

# Ways towards an accelerated formation of protective layers on CuNi 90/10 in artificial seawater

S. Friedrich, M. Langer

*Institut für Korrosionsschutz Dresden GmbH, D-01217 Dresden, Germany  
Tel. +49 351 871 7109, Fax. -7150, [mlanger@iks-dresden.de](mailto:mlanger@iks-dresden.de)*

## Abstract

The formation of thin protective layers on the inner surface of copper nickel tubes, which were contacted by flowing artificial and natural sea water, was studied by means of electrochemical, metallographical, REM-/ EDX- and X-ray techniques. The found effects of variable pH, temperature and oxygen concentration on this process are discussed in terms of the layer's thickness and morphology, elemental distribution, structure and its formation mechanism. Sulphide loading served as indicator for the layer quality.

**Keywords** Copper alloy, marine corrosion, laboratory test, polarisation resistance sulphide

## Introduction

The CuNi 90/10 (UNS C70600) alloy is widely used in sea water service as piping material for heat condensers, desalination equipment, water supply lines and in other tube applications [1-3]. The excellent corrosion protection behaviour of the alloy is due to the formation of a thin, compact and adherent corrosion protective layer mainly consisting of cupric and cuprous oxides which separates the alloy's surface from the sea water and decrease the electric conductivity. The formation of films with sufficient thickness in natural sea water usually takes about 8 to 12 weeks [4-5]. Another important feature of CuNi 90/10 is its high resistance to biofouling [6], mainly due to the release of copper ions. Hence, in many cases an additional chlorination is dispensable. On the other hand, there is an enhanced susceptibility to localised corrosion in polluted water and under deposits. Pitting or crevice corrosion may result in sulphide containing (brackish) water and under deposits, where an enrichment of aggressive substances (sulphide, organic acids) and depletion of oxygen (e.g. under biofilms) can occur, respectively [7,8,9].

The examination of the corrosion behaviour of the CuNi 90/10 alloy and its improvement under critical conditions with present pollutants like sulphide makes it necessary to form protective layers in the lab, in artificial sea water, and within shorter periods. In the literature no method for an accelerated film formation is described.

For those reasons a test loop installation for the lab scale formation of protective layers on CuNi 90/10 tubes in circulating artificial seawater was set up. The aim was to find ways for accelerating the film growth and to simulate the well known process in natural sea water.

Based on a comprehensive literature research, the parameters pH and temperature were defined. The effect of the parameter variation on the layer formation was first tested electrochemically in a measurement cell. Afterwards tests in a new built test loop were performed. Tests with natural seawater are performed to evaluate the correlation between experiments in natural and in artificial seawater. In addition to the latter test program the corrosion protection properties of the formed protective layers in sulphide contaminated sea water were tested.

## Experimental

Tube samples of the alloy CuNi10Fe1,6Mn (UNS C70600), seamless drawn, solution-annealed and according to DIN 86019 and DIN 85004 T4, were inserted into a test loop with a 1 m<sup>3</sup> tank, containing artificial sea water (ASTM D 1141-98). Constant values of temperature, pH and flow rate were set, the oxygen content was controlled electrochemically. Water analysis was performed once a week. The integrated corrosion meter enabled the monitoring of the corrosion rate and pitting tendency. After 1, 2, 4, 8 and 12 weeks of testing samples were dismantled, analysed electrochemically, metallographically and by AAS-, REM-/ EDX- and X-ray techniques. The tests with natural sea water (North Sea) were performed on Helgoland for 8 weeks.

## Results and Discussion

Tab. 1 gives the parameters used in the test loop. The two temperatures and pH values were chosen from polarisation measurements with the raw material in a test cell. *Efird* [10] found the alloy CuNi 90/10 to be passive at pH > 8,5 in seawater, but in an active corroding state below that value, as in natural seawater (pH 7,8...8,3). So it was interesting, how a pH shift from 8,2 to 8,6 would influence the formation of the protective film. Known from the above mentioned literature, due to its higher nickel content, CuNi 70/30 is passive under the conditions of natural sea water, having a distinct lower initial corrosion rate in comparison to CuNi 90/10.

Tab. 1 Test parameters

tank volume	1	m <sup>3</sup>
number of test lines	2	
flow rate in the tubes	1.54-1.58	m/s
temperature	25 / 40	°C
pH (25 °C)	8,2 / 8,6	
O <sub>2</sub> -content	3.6-6.1	mg/l

On the other hand, temperature increase to 40 °C should accelerate the process, as stated by *Ijsseling* et al. [11]. However, the oxygen saturation content decreases with increasing temperature. So a supersaturation would be necessary not to suppress the formation of the copper and nickel oxides.

Figure 1 shows the result of parameter variation in the test loop in terms of corrosion rate, plotted against the time. The basic experiment (pH = 8,2 / 25 °C) shows a slow decrease of the corrosion rate with reaching a low level only after about 30 days. In comparison, the higher temperature (40 °C) results in a much faster decrease with the corrosion rate being at a low level after 10 days of running.

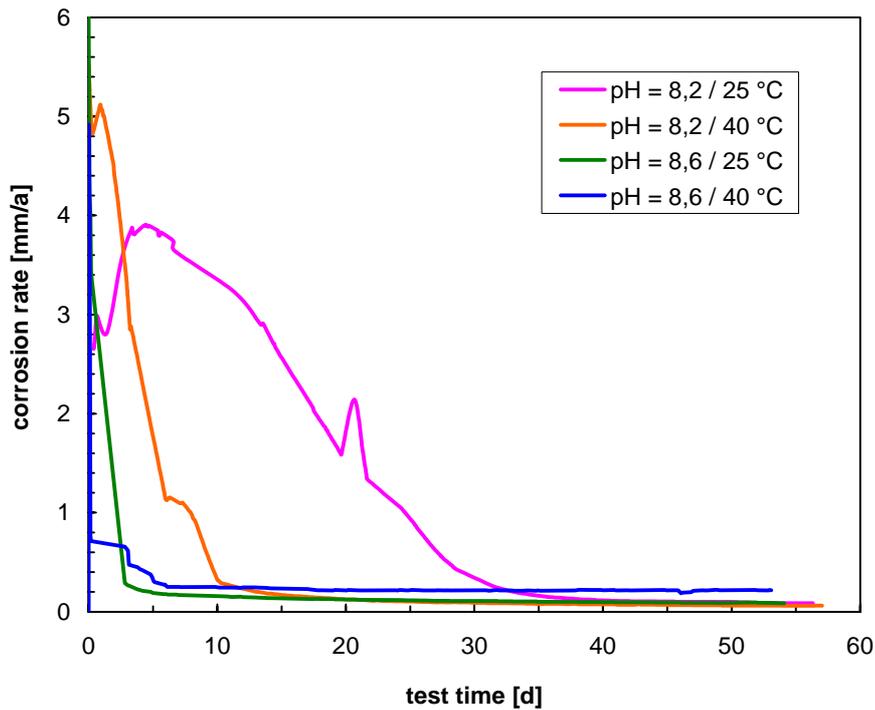


Fig. 1 Corrosion rates for the 8-weeks tested tube samples, plotted against the time

With a pH = 8,6 set, we obtained a very fast drop of the curve within 3-5 days. In case of the higher temperature, small verified effects on a low level of corrosion rate occur, also at a pH = 8,2 / 25 °C and 40 °C. Presumably this can be ascribed to the dynamic process of layer growth with temporarily appearing instabilities, also indicated by pitting measure.

The REM images of the film, formed in the basic experiment (Fig. 2), shows a compact layer with a thickness of about 8 μm, being well adherent to the alloy surface. Due to drying, clefts occur. The layer morphology was comparable with that formed in the North Sea water.

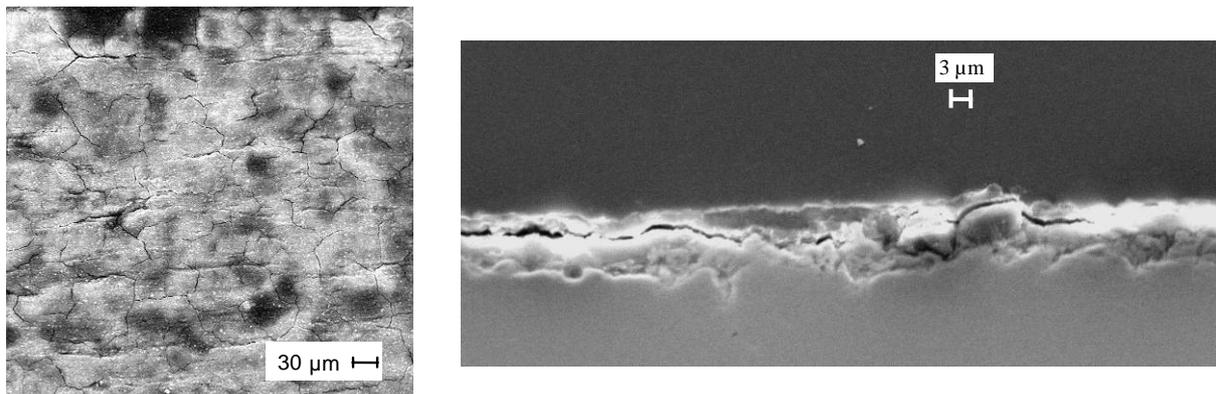


Fig. 2 REM images of the protective layer, formed at pH = 8,2 and 25 °C; surface (left) and metallographic cross-section (right)

The other loop test layers have a thickness of 3-4 μm, the layer grown in natural sea water is 6 μm thick. All are well adherent, but with different appearances.

The average elemental composition of the most important film elements were analysed by means of EDX technique. In Tab. 2 the results for all loop test experiments and the test with natural sea water (Helgoland) are summarised. Nickel enrichment can be observed for all 3 loop tests with variations from the basic set (pH = 8,2 / 25 °C) The Cu/Ni ratio changes from about 6 (basic experiment) over 2 (pH = 8,6 / 25 °C, pH = 8,6 / 40 °C) to 1 (pH = 8,2 / 40 °C). In natural sea water a film forms with a Cu/Ni ratio of about 3. Here the iron content is very high, which can be ascribed to the sea water supply via a steel pipe, whereas no iron contamination is possible in the test loop installation.

Amazingly only the film corrosion products of the basic experiment (pH = 8,2 / 25 °C) contain chloride. At higher temperatures the chloride containing compounds of copper have a higher solubility, so they cannot form films. This effect was also found in the literature [11]. The reason for the missing chloride in the corrosion product formed at pH = 8,6 / 25 °C and in the natural sea water, is not obvious so far.

Tab. 2 EDX-Analysis; surface of film; pH = 8,2 / 25 °C

Element [atom-%]	pH = 8,2 / 25 °C	pH = 8,2 / 40 °C	pH = 8,6 / 25 °C	pH = 8,6 / 40 °C	nat. sea water*
Cu	28,1	10,4	20,1	20,5	16,5
Ni	4,4	9,4	11,4	12,4	6,1
Fe	6,1	7,0	2,9	2,6	16,3
Mg	-	4,3	4,5	9,7	-
Ca	-	-	-	-	0,6
C	-	4,7	9,3	5,7	-
O	51,6	60,5	49,9	43,1	57,1
Cl	9,0	-	-	-	-

\* pH = 7,5 / 7 °C

The installation for testing with natural sea water shows Fig. 3. The water was not filtered, thus it has a more erosive effect due to moving sand particles. The temperature of the water was 7 °C with an oxygen content of 8,4 mg/l, its pH was 7,5.



Fig. 3 sea water flow installation on Helgoland

Exposure in sulphide containing sea water over 5 weeks results in a general flaking of the thin films, in combination with tarnishing effects of the substrate.

X-Ray structure investigations yet proceed, but indicate, that the films have a high fraction of amorphous compounds. Crystalline copper oxides have already been detected.

## Conclusions

The test results show that protective layers form in the test loop, operated with circulating artificial sea water. The parameters temperature, pH, and concentration of dissolved oxygen effect the thickness, the chemical and phase composition of the protective layers. An acceleration of film formation is able by means of setting certain pH and temperature conditions. The elemental distribution differs widely, especially in terms of Cu/Ni ratio. Chloride was only found in the basic loop test experiment. Sulfide exposure test showed general effects well known from the literature. The results obtained in natural sea water show the complexity of different influencing factors like the water composition, pH, temperature and oxygen content, which has to be evaluated more intensive. The Structure investigations proceed.

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