PASSIVATION TREATMENTS FOR COPPER-NICKEL ALLOYS EXPOSED TO SEAWATER

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ABSTRACT

The US Navy uses copper nickel (CuNi) piping and tubing in various seawater applications. The current standard for passivation of CuNi in seawater requires a minimum of three to six weeks of exposure in clean seawater. However, due to issues with pollution in port and estuary environments and the rapid timelines required during construction or overhaul, new environmentally friendly chemical passivation treatments, which can achieve passivation within one week have been investigated. Five passivation chemistries were examined for amount of copper released and film thickness, which provide insight into the passive film's ability to protect the CuNi surface from corrosion. Future work includes durability testing to determine how long the passive films last under normal operating conditions and resistance to sulfide poisoning.

INTRODUCTION

Copper nickel alloys are used in piping and tubing flowing seawater applications such as for heat exchangers and fire main systems. Currently, the Naval Sea Systems Command requires tubing to be passivated for 21 days in clean, flowing seawater prior to first use. However, due to issues with pollution in port environments, the cost of delivering clean, natural seawater for this operation can be prohibitive to completing this passivation. Additionally, after chemical cleaning operations that require repassivation of tubing, the 21 day requirement can cause difficulty in maintaining ships' schedules. Therefore, an investigation into chemicals that can be added to seawater to achieve passive film formation within seven days was conducted.

Another issue which must be considered is if chemicals can be applied in an open loop system where seawater is pumped on to the ship, circulated, then discharged overboard. The concept of additions in an open loop system is chemicals are added at an inject port near the system to be passivated and chemical and seawater are discharged overboard, requiring minimal modification to the existing system and minimal manpower to monitor treatment.

Chemicals that cannot be discharged overboard would be required to be applied using a closed loop system. A closed loop system requires a tank on the pier with sufficient piping/tubing run into the ship and patched in to the system to be passivated. Circulation is completed to/from the tank on the pier using a pump external to the ship and the chemicals used for passivation are monitored and adjusted at the tank. This system requires more manpower and monitoring than an open loop system.

A final goal of any passive treatment is a color change of the surface film in order to determine if the surface is present. Most commonly borescope is used to determine color of any surface film present in copper nickel tubing. Therefore, developing a technology that creates sufficient color change to provide the ability to positively identify the existence of the surface film is necessary.

BACKGROUND

Passivation of copper-nickel alloys results from the formation of a duplex oxide film structure, with initial growth of an inner cuprous oxide (Cu_2O) film on the surface followed by slower growth of cupric oxide (CuO) or cupric hydroxychlorides ($Cu_2(OH)_3Cl$) on top of the Cu_2O layer [1-7]. It has been well documented that this film requires time to form for best protection from corrosion [4,5,8]. Furthermore, it has been theorized that the potential and presence of chlorides and other species can affect the structure of these films and ultimately influence the stability of the species present [9]. Breakdown of the passive film occurs when copper nickel alloys are exposed to aggressive and/or acidic environments, especially in the presence of chemicals like hydrochloric acid, sulfuric acid, or dissolved sulfides [2,5,10]. Typically, this occurs via adsorption of anions to the Cu_2O/CuO/CuOHCl surface which then catalyze dissolution reactions between Cu atoms and reactive H^+ ions.

Enhancing the protective behavior of Cu_2O in such environments has been a goal of research over the past several decades. One major approach to do so has been to identify chemical additives which develop adsorbed films on the Cu_2O layer in lieu of growth of CuO [2,4,5,10,11]. In regards to this approach, potassium iodide with L-leucine, propargyl alcohol, and citric acid were chosen as chemical additives for this study.

Many of these additives are organic molecules with polar elements such as O, N, or S which bind to Cu atoms at the surface, leaving the remainder of the molecule as a barrier which prevents harmful species from contacting the Cu_2O. Azoles and chemical derivatives thereof have seen extensive research into inhibition of copper corrosion due to superior performance in hydrochloric acid, salt, and sulfate environments [2,10]. Allam et al. reported maximum inhibition efficiency can be achieved with benzotriazole within 4 days of immersion, but their results also suggest azoles do not protect copper nickel alloys well from sulfuric acid or sulfide environments [10]. Furthermore, environmental and economic concerns that would result from large-scale use of these chemicals eliminates them as candidates in this study.

Effective passivation of copper nickel using environmentally friendly amino acids was looked at by Badawy et al. in 2005 [11]. Their results showed that amino acids can effectively protect copper when mixed with halide anions, and they identified a mixture of amino acid L-leucine with iodine as optimal to form an effective corrosion barrier within a few hours of immersion. Propargyl alcohol is an acetylenic molecule that has seen study for corrosion inhibition not just of copper nickel [2,5], but also steel and aluminum alloys as well [12-14]. For all three systems, propargyl alcohol greatly improves corrosion resistance in sulfuric acid environments, though data is lacking on whether the chemical also limits sulfide poisoning. Citric acid has not seen detailed research as a corrosion inhibitor for copper nickel, but it is a naturally abundant chemical with polar O bonds that make it a potential candidate for an environmentally and economically feasible solution to passivation of copper nickel alloys.

The second major approach to improve passivation in copper nickel alloys is to identify chemical additives which promote more rapid growth of a modified outer layer film [2,5-7,15]. In regards to this approach, nickel hydroxide and nickel sulfate were chosen as chemical additives for this study.

These types of additives are inorganic salts with metal cations chosen either to alter the growth of the oxide at the surface of the alloy or to interfere with the chemical reactions of corrosion [2,15]. The use of nickel cations encourages deposition of Ni atoms to the Cu_2O surface and promotes growth of a mixed $Ni(OH)_2$/NiO/CuO film that protects the alloy from corrosion more strongly than just CuO [5,7,15]. Brizuela et al. suggest this is in large part due reduced surface defects and improved electronic and ionic resistance of the Ni-based films [7]. The anions of these salts also confer corrosion resistance, and it is believed this is due to adsorption behavior which limits chemical attack on the metal atoms at the surface [6,13,14]. Ismail et al. documented passive behavior in four Cu_xNi_{1-x} alloys (x = 5, 10, 30, 65 wt. %) at an optimum concentration of 25 mM sulfate anions [6], though it was not made clear how exactly passivation was achieved.

The goal of this initial study is to determine if any of these chemical additions to seawater can, within seven days, provide equivalent protection to copper nickel that has been exposed to clean seawater for 21 days. A secondary goal is to find a passivation aid that can be discharged overboard while meeting the first requirement. A tertiary goal is to find a passivation aid where application is easy to identify via borescope inspection.

EXPERIMENTAL PROCEDURE

Alloy

Copper nickel alloy UNS C70600 was used in extruded, annealed bar form with 3/8 inch outer diameter. Specimens were cut from the bar to a thickness of 0.125 inches. All specimens were ground to 600 grit silicon carbide with water, rinsed in ethanol, rinsed in deionized water, and air dried. Specimens were stored in a vacuum sealed desiccator prior to testing.

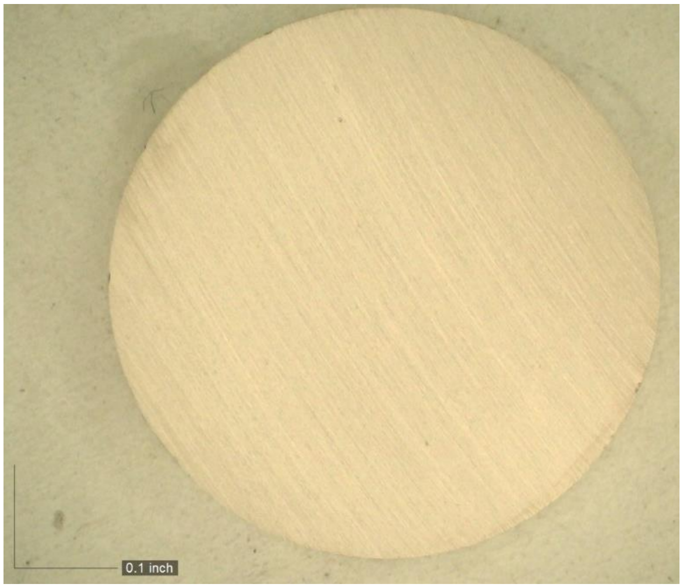

Figure 1 Representative photo of specimen after grinding to 600 grit SiC and cleaning, prior to exposure.

Passivation Chemistries

The chemistries and concentrations of chemical additives tested are found in Table 1. All solutions were made with reagent grade chemicals and 6 M ASTM SW without any additions was used as a control chemistry. All ASTM SW was mixed from salt as supplied by Lake Products, Inc[1].

Table 1 Chemistries of passivation aids examined.

Chemistry + ASTM SW	Concentration
Citric acid ($C_6H_8O_7$)	5 mM
Nickel hydroxide ($Ni(OH)_2$)	0.5 mM
Potassium iodide (KI) + L-leucine ($C_6H_{13}NO_2$)	1 μM KI + 5 μM $C_6H_{13}NO_2$
Nickel sulfate ($NiSO_4$)	12.5 mM
Propargyl alcohol (C_3H_4O)	1 mM

Exposures

Two types of exposures were conducted: quiescent and flowing. Quiescent exposures were conducted by placing the specimen in the bottom of a 50mL beaker with one face of the disc facing up and filling the beaker with 40mL of the test solution. Flowing exposures were conducted similarly, but beakers were placed on an orbital shaker set to 100 rotations per minute speed. All beakers were covered to prevent loss of solution due to evaporation during testing. Temperature was not controlled during the experiment; exposures were at laboratory temperature. Four replicates of each exposure condition and chemical additive were completed (eight total per chemical additive). All tests were run for seven days, except the control chemistry (ASTM SW); the ASTM SW specimens were exposed for 7 and 21 days (two separate

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[1] Lake Products Inc., 745 Saint Anthony Lane, Florissant, MO, 63033.

tests and sets of specimens). After exposure, samples were rinsed in deionized water and stored in a vacuumed desiccator until characterization.

Characterization

Each specimen was photographed prior to and after exposure on a stereoscope. Scanning electron microscope images of the surfaces were taken post exposure for one sample from each exposure and chemistry condition.

Copper ion concentration post exposure was measured for all solutions with the USEPA Copper Bicinchoninate Method Method 8026 using a Hach[2] DR 1900 spectrophotometer and chemicals. Solution samples were adjusted to pH 2 or lower using concentrated hydrochloric acid to digest any undissolved copper, then pH was readjusted to between pH 4 and 6 using sodium hydroxide prior to testing. Due to the high level of copper concentration, some solutions were required to be diluted for measurement. All solution dilutions (including those for pH adjustment) were accounted for using dilution factors and readings were multiplied by the appropriate dilution factor. Measurements reported are averaged from a minimum of four measurements per exposure condition and chemical additive. These measurements are not intended to be statistically significant, but provide a rough order of magnitude of copper dissolution during the exposure period.

Electrochemical impedance spectroscopy (EIS) was also conducted on two specimens after exposure. Scans were run in ASTM SW with a saturated calomel reference electrode and carbon counter electrode. Scans were run from 10^5 Hz to 10^{-2} Hz at an amplitude of 10 mV about the open circuit potential on a Gamry G300 potentiostat. Open circuit potential for each specimen was allowed to stabilized for one hour prior to the start of EIS. EIS data was used to attempt to determine passive film thickness.

RESULTS

Images

Stereoscopic images of post exposure surfaces are shown in Table 2. ASTM SW after 21 day exposures show the formation of a dark brown film for both the quiescent and flowing samples. The ASTM SW quiescent sample shows evidence of possible copper hydroxychloride (green areas). ASTM SW after seven day exposures show optical interference coloring (iridescence) on the quiescent exposure and a similar dark brown film to the 21 day specimen for flowing exposure. The citric acid exposed samples look similar to the flowing ASTM SW 21 day exposure, with the dark brown film. Nickel hydroxide formed films show an iridescence of the quiescent specimen while the flowing specimen shows a dark brown film. The potassium iodide plus L-leucine specimens show behavior similar to that of the nickel hydroxide with iridescence of the quiescent specimen and dark brown film on the flowing specimen. The nickel sulfate specimens both show a brown tinted film with some iridescence that is transparent enough to see the copper-nickel surface. The propargyl alcohol specimens show a yellow film.

Secondary electron images of the post exposure surfaces are presented in Table 3. The images show what appears to be similar structure surface films for all specimens except the propargyl alcohol exposed specimens. The propargyl alcohol formed surface films look similar to a polymeric type film. See Figure 2 and Figure 3 for higher magnification images of the nickel hydroxide and propargyl alcohol films where the structure differences are clearly seen. The nickel hydroxide film, Figure 2, shows a uniform structure. The propargyl alcohol film, Figure 3, shows “rod” shapes and “nodule-like” shapes that are incorporated in a non-uniform film.

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[2] Hach Company, P.O. Box 389, 5600 Lindbergh Drive, Loveland, CO, 80539.

Table 2 Stereoscope images of specimens post exposure. All exposures were 7 days except ASTM SW, which were 21 days.

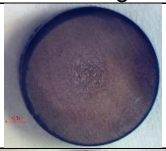
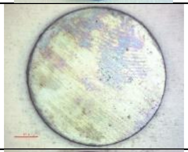
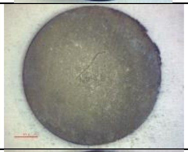
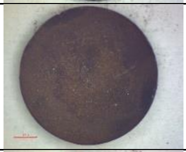
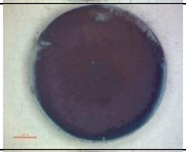
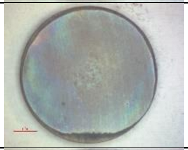
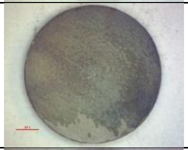
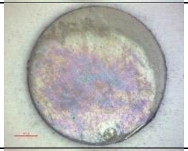
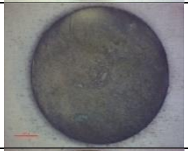
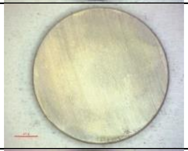
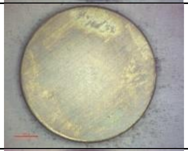
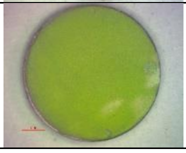
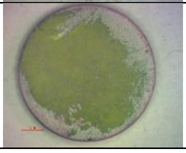
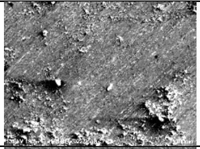
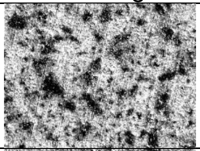
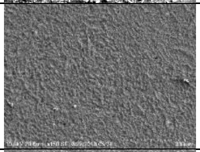
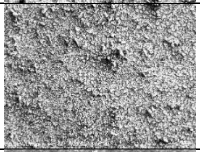
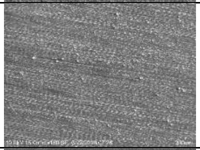
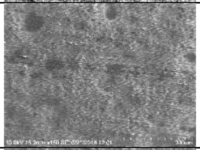
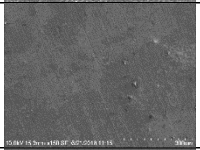
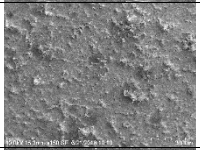
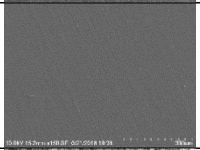
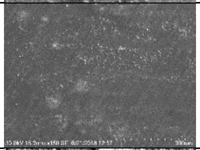
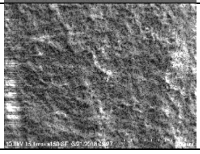
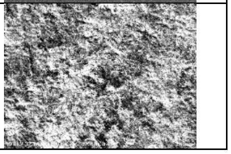
Chemistry	**Post Exposure Photographs**	
	Quiescent	Flowing
ASTM SW (21 d)		
ASTM SW (7 d)		
5 mM Citric Acid in ASTM SW		
0.5 mM Nickel Hydroxide in ASTM SW		
1 mM Potassium Iodide + 5 mM L-leucine in ASTM SW		
12.5 mM Nickel Sulfate in ASTM SW		
1mM Propargyl Alcohol in ASTM SW		

Table 3 Scanning electron microscope, secondary electron images for specimens post exposure. All exposures are 7 days.

Chemistry	Post Exposure SEM Micrographs	
	Quiescent	Flowing
ASTM SW (7 d)		
5 mM Citric Acid in ASTM SW		
0.5 mM Nickel Hydroxide in ASTM SW		
1 mM Potassium Iodide + 5 mM L-leucine in ASTM SW		
12.5 mM Nickel Sulfate in ASTM SW		
1mM Propargyl Alcohol in ASTM SW		

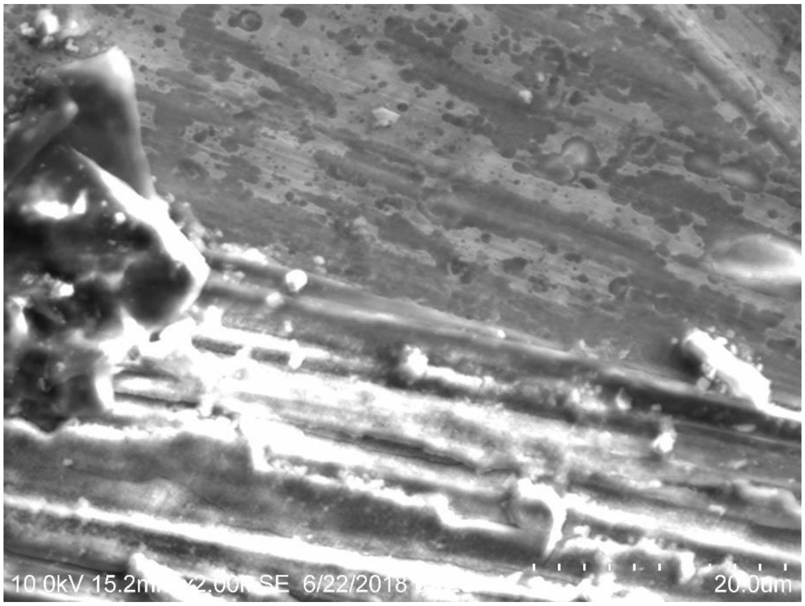


Figure 2 Secondary electron image of surface of nickel hydroxide exposed specimen.

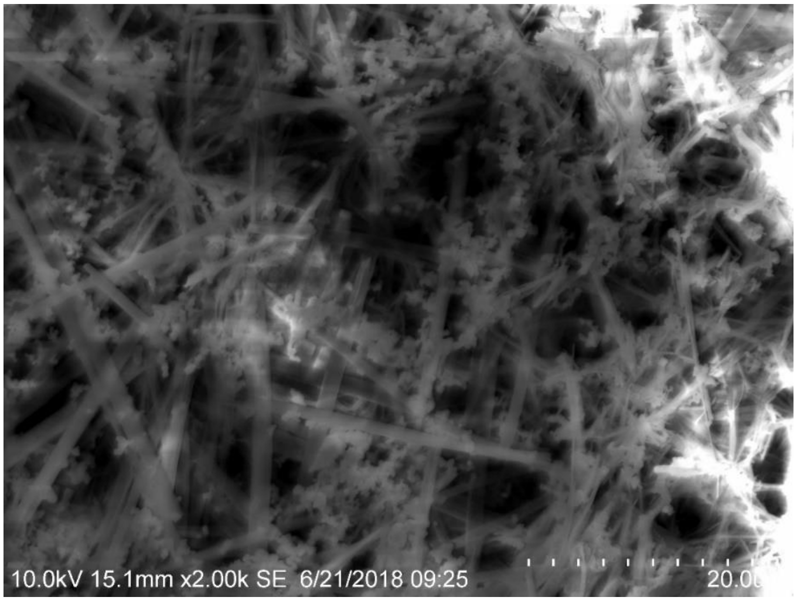


Figure 3 Secondary electron image of surface of propargyl alcohol exposed specimen.

Copper Ion Testing

Copper ion content of effluent has been shown to be an indirect measure of passive film formation on copper nickel alloys [8]. Copper ion concentration after exposure is reported in Table 4. Copper ion concentration prior to exposure was 25-30 μg/L and was not subtracted from the values reported in Table 4. Copper (Cu) ion concentration for ASTM SW 21 day exposures were 45.01 mg/L Cu for the quiescent exposure and 27.09 mg/L Cu for the flowing exposure. For the ASTM SW seven day exposures, the Cu ion concentration was 31.04 mg/L Cu for the quiescent exposure and 25.02 mg/L Cu for the flowing exposure. Copper ion concentrations for all chemistries tested ranged from 3.25 – 16.74 mg/L Cu for quiescent exposures and 2.43 – 18.30 mg/L Cu for flowing exposures for all chemistries, which are lower than the ASTM SW exposures.

Table 4 Copper ion concentration in solution after exposure.

Chemistry	**Post Exposure Copper Ion Concentration (mg/L Cu)**	
	Quiescent	Flowing
ASTM SW (21 d)	45.01	27.09
ASTM SW (7 d)	31.04	25.02
5 mM Citric Acid in ASTM SW	16.74	18.30
0.5 mM Nickel Hydroxide in ASTM SW	5.20	5.17
1 mM Potassium Iodide + 5 mM L-leucine in ASTM SW	16.60	13.11
12.5 mM Nickel Sulfate in ASTM SW	3.44	2.43
1mM Propargyl Alcohol in ASTM SW	3.25	3.63

Electrochemical Impedance Spectroscopy

Film capacitance was calculated from electrochemical impedance spectroscopy data. The EIS data set has been reported elsewhere [16]. At 0.16 Hz, log |Z| = - log C, where Z is impedance modulus and C is the film capacitance or

$$C = \frac{1}{|Z|}. \qquad \textbf{Equation 1}$$

Passive film thickness was calculated from film capacitance at 0.16 Hz following the work of Cottis and Turgoose [17] and Shaw et al. [18] where film thickness can be calculated from

$$t = \frac{\varepsilon\varepsilon^0}{C}, \qquad \textbf{Equation 2}$$

where t is the film thickness, ε is the dielectric constant of the film, ε^0 is the permittivity of free space, and C is the capacitance of the film at 0.16 Hz. All films were assumed to be a form of cuprous oxide (ε=7.6 [19] except for propargyl alcohol exposed specimens which were assumed to be a copper complexed propargyl alcohol (ε=25.4, [20]). Film capacitance is also reported, so data can be viewed independent of the dielectric constant assumption. Capacitance and film thickness data are reported in Table 5.

Table 5 Film capacitance and thickness as calculated from electrochemical impedance spectroscopy data.

	Post Exposure Film Capacitance at 0.16 Hz (μF)		**Post Exposure Film Thickness (μm)**	
Chemistry	Quiescent	Flowing	Quiescent	Flowing
ASTM SW (21 d)	228	128	0.295	0.526
ASTM SW (7 d)	278	452	0.242	0.149
5 mM Citric Acid in ASTM SW	920	783	0.073	0.086
0.5 mM Nickel Hydroxide in ASTM SW	119	132	0.566	0.511
1 mM Potassium Iodide + 5 mM L-leucine in ASTM SW	176	130	0.383	0.516
12.5 mM Nickel Sulfate in ASTM SW	32.2	68.6	2.09	0.981
1mM Propargyl Alcohol in ASTM SW	189	172	1.19	1.30

DISCUSSION

Specimens exposed to ASTM SW after 21 days and 7 days, respectively, show film thicknesses of 0.295 and 0.242 μm in a quiescent environment and 0.526 and 0.149 μm in a flowing environment. There is a 3.5 times increase in film thickness in the flowing environment from day 7 to day 21. The copper dissolved in the quiescent environment increased from 31.04 to 45.01 mg/L Cu and in the flowing environment from 25.02 to 27.09 mg/L Cu. The increase in film thickness from day 7 to day 21 and only small increase in copper dissolution over this period support the argument that time is needed to form protective passive films on 90/10 copper-nickel. This concept has been documented in the literature [1,8] and captured by US Navy technical documents [21]. However, identifying the presence of this film is difficult to accomplish visually (see Table 2).

In order to provide a new passivation chemistry, chemistries should demonstrate film thicknesses equivalent to or greater than the ASTM SW 21 day exposure, equivalent or lower Cu ion concentrations, and a color change within seven days of exposure.

Citric Acid

Citric acid exposed specimens did not form surface films thicker than the ASTM SW formed films. However, the amount of Cu dissolved in solution did decrease. The surface films were not noticeably different from those formed on 90/10 CuNi in seawater. Therefore, citric acid is not considered a suitable candidate for passivation of 90/10 copper nickel.

Nickel Hydroxide

Nickel hydroxide exposed specimens formed surface films 0.271 μm thicker than the ASTM SW formed films in quiescent exposures and equivalent to those formed in ASTM SW in flowing exposures (0.015 μm difference). The amount of Cu dissolved in solution decreased by 39.81 mg/L Cu from ASTM SW exposed for 21 days in quiescent exposures and by 21.92 mg/L Cu in flowing exposures. The amount of copper detected in quiescent and flowing exposures was fairly equivalent (5.20 mg/L Cu quiescent, 5.17 mg/L Cu flowing). The surface films were not noticeably different colors from those formed on 90/10 CuNi in ASTM SW. Even without the desired color change nickel hydroxide may prove a viable seven day passivation solution for 90/10 copper nickel. However, nickel hydroxide is not environmentally friendly and would require application with a closed loop system.

Potassium Iodide plus L-leucine

Potassium iodide plus L-leucine exposed specimens formed surface films 0.088 μm thicker than the ASTM SW formed films in quiescent exposures and equivalent to those formed in ASTM SW in flowing exposures (0.010 μm difference). The amount of Cu dissolved in solution decreased by 28.41 mg/L Cu from ASTM SW exposed for 21 days in quiescent exposures and by 13.98 mg/L Cu in flowing exposures. The surface films were not noticeably different colors from those formed on 90/10 CuNi in ASTM SW. Without the desired color change potassium iodide plus L-leucine may prove a viable seven day passivation solution for 90/10 copper nickel. This chemistry has the added benefit of being environmentally friendly (able to be discharged overboard).

Nickel Sulfate

Nickel sulfate exposed specimens formed surface films 1.795 μm thicker than the ASTM SW formed films in quiescent exposures and 0.455 thicker to those formed in ASTM SW in flowing exposures. The amount of Cu dissolved in solution decreased by 41.57 mg/L Cu from ASTM SW exposed for 21 days in quiescent exposures and by 24.66 mg/L Cu in flowing exposures. The surface films were not noticeably different colors from those formed on 90/10 CuNi in ASTM SW. Without the desired color change nickel sulfate may prove a viable seven day passivation solution for 90/10 copper nickel. However, nickel sulfate is not environmentally friendly and would require application with a closed loop system.

Propargyl Alcohol

Propargyl alcohol exposed specimens formed surface films 0.895 μm thicker than the ASTM SW formed films in quiescent exposures and 0.774 μm thicker to those formed in ASTM SW in flowing exposures. The amount of Cu dissolved in solution decreased by 41.76 mg/L Cu from ASTM SW exposed for 21 days in quiescent exposures and by 23.46 mg/L Cu in flowing exposures. The surface films were noticeably different color, yellow, from those formed on 90/10 CuNi in ASTM SW (translucent with interference colors to brown). Propargyl alcohol may prove a viable seven day passivation solution for 90/10 copper nickel. However, propargyl alcohol is not environmentally friendly and would require application with a closed-loop system.

SUMMARY

Surface films formed within seven days when exposed to the various chemistries show equivalent or improved performance when measured by copper ion concentration after exposure and film thickness except for films formed when exposed to citric acid. The lowest copper ion concentration and thickest films were formed in solutions with nickel sulfate and propargyl alcohol. The propargyl alcohol also provides a distinct color change from the alloy, making application easy to identify. However, propargyl alcohol is not environmentally friendly. Of the environmentally friendly (able to be discharged overboard) chemical additives examined, only the potassium iodide plus L-leucine performed adequately.

FUTURE WORK

Further work is needed to down select the four chemistries presented here that performed well when compared to 21 day exposures in ASTM SW. Studies include compatibility with 70/30 CuNi (UNS C71500) and investigation into barrier properties of the films formed using EIS. Additional work on the composition of the films formed will be accomplished via x-ray photoelectron spectroscopy and other surface characterization techniques in order to verify the protection mechanisms (modified outer layer film or molecular barrier). The final technologies selected will need to take into account the durability of the films in flowing seawater and resistance to sulfide poisoning.

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