on ammonia-induced brittle SCC failures was also reported by D.C. Agarwal et al. [27,28]. As shown in Figure 3, the Cu-30Ni experiences pitting corrosion upon exposure to seawater and seawater + NH_4^+. With the further application of stress, cracks developed on the surface [13]. Note that Figure 3 has a lower magnification than Figure 3a,b to show the full morphology of the formed crack. Ammonia initiates an SCC attack at the surface via an intergranular mechanism, and crack propagation may transition to a transgranular mode [25,27,28]. Once the crack is initiated, it can propagate to failure unless $MgCl_2$ is added and plays a mitigating effect.

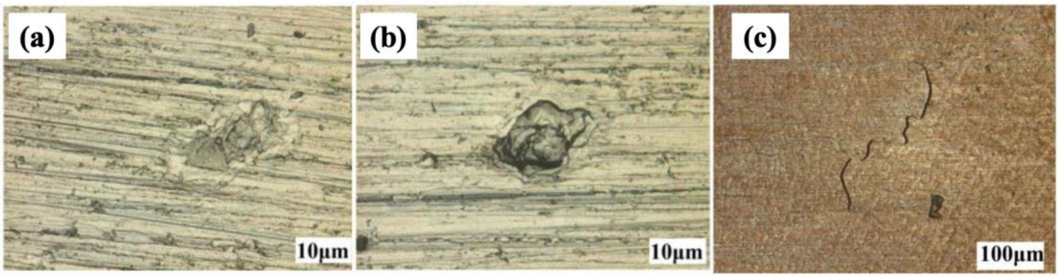

Figure 3. Optical images of Cu-30Ni alloy surfaces after corrosion and corrosion product removal in different environments: (**a**) seawater, (**b**) seawater with NH_4^+, and (**c**) seawater with NH_4^+ under stress [13].

H. Y. Xing et al. [13] reported the synergistic effects of stress and NH_4^+ on the pitting corrosion of the Cu-30Ni alloy. NH_4^+ destroys the oxide film on the surface of the Cu-30Ni alloy, hindering the restoration process of the oxide film, and thereby diminishing the quantity of protective Cu_2O and NiO in the corrosion products of the specimen. After the application of load stress, the pitting depth of the specimen intensifies, indicating the onset of stress corrosion cracking.

3.2.3. Sulfide + Ammonium$^-$

H. Ardy et al. [29] studied the corrosion behavior of Cu-10Ni alloy in a solution containing a mixture of both ammonia and sulfide. No SCC behavior was observed, as the specimens were still in the initial stage of SCC where the slip dissolution mechanism occurs, accompanied by pitting and intergranular corrosion [29]. Further studies are still needed to confirm the synergistic effects of NH_4^+ and S^{2-} on SCC.

3.2.4. Strain Rate

SCC is also found to be associated with the tensile strain rate. A. A. Nazeer et al. [30] investigated SCC behaviors of Cu-10Ni alloys at room temperature in a 3.5% NaCl solution containing sulfide ions at various strain rates during the SSRT tests. The study suggested that similar SCC behavior may be observed when using strain rates of 1.8×10^{-6}, $2.5 \times 10^{-6,}$ and 5×10^{-6} s^{-1}, with the most severe SCC occurring at a strain rate of 5×10^{-6} s^{-1} and a concentration of 20 ppm S^{2-}.

3.2.5. Temperature

It is also noted that the testing temperature played a significant role in influencing the SCC of Cu-Ni alloys. K. Habib et al. [31] evaluated the SCC of Cu-10Ni and Cu-30Ni in natural seawater polluted with sulfides at temperatures ranging from 25 to 70 °C. The most severe SCC deterioration of the Cu-10Ni specimens at 39% was in polluted seawater containing 200 ppm sulfide at 70 °C. In contrast, the Cu-30Ni specimen exhibited a maximum deterioration percentage of 27% in polluted seawater with 3120 ppm sulfide at 70 °C. H. M. Shalaby et al. [32] also reported similar findings, indicating that Cu-30Ni was more susceptible to transgranular SCC at 90 °C than 60 °C in 18% monoethanolamine solutions. This cracking phenomenon was attributed to the stress-assisted dissolution of copper from the alloy matrix.

3.3. SCC Mechanisms

As can be found in Reaction 2, the cathodic reaction during Cu-Ni corrosion is oxygen adsorption rather than hydrogen evolution. This feature is decided by the high reduction potential of H on the Cu surface. Therefore, the hydrogen embrittlement theory, which is popular for other metals such as Fe- and Mg-based alloys is not applicable to Cu-Ni alloys. Actually, there are two widely accepted SCC failure mechanisms of Cu-Ni alloys: the film-rupture theory and the dealloying theory.

Based on the film rupture theory, the Cu-Ni alloys develop a corrosion product upon exposure to aqueous environments. Under the synergistic effect of tensile loading, cracks are prone to develop within the film, thus providing a short-circuit path for the inwardly diffused corrosive solution. The exposed underlying substrate at the crack tip experiences severe corrosion; however, repassivation is inhibited due to the presence of external stress. In this way, the SCC crack develops at a fast speed.

As for the dealloying theory, selective dissolution of certain elements at the crack tip is the main contributor to SCC. For instance, in S^{2-}-polluted seawater, Cu-10Ni experienced severe SCC due to the selective dissolution of Cu induced by S^{2-} [16]. Theoretical tools such as Pourbaix diagrams and the solubility database should be used to predict the tendency of dealloying or selective dissolution of certain metallic elements in the presence of other corrosive ions, thus evaluating the SCC susceptibility in various aqueous environments [8].

Based on a comprehensive literature survey, all the SCC studies of Cu-Ni alloys in various environments are summarized and presented in Appendix A. It is intended not only for literature citation and searching but also for the setup of a database covering all related details of SCC for future reference.

4. Corrosion Cracking Mitigation

Currently, the established strategies for mitigating stress corrosion cracking primarily encompass the incorporation of corrosion inhibitors, regulation of alloying elements, and heat treatment [8].

4.1. Inhibitors

A. A. Nazeer et al. [30] reported that the susceptibility to SCC of Cu-10Ni alloy can be effectively inhibited by adding glycine, which results in an alteration of the failure mechanism, from brittle transgranular cracking to ductile failure in 3.5% NaCl solutions containing sulfide ions. As shown in Figure 4a, the Cu-10Ni sample experiences ductile failure in the air since a lot of dimples can be found on the fracture surface. In Figure 4b,c, the application of S^{2-} and higher strain rate lead to brittle fracture, as indicated by the transgranular morphology and more cracks. With the future addition of glycine, the fracture mode shifts back to ductile, as shown in Figure 4e. The inhibition effect of glycine is ascribed to its adsorption on the alloy surface, which delays the anodic dissolution of the alloy by blocking the active sites on the alloy surface and thereby mitigating the SCC. In addition, Benzotriazole (BTA) was demonstrated to act as a SCC inhibitor for Cu-27Ni alloys, leading to an alteration of the failure mechanism, from brittle intergranular cracking to ductile failure in Mattsson's solution [26]. The comparative results are shown in Figure 2. Based on the top and side views of the fractured sample, it is found that the addition of BTA can increase the number of dimples (top view, indicated by the yellow arrow and red circle in Figure 2e) and reduce the number of cracks (side view). BTA can form a protective film on the surface of the Cu-27Ni alloy and shift the corrosion potential to nobler states. The crack propagation regime is controlled by the concentration of BTA.

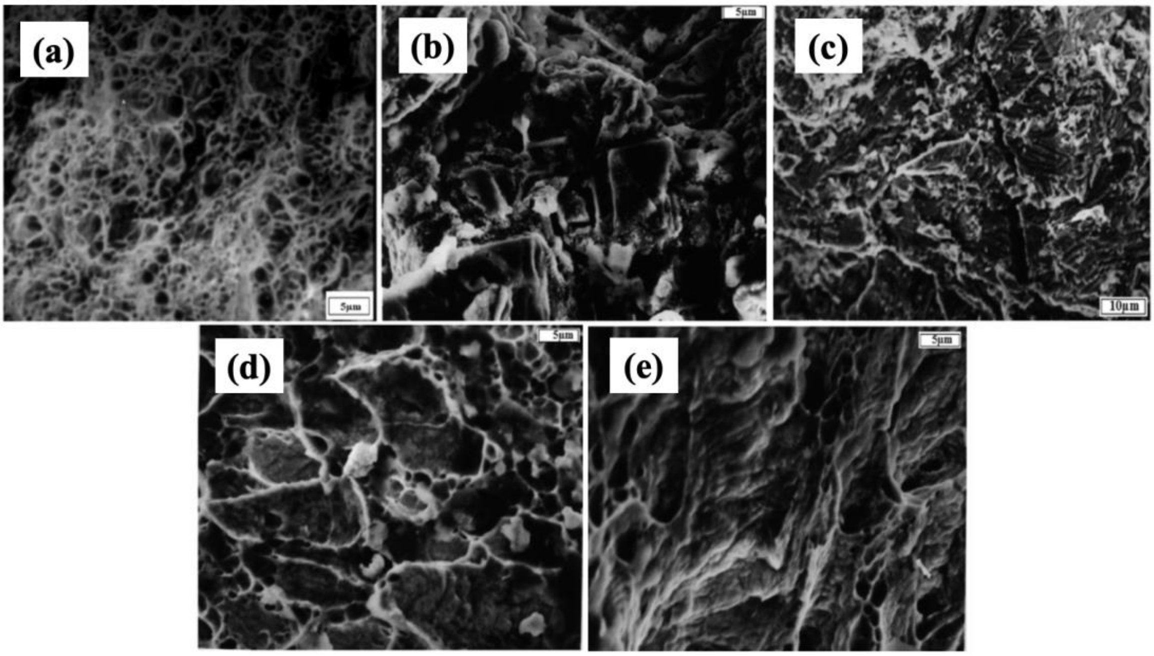

Figure 4. Fractography of Cu-10Ni alloy after SCC tests in different environments: (**a**) air, (**b**) 3.5% NaCl + 20 ppm S^{2-} at a strain rate of 2.5×10^{-6}, (**c**) 3.5% NaCl + 20 ppm S^{2-} at a strain rate of 5×10^{-6}, (**d**) 3.5% NaCl + 20 ppm S^{2-} + 500 ppm glycine, and (**e**) 3.5% NaCl + 20 ppm S^{2-} + 500 ppm gly + 100 ppm KI. Adapted from reference [30].

The presence of $MgCl_2$ can be beneficial for the SCC when low nickel–copper alloys (Cu-5.37Ni) are exposed to 3.5%NaCl solutions containing ammonia [33,34]. The brittle intergranular SCC was entirely eliminated when the concentration of $MgCl_2$ reached 7.5%. The results were attributed to the formation of a thick, sticky protective corrosion layer on the sample surfaces in the presence of $MgCl_2$, which can withstand the corrosive attack by ammonia [27,28].

4.2. Alloying Elements

The addition of Ni to copper can enhance the SCC resistance in ammonia and sulfide environments [8,9]. Previous studies reported that Cu-30Ni has higher SCC resistance than Cu-10Ni in ammonia and sulfide-containing environments [9]. In another study. different contents of Fe were added into Cu-10Ni and then tested SCC in a moist NH_3 atmosphere [35]. At a relatively low value, Fe was in a solutionized state, and it can increase the SCC resistance by doping the Cu_2O corrosion product film and reducing the growth rate of the tarnish film ahead of the advancing crack. However, once beyond the critical value, further addition of Fe results in precipitates, which reduce the SCC resistance by decreasing the availability of Fe in the matrix for doping the corrosion product film. The precipitate also further accelerates the crack growth rate via a galvanic effect [35]. It seems that adding minor alloying elements in Cu-Ni alloys can improve the corrosion resistance. For instance, Al, Cr, Co, and Ti were proven to their beneficial effects on improving corrosion resistance. Future work shows enlarge the element database and figure out the specific improving mechanisms.

4.3. Remove or Reduce the Stress Level

The stress-induced SCC basically originates from two sources: external ones from the service environments and internal ones due to material manufacturing and processing [36]. To reduce the SCC susceptibility, an effective way is to remove or reduce the stress level. The external stress can be reduced via rational geometrical design of the components and reasonable stress distribution during service, while the internal stress can be inhibited by optimizing the materials processing (such as welding) and appropriate material treatment such as annealing [37], vibration stress relief [38], tempering [39], natural aging, mechanical loading, and so on.

5. Summary and Future Directions

5.1. Summary

Cu-Ni alloys such as Cu-10Ni and Cu-30Ni exhibit high corrosion/wear resistance, high mechanical strength, bio-fouling resistance, and good processability, thus showing potential applications in marine, electric, chemical engineering, and other fields. The good corrosion resistance of Cu-Ni alloys lies in the formation of a compact Cu_2O surface oxide layer. The appropriate addition of Ni improves corrosion resistance by reducing the number of Cu^+ vacancies and forming Ni oxide/hydroxide, which increases the compactness and protectiveness of the surface oxide layer.

While Cu-Ni alloys generally show acceptable corrosion resistance to Cl^--containing environments, the simultaneous presence of other ions such as S^{2-} and NH^{4+} will make them susceptible to stress corrosion cracking. Based on the literature survey, the following conclusions can be drawn:

S^{2-} can react with Cu^+ to form non-protective Cu_2S. Higher S^{2-} concentration will intensify SCC. The rupture of brittle Cu_2S may expose the underlying substrate and accelerate the SCC degradation.

$NH_4{}^+$ has a high affinity to both Cu and its oxides. By destroying the surface Cu_2O, $NH_4{}^+$ induces localized corrosion such as pitting on Cu-Ni alloys. With the assistance of external stress, $NH_4{}^+$ selectively dissolves Cu at the crack tip, causing intergranular corrosion.

The combination of S^{2-} and $NH_4{}^+$ increases the susceptibility by acting as SCC initiators. In addition, a higher strain rate and testing temperature will enhance SCC.

The SCC can be mitigated by using corrosion inhibitors (glycine, Benzotriazole, $MgCl_2$, etc.), adding appropriate amounts of alloying elements (such as Ni, Fe, Al, Cr, Co, Ti), and reducing the stress levels.

5.2. Future Directions

To fully understand the SCC mechanisms and formulate effective mitigating strategies, the following directions should be considered for future studies.

- Using advanced characterization techniques to characterize the structure degradation mechanisms at the atomic level, especially for the atoms at the crack tip.
- Enlarging the SCC testing environments. More testing factors, such as the presence of NO_3^- or other ions, a wider range of testing temperature, and flow conditions, should be taken into consideration during the SCC tests.
- Exploring other corrosion protection methods, such as coatings, to reduce SCC susceptibility. The related SCC mechanisms with coatings should also be illustrated. In addition, effective surface modification methods, such as laser processing [40], might also be used to inhibit the initiation of SCC cracks.
- Making modifications to the current operating practices and reducing the possibility of crack growth. In addition, finding effective methods to repair the existing cracks.

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Appendix A. A Summary of the SCC of Cu-Ni Alloys in Different Environments

Year	Materials	Solution	Temperature	SCC Test Method	Time to Failure	Main Finding-	References
1961	Cu-Ni	seawater	-	-	-	Immune to SCC	[18]
1968	α Cu	$Cu(NO_3)_2$	-	-	-	Susceptibility of Cu–Ni alloys to intergranular SCC in $Cu(NO_3)_2$ solutions.	[41]
1973	Cu-10Ni	moist NH_3	-	U-bend	1000 h	Stress corrosion resistance was improved by solutionized Fe, but damaged by precipitation of Fe.	[35]
1974	Cu-Zn-Al	pure water/steam	150–300 °C	-	1000 h	Low-Zn alloys: intergranular SCC high-Zn: layer corrosion, immune to IGSCC.	[42]
	Cu-10Ni/30Ni		300–350 °C		500 h	Accelerated intergranular SCC due to the equilibrium grain boundary segregation of active metals.	
	Monel metal		350 °C			No SCC (due to metallurgical factors and service duration).	
1975	25 copper-base alloys	industrial and marine environments.	-	-	-	Only a few are susceptible to SCC	[19]
1979	-	-	-	SSRT	-	Strain rates between 10^{-7} and 10^{-5} s^{-1} promote SCC	[43]

Year	Materials	Solution	Temperature	SCC Test Method	Time to Failure	Main Finding-	References
1987	CuZn\CuZnMn\CuZnNi	PH4-14 Mattsson's solution	RT	U-bend	-	Stress corrosion of copper alloys is controlled by anodic crack tip dissolution	[44]
1991	Cu-10Ni	Na$_2$S	RT	SSRT	-	Cu-10Ni is susceptible to intergranular SCC in concentrated pure sulfide solutions, but not in dilute solutions	[22]
1992	Cu-10Ni, Cu-30Ni	chloride + sulfide	-	-	-	No SCC. The passive surface is responsible for the resistance to chloride and sulfide SCC.	[45]
1994	Cu-30Ni	NaCl + S^{2-}	25–70 °C	SSRT	-	The most severe SCC on a Cu-30Ni in seawater with 3120 ppm S^{2-} at 25 °C.	[21]
	Cu-10Ni					SCC of Cu-10Ni is not affected by S^{2-} or T.	
1997	Cu-10Ni	NaCl + S^{2-}	20 °C	SSRT	97 h for 100 ppm; ~41 h for 1000 ppm	Two SCC mechanisms: anodic dissolution-low c(S^{2-}), hydrogen embrittlement-high c(S^{2-}).	[16]
2002	Cu-5.37Ni	5% NH$_3$	26 ± 1 °C	SSRT	16–17 days	Brittle transgranular SCC. MgCl$_2$ is beneficial when low nickel copper alloys are exposed to ammonia.	[34]
		NaCl + NH3 + MgCl$_2$			20–21 days		
		air			26 days		
2002	Cu-5.37Ni	air	28 ± 1 °C	SSRT	24 days 18 h	NO SCC.	[46]
		NaCl + MgCl$_2$			23 days 0 h	NH$_3$ reacts directly with Cu and Ni resulting in blue–green complexes and shows corrosion-assisted failure. No clear evidence of SCC.	
		NaCl + MgCl$_2$ + NH$_3$			17 days 2 h		
2002	Cu10Ni	NaCl + Na$_2$S	24 ± 1 °C	SSRT	0.98/0.70	Susceptible to SCC, mainly intergranular. Mechanism: sulfide stress corrosion cracking assisted with pitting corrosion for Cu10Ni at slip steps.	[47]
2002	90Cu-10Ni	NaCl + S^{2-}	25/50/70 °C	SSRT	40.8/27.8/25.0 h	The deterioration percentage of SCC of the Cu-10Ni specimen in polluted seawater was found to range between 19.6 and 39% (200 ppm, 70 °C)	[31]
	70Cu-30Ni				95.3/73.1/74.2 h	70Cu-30Ni -between 19.4 and 27.3% (1000 ppm, 50 °C; 3120 ppm, 70 °C)	
2003	Cu-5.37% Ni	3.5 wt.% NaCl + 10.0 wt.% MgCl$_2$ + 1.0 wt.% NH$_3$	28 ± 1 °C	SSRT	62.93 h	1. With NH$_3$, failure changed from ductile to brittle intergranular SCC. 2. Inhibition of SCC by MgCl$_2$.	[33]
2003	Cu-5.37Ni	air/5/10% NH$_3$	28 + 1 °C	SSRT	75.54/57.26/52.14 h	Intergranular SCC was observed to occur below the elastic limit in the presence of the superimposed cyclic stress, which propagates by transgranular SCC mechanism.	[25]
2004	CuAl$_9$Ni$_3$Fe$_2$	sea water	-	SSRT	Cross-section reduced by 20% in 3 weeks	Intergranular crack; second phases play a key role.	[48]
2005	Cu-Ni-Al-Mn-Nb	NaCl + acetic acid + hydrogen sulfide	82 °C	SSRT	720 h	Brittle intergranular failure. With Ni up to 25%, it is resistant to hydrogen embrittlement, sulfide stress corrosion, and stress corrosion in NH$_3$.	[49]
	MTA150 (Cu-Ni14.9-Sn7.9-C72900)				180 h	Susceptibility to stress corrosion; brittle intergranular fracture	
2005	Cu-5.37%Ni	NH$_3$/NH$_3$ + NaCl/NH$_3$ + NaCl + MaCl$_2$	28 ± 3 °C	SSRT	57.26/57.37/62.73 h	Brittle SCC failures. Superimposed cyclic stresses on prestressed specimens accelerate the stress corrosion failures in an ammoniacal environment.	[27]
2005	Cu-5.37%Ni	10% NH$_3$ + x% MgCl$_2$	28 ± 3 °C	SSRT	40.91–97.58 h	Intergranular SCC. Beyond 7.5% MgCl$_2$ completely restores the ductility loss that was observed under the influence of ammonia alone.	[28]
2006	Cu-10Ni	wet H$_2$S	35–120 °C	-	-	The failure of a Cu-10Ni bundle used in the overhead condenser of a steam cracker unit was attributed to intergranular SCC caused by wet H$_2$S condensed in the overhead column.	[50]
2007	UNS C72900	ISO 15156-3 [51]	RT	-	30 days	Cold-worked and hardened UNS C72900 is more prone to SSC and SCC than hot-worked and hardened, and exhibited intergranular fracture with transgranular branching.	[52]

Year	Materials	Solution	Temperature	SCC Test Method	Time to Failure	Main Finding-	References
2007	Cu-30Ni	18% monoethanolamine (MEA)	60/90 °C	constant extension rate test (CERT) technique	81/65 h	Susceptible to transgranular SCC in the 90 °C aerated MEA solution of pH 9. Cracking mechanism: stress-assisted dissolution of copper from the alloy matrix.	[32]
2009	Cu-10Ni	7.5% NH_3/Na_2S	RT	SSRT	67.57 h/26.12 h	Crack propagation depends on the concentration and the exposure to the environment post-crack initiation. Better SCC resistance due to higher Ni.	[9]
2011	Cu-10Ni	NaCl + S^{2-}	RT	$5.0 \times 10^{-6} s^{-1}$	397 min	S^{2-} increases the susceptibility of brittle transgranular SCC at different strain rates.	[30]
		NaCl + S^{2-} + glycine			420 min	Glycine is a great SCC inhibitor. Surface adsorption inhibits anodic dissolution	
		NaCl + S^{2-} + glycine + KI			430 min	Synergistic effect of KI and glycine improves SCC resistance in sulfide-polluted saltwater	
2011	Cupronickel	NH_3/S^{2-}	-	-	-	1. Ni in Cu enhances the SCC resistance, while Zn decreases it. 2. Two SCC mechanisms: Passive-film rupture and de-alloying. 3. Mitigate the SCC: heat treatment and inhibitors.	[8]
2013	C70600\C76400	-	-	ISO 6957 [53]	1 year	NO SCC. Corrosion rates under tensile timevarying load is 39% higher than untensioned fixed configuration.	[4]
2018	CuNiSn	sour H_2S	150 ± 5 °C	4PB	720 h	SCC: cracks up to 3 mm deep, severe depletion of Cu close to the cracks due to selective corrosion	[54]
		simulated seawater				NO HSC.	
2019	KS C1220, UNS C12200	heating water supply system of a residential building	10 °C	U-bolt	-	Susceptible to SCC and exhibits 4-stage fracture process.	[55]
2021	Cu-27%Ni	Mattsson's solution	-	SSRT	2301/7037 sec without/with BTA	1. BTA as a SCC inhibitor by forming a protective surface film. 2. Crack propagation regime is controlled by the BTA concentration. 3. Fracture type changes from intergranular brittle to ductile.	[26]
2021	Cu-10Ni (UNS C70600)	10% NH_3/10% Na_2S/mixture of both	RT	C-ring	15 days	1. In the incubation stage of SCC with slip dissolution mechanism accompanied by pitting and intergranular corrosion. 2. No well-defined effect of tensile stress on the corrosion rate.	[29]
2023	Cu-30Ni	NH_3	65 ± 0.2°C	C-rings	7 days	1. NH_4^+/stress increases the depth and diameter of the pits and the number of pits in the specimens. 2. Pitting is the synergistic effect of stress and NH_4^+.	[13]
2023	Phosphorus deoxidized copper	3.5 wt%NaCl	RT	SSRT	2 days (BJ)/4.5 days (MJ)	Worse SCC and poorer fracture toughness on Brazed joint (BJ) than mechanical joint (MJ) due to a brittle surface copper oxide layer	[17]

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