

Effect of Alloying on the Resistance of Cu-10% Ni Alloys to Seawater Impingement

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ABSTRACT

Cu-Ni castings and wrought pipes nominally contain 1% Fe to 2% Fe, which is added to improve the Cu-Ni alloy's erosion-corrosion resistance. After fabrication, Cu-Ni products are solution heat-treated to dissolve the iron uniformly and form a single-phase alloy. During welding, however, iron can precipitate from solid solution onto grain boundaries in the heat-affected zones (HAZ). During seawater service, these iron-rich precipitates can dissolve preferentially (galvanically), leading to intergranular corrosion of the HAZ. The present report described 90-10 Cu-Ni alloys in which different soluble elements were substituted for iron. Jet-impingement testing in filtered natural seawater showed that 2% In also promoted improved erosion-corrosion resistance. Because indium is very soluble in copper, it should not precipitate in the HAZ during welding and cause intergranular corrosion of the HAZ during seawater service. The present study reviewed the literature on the mechanisms by which iron is believed to improve the erosion-corrosion resistance, and proposed a different model based on doping of the thin surface oxide film.

KEY WORDS: copper-nickel alloys, cupronickel, erosion-corrosion, film, heat-affected zone, intergranular corrosion, iron, jet impingement, seawater

INTRODUCTION

Cu-Ni alloys (also known as cupronickels) have been used for over 50 years for seawater piping and heat exchangers because they have good seawater corrosion resistance and excellent marine fouling resistance.¹ Although pipes made from stainless steel or titanium alloys have a higher erosion-corrosion resistance, they are subject to biofouling, which requires that the intake seawater be chlorinated or ozonated. Ship designers prefer to use the cupronickel alloys because of their natural fouling resistance, resulting from their very high copper content. It would be of great value to the maritime fleet if the erosion-corrosion resistance (and the resistance to sulfide-polluted water) could be improved. Such an improvement would extend the service life and lower the copper discharge rate, which also would benefit the commercial utilities and environment, since many land-based power plants use cupronickel tubing.

Commercial Cu-Ni alloys contain 1% Fe to 2% Fe, which improves their erosion-corrosion resistance (i.e., Cu-10% Ni-2% Fe [UNS C70600]⁽¹⁾ and Cu-30% Ni-1% Fe [UNS C71500]). In 1951, Bailey published a report outlining the development of the Cu-Ni-Fe alloys and the experimental determination of the optimum iron content.² Bailey reported that Cu-30% Ni alloys with 0.3% Fe to 4.0% Fe were resistant to impingement attack in flowing seawater, with 4% Fe being the upper limit (however, alloys with > 2% Fe were subject to pitting). Bailey reported that the optimum composition was Cu-30% Ni-1% Fe. For

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⁽¹⁾ UNS numbers are listed in *Metals and Alloys in the Unified Numbering System*, published by the Society of Automotive Engineers (SAE) and cosponsored by ASTM.

the low nickel range, Bailey reported the optimum composition to be Cu-10% Ni-2% Fe. The protective oxide on these alloys was thin, golden, and almost transparent. X-ray patterns of the scrapings identified the oxide as cuprous oxide (Cu_2O). Bailey also reported that 0.25% Mn to 2.0% Mn was beneficial in improving impingement attack for cupronickel alloys with < 0.3% Fe.

The earliest attempt to understand the role of iron in improving erosion-corrosion resistance was reported by North and Pryor.³ They used potentiodynamic polarization to demonstrate that Cu-Ni-Fe alloys were not truly passive in sodium chloride (NaCl) solutions. North and Pryor postulated that the iron increased the electronic resistance of the Cu_2O oxide. They demonstrated this concept by boiling copper, Cu-10% Ni-Fe, and Cu-30% Ni-Fe in a 3.4% NaCl solution for 30 days, and then measuring the resistance of the surface film galvanostatically in 3.4% NaCl at 25°C. The film on copper showed the lowest resistance, next was Cu-10% Ni-Fe, and the highest resistance was Cu-30% Ni-Fe. North and Pryor hypothesized that nickel and iron were incorporated into the Cu_2O film, occupied cation vacancies, and thus, reduced the cation vacancy concentration, which increased the resistance.³ However, North and Pryor's explanation ignores the oxide anion (O^{2-}) that must accompany the nickel or iron substitution into the Cu_2O lattice. Consideration of the O^{2-} implies that the addition of nickel oxide (NiO) and hematite (Fe_2O_3) into Cu_2O will not annihilate cation vacancies but will create them.

A 1972 review by Pearson reported that the iron addition increases erosion-corrosion resistance of cupronickels in flowing seawater, but only if iron remains in solid solution.⁴ Pearson reported that increasing the iron concentration increases the resistance to impingement attack (erosion-corrosion) but decreases the resistance to localized attack (pitting and crevice corrosion). The maximum iron content of Cu-10% Ni was recommended as 2% Fe because more iron was difficult to keep in solid solution and its precipitation increased localized corrosion. Pearson reported that if subsequent thermal treatment during the forming operation allowed the iron-rich phase to precipitate from solution, then resistance to erosion-corrosion was reduced. Frick et al., reported that heat from welding can cause precipitation of the iron-rich phase in the heat-affected zones (HAZ) and lead to intergranular attack adjacent to the welds.⁵ Although Cu-10% Ni is single-phased at room temperature, Cu-Fe alloys are generally two-phase alloys as shown in the binary alloy phase diagrams.⁶ At 1,000°C, 4% Fe can dissolve into copper, but this iron precipitates out at lower temperatures and there is almost zero solubility at room temperature. Cu-Ni-Fe alloys must be

quenched rapidly to room temperature to retain the iron in solid solution.

Some researchers believe that iron forms a protective layer of iron oxide on the surface of the Cu-Ni piping. A 1976 review by Vreeland dealt mostly with the attack of the cupronickels by sulfides in polluted seawater.⁷ He reported that ferrous sulfate (FeSO_4) was an effective inhibitor; the mechanism was related to the deposition of a thin, brown layer of lepidocrocite ($\gamma\text{-FeOOH}$) on the piping. A number of workers have postulated that a duplex oxide layer is formed on these alloys. Using x-ray and electron diffraction, Popplewell et al., reported that the Cu-10% Ni passive oxide in quiescent NaCl solutions was a duplex oxide with a reddish Cu_2O inner layer, and a greenish trihydroxo copper (II) monochloride ($\text{Cu}_2(\text{OH})_3\text{Cl}$) outer layer.⁸ The outer $\text{Cu}_2(\text{OH})_3\text{Cl}$ layer was believed to be deposited from the solution. Its mechanical removal had little effect on the corrosion resistance of the sample. The inner Cu_2O layer was identified as the barrier layer. Notably, this barrier layer could dissolve up to 30% Ni and 10% Fe with no apparent change in structure. Popplewell's explanation for the protection provided by the layer was similar to North and Pryor's.³ Namely, nickel and iron incorporate into the Cu_2O lattice and reduce the cation vacancies, thereby increasing the ionic and electronic resistance.⁸ Pearson also reported that cupronickels used in seawater service develop a brown, adherent Cu_2O film on their surface.⁴ Kato, et al., studied corrosion resistance of Cu-9.4% Ni-1.7% Fe alloys in NaCl solution from 1980 to 1984 and reported that the surface had a duplex oxide layer,⁹⁻¹² similar to the observations of Popplewell.⁸ The outer layer was green, porous $\text{Cu}_2(\text{OH})_3\text{Cl}$, and the inner layer was the barrier oxide, high in copper and chlorine, and also contained iron and nickel. Kato, et al., reported that the inner layer was protective because it restricted the cathodic oxygen reduction reaction.¹² Sulfides had an impairing effect of forming a copper sulfide (Cu_2S), which acted as a catalyst and accelerated the oxygen reduction reaction.

Alloy UNS C72200 (Cu-16% Ni-0.8% Fe-0.5% Cr-0.5% Mn) showed superior erosion-corrosion resistance over Cu-10% Ni-Fe and Cu-30% Ni-Fe.¹³ Cr^{3+} is postulated to be a dopant with an effect similar to that of Fe^{3+} . Cr only works while in solid solution, and any precipitation causes serious pitting problems.¹⁴ Since Cr has very low solubility in copper < 800°C,⁷ there are production problems in welding and fabricating piping from this alloy. UNS C72420 is a Cu-15% Ni with 1% Al to 2% Al. Cu-Ni-Al has been reported to have greater erosion-corrosion resistance but no market¹⁴ because of difficulties with the aluminum oxide (Al_2O_3) scale and the nickel aluminide (Ni_3Al) precipitates that form during hot-working.¹⁵

In 1988, Parvizi, et al., reviewed over 400 publications on the corrosion of Cu-Ni alloys, but provided

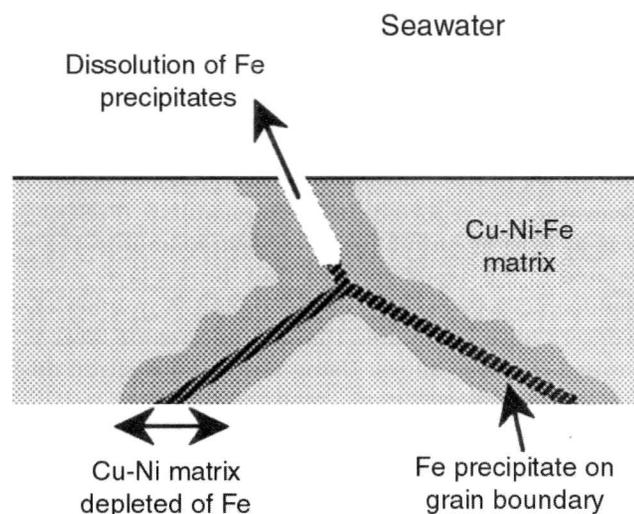


FIGURE 1. Intergranular corrosion of the Cu-Ni-Fe alloy was hypothesized to occur because iron precipitates onto the HAZ grain boundaries during welding or heat-treating, then iron preferentially (galvanically) can dissolve during immersion in seawater.

no conclusive evidence on the mechanism by which iron improves erosion-corrosion resistance.¹⁶ Parvizi summarized the literature by stating that the corrosion product had a layered structure and that good corrosion resistance was imparted by the thin, inner layer, which had high adherence and high resistivity.¹⁶ High resistivity of this layer slowed electron transport, and thus, inhibited the oxygen reduction reaction. Why iron would improve the adherence and the resistivity was not explained.

There are many problems associated with the iron addition. Although iron in solid solution improves the impingement corrosion resistance, iron is not soluble in copper at room temperature.⁶ Therefore, the alloy must be homogenized at 850°C to 1,000°C and quenched to be kept in solution.^{4,17} If there is subsequent thermal treatment of the alloy, an iron-rich phase can precipitate out on the grain boundaries where it can lead to localized attack of the depleted zone (Figure 1). Bailey's investigations showed that > 2% Fe tended to cause crevice corrosion and > 4% Fe promoted pitting.² Admiraal, et al., demonstrated that heating at 650°C for 10 min or 400°C for 100 h could produce grain boundary precipitates with a subsequent deterioration in corrosion resistance.¹⁷ Welding can provide sufficient thermal input for grain boundary precipitation to occur in the HAZ of the weld. Frick, et al., showed that the intergranular attack of the HAZ corresponded to precipitation of iron-rich grain boundary precipitates in the HAZ.⁵ These phenomena place severe restrictions on the use of cupronickel alloys since ease of fabrication and assembly are requirements for seawater piping.

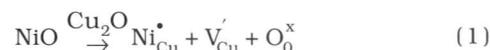
Hypothesis

The literature supports the notion that the cupronickel resistance to erosion-corrosion is caused by the properties of a barrier oxide, reportedly Cu_2O , which forms on the surface. The questions to be asked are two-fold:

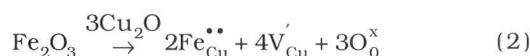
— Why does alloying with nickel, iron, or chromium improve the impingement resistance of the barrier oxide?

— Can this effect be duplicated with an element that is soluble in copper at room temperature so that adverse effects such as precipitation (which leads to localized corrosion) is avoided?

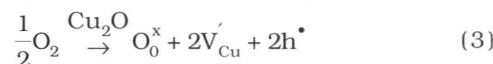
Insight into the properties of the doped Cu_2O film may be gained by analyzing the effect of ion substitutions into the oxide by using mass, charge, and site balances based on the Kröger-Vink notation.¹⁸ Addition of NiO or Fe_2O_3 into Cu_2O was shown to cause an increase in the cation vacancies, not a decrease. If NiO or Fe_2O_3 were placed in a Cu_2O lattice, then the charge, mass, and site balance required the creation of cation vacancies (V_{Cu}'). For the NiO substitution into Cu_2O :



Equation (1) shows that NiO placed in a Cu_2O site will result in a nickel atom on a copper site with a positive charge ($\text{Ni}_{\text{Cu}}^{\bullet}$), plus a copper site vacancy with a negative charge (V_{Cu}'), and an oxygen on an oxygen site with zero charge (O_0^{\times}). For the Fe_2O_3 substitution into Cu_2O :



Equation (2) shows that Fe_2O_3 placed in three Cu_2O sites will result in two iron atoms on copper sites having a double positive charge ($2\text{Fe}_{\text{Cu}}^{\bullet\bullet}$), plus four copper site vacancies with a negative charge ($4V_{\text{Cu}}'$), and three oxygen atoms on oxygen sites with zero charge (3O_0^{\times}). If one considers the incorporation of oxygen into the Cu_2O lattice, the relationship is the following:



Equation (3) states that oxygen placed in a Cu_2O lattice will result in an uncharged oxygen on an oxygen site (O_0^{\times}), plus two copper site vacancies with a negative charge ($2V_{\text{Cu}}'$), and two positively charged electron holes ($2h^{\bullet}$). Equation (3) gives the relationship that at

a constant pressure of oxygen, the following proportionality holds:

$$\left[V_{\text{Cu}}' \right] \left[h^{\bullet} \right] \propto P_{\text{O}_2}^{0.25} \quad (4)$$

Equation (4) is a constant for a given oxygen pressure. Therefore, if the concentration of cation vacancies increases, then the concentration of electron holes must decrease. In other words, the addition of NiO and Fe₂O₃ will increase the number of copper vacancies and decrease the number of electron holes. NiO and Fe₂O₃ act as n-type dopants. The manner by which nickel and iron improve erosion-corrosion resistance of the passive film could be related to the decrease in electron holes (Cu₂O is a p-type semiconductor), resulting in an increased electrical resistivity.

Therefore, to improve corrosion resistance of copper-based alloys, elements should be added that would be n-type dopants and are soluble in copper. If a metal (M) with +3 valence is selected, which forms M₂O₃ or M(OH)₃ in water (based on the Pourbaix diagrams¹⁹), and forms a solid solution with copper at room temperature (based on the alloy phase diagrams⁶), the initial choices for M would be gallium, aluminum, and indium. The second choices would be elements with valence states +3 or +4, such as manganese and germanium. (Bailey recommended in 1951 the use of manganese in the Cu-Ni alloys, and manganese is still being used.²)

EXPERIMENTAL

The candidate cupronickel alloys were induction melted as 30-g ingots in the first iteration, and the more promising ones were cast as 300-g ingots in the second iteration (Table 1). All ingots were homogenized at 1,000°C for 1 h and cold water-quenched. The 300-g ingots were all cold-rolled to a final thickness of several millimeters and cut into specimens for corrosion testing. The starting materials for all ingots were minimum 99.9% pure, except the copper that was 99.999% pure. Table 1 lists compositions of the 300-g candidate ingots. All percentages were wt%. Final compositions of the 300-g ingots were based on analyses.

The 300-g candidate alloys were jet impingement tested at the LaQue Center for Corrosion Technology.⁽²⁾ The test technique was 30 days of filtered seawater jet impingement at ≈ 22 ft/s (6.7 m/s). Samples were photographed and weighed before and after the test.

Additional tests, such as potentiodynamic polarization, electrochemical impedance spectroscopy,

⁽²⁾ LaQue Center for Corrosion Technology, Inc., PO Box 656 (Corner Hwy 76 and Auditorium Circle), Wrightsville Beach, NC 28480.

TABLE 1
Compositions of 300-g Ingots
of the Candidate Cupronickel Alloys

Alloy Designation	wt%
0.0%	90.1% Cu-9.82% Ni
1.9% Fe	88.1% Cu-9.93% Ni-1.92% Fe
1.0% Al	89.0% Cu-9.97% Ni-0.95% Al
1.0% Ga	89.2% Cu-9.74% Ni-0.99% Ga
1.9% Ga	88.1% Cu-9.98% Ni-1.90% Ga
1.5% Ge	88.2% Cu-10.19% Ni-1.51% Ge
2.1% In	88.0% Cu-9.90% Ni-2.07% In

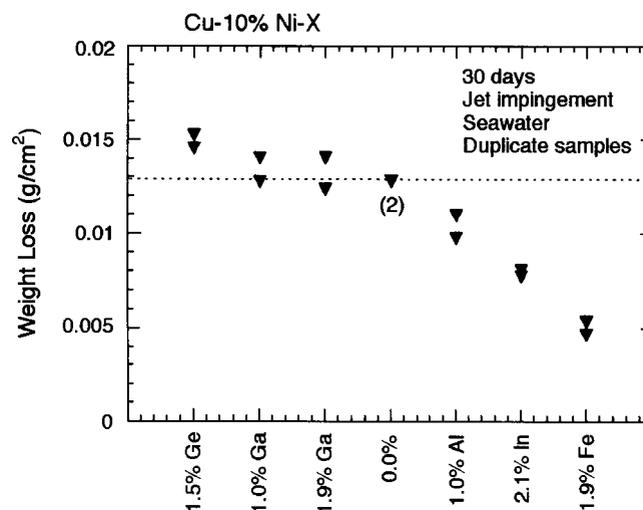


FIGURE 2. Weight loss results after 30 days of seawater jet impingement.

photoelectrochemistry, voltage-capacitance analysis, and x-ray photoelectron spectroscopy also were conducted, but results were not as conclusive.

RESULTS AND DISCUSSION

After 30 days of jet impingement in filtered seawater, all Cu-Ni candidate samples were green except for the Cu-Ni-Fe samples, which were brown. The center of each sample had a discolored spot where the seawater jet-impinged. This site was worn deeper and had a very thin (different color) oxide layer.

Weight loss data for the duplicate samples are shown in Figure 2. Candidate alloys containing indium, aluminum, and iron were all improvements over the binary cupronickel alloy 90% Cu-10% Ni (0%). Cu-Ni-Fe (1.9% Fe) and Cu-Ni-Al (1% Al) were similar to commercial alloys, but Cu-10% Ni-2% In (2.1% In) was a new alloy. Relating this to the hypothesis, indium, aluminum, and iron all formed trivalent oxides (M₂O₃), which can act as electron donors when dissolved in Cu₂O film. The sample with the least weight loss was Cu-10% Ni-1.9% Fe, which

was similar to the commercial cupronickel alloy UNS C70600. The important result was that the candidate alloy Cu-10% Ni-2% In was the second best and consistently better than the control alloy (0%). The 1% Ga, 2% Ga, and 3% Ge samples all showed no improvement over the control sample. Although the 1% Al sample showed improved performance over the control, this 1% Al was similar to alloy UNS C72420 (Cu-15% Ni with 1% to 2% Al). The optimum composition for Cu-Ni-In alloy was not determined.

CONCLUSIONS

- ❖ 10% Ni (wt%) were cast, cold-rolled, and solution heat-treated. Subsequently, they were tested for erosion-corrosion resistance.
- ❖ The candidate alloys were chosen on the basis that: (1) they formed trivalent oxides (M_2O_3) to act as an n-type dopant when dissolved in the copper oxide film, and (2) they had significant solid solubility in copper even at room temperature.
- ❖ The erosion-corrosion test technique was 30 days of seawater jet impingement at 22 ft/s. Results showed that the indium, aluminum, and iron were all improvements over the binary Cu-Ni alloy 90% Cu-10% Ni. The Cu-Ni-Fe and Cu-Ni-Al were registered commercial alloys, but the Cu-Ni-In was a new alloy whose solid solubility is superior to the Cu-Ni-Fe alloy. Because the indium is still 2% soluble in copper at room temperature, it should not precipitate onto the grain boundaries during welding and hot forming. Hence, it should not be susceptible to intergranular corrosion (such as occurs with the iron or chromium). The Cu-Ni-In alloy also should not form the tenacious oxide film that formed on the Cu-Ni-Al alloys.

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