EFFECTS OF SEA WATER BIOCHEMISTRY ON BIOCORROSION OF MODIFIED STAINLESS STEELS

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ABSTRACT

Natural, synthetic and sterile sea water were used as electrolytes to study the performance of a new type of stainless steels. The steels were alloyed with poison alloying elements such as Cu, Sn and As in order to diminish the

microbial attack in sea water. The results obtained in this work showed that the behavior of the stainless steels was different in all the solutions used. In both synthetic and sterile sea water, the steels showed a good corrosion resistance compared to the results obtained in natural sea water, in which the steels were more corroded. The results led to the conclusion that using modified sea water to represent real sea water could lead to false results since in different solutions the biofilm formed on the surfaces did not have the same effect on the surfaces. On the other hand the microbial metabolism as well as the microbial interactions could be different because of the biochemistry of the water.

1. INTRODUCTION

Several works regarding biocorrosion have been performed in different media /1-3/. In many of them natural sea water was used as electrolyte. In many others, synthetic sea water and sterile sea water were inoculated with a specific strain and different carbon sources. Some others used just culture media.

Microorganisms tend to react in very different ways according to the surrounding environment. In many cases, for practical reasons, synthetic sea water has been used to represent real sea water. However, the results obtained demonstrated that in most cases, there is not good agreement with those obtained in natural conditions. One reason for this disagreement is the simplification of the sea water's biochemistry which is, in reality, very complex. Sea water could be considered as a "living solution" that cannot be easily simplified. In addition, microbial interactions in sea water are extremely complex and numerous.

The aim of this publication is not to describe these interactions but to show, using electrochemical measurements, the behavior of the stainless steels in different solutions which were intended to simplify sea water.

3. MATERIALS AND METHODS

A 316L SS was taken as a reference. Three different alloys were obtained from the 316L SS which was remelted and alloyed with Cu (3%), Sn (3%) and As (1%) to obtain the different alloys:

- 316L + Cu

- 316L + As

These alloys were tempered up to 1100°C and then cooled with water. One experimental specimen of each alloy was fabricated, from which small specimens (1 cm^2) were cut off for the multiple experiments.

Each specimen was ground with emery paper gradually up to number 800, before exposure in the solutions.

For all measurements, the saturated calomel electrode (SCE) was used as a reference electrode and the platinum electrode was used as counter-electrode.

Four solutions were used:

1. Synthetic sea water (ASTM D 1141).
2. Synthetic sea water (ASTM D 1141) inoculated with bacteria present in the oxides of a corroded steel in sea water. The objective was to have in the solution a representative colony of marine bacteria which took part directly in the corrosion of the steel. The procedure to obtain the bacteria from the oxides was as follows: the oxides were put in a solution containing phosphates in order to open the spores and to reactivate the bacteria. After that, bacteria were cultivated in phosphate media and inoculated in the solution. Culture media was also added to the solution on a weekly basis.
3. Natural sea water taken directly from the ocean at Brest in Brittany, France during September and October, 1988 and filtered with a 2 μm filter. A sea water circulating system, in the laboratory, was built up. The flow rate was 0.5 ml/h. The pH and temperature of the water were 8.2 and 18°C, respectively.
4. Natural sea water was taken and filtered with a 1 μm filter and then autoclaved during 20 minutes to 120°C and 1 bar of pressure. 10 mg/l of yeast extract was added in the electrochemical cell through two 10 l *hermetic glass containers* which were installed and connected to a peristaltic pump to obtain a circulating flowing system. The flow rate was 0.5 ml/h. The medium was renewed every week. Both containers were inoculated with aerobic bacteria type *Vibrio natrigens*, taken from a 24 h culture which was in an EM10 culture medium. The system was left for 21 days in order to create a thick biofilm. After that, SRB type *Vibrio vulgaris* taken from a 5 days culture and contained in an anaerobic liquid of lactate and yeast extract was inoculated. This was done in order to reproduce, in a simplified way, the biofilm formed in the ocean, which has both an aerobic and an anaerobic region.

2.1. Electrochemical tests

Open circuit potential versus time plots (OCP)
Potential measurements were made by using the saturated calomel electrode. These measurements were taken on a daily basis. For all the solutions, the open circuit potentials were taken by using the same reference electrode which was installed in the electrochemical cell from the beginning.

Polarization curves
The polarization curves were outlined by making a scanning potential from the open circuit potential to −1000 mV/SCE, then returning towards the noble potential until either the current reached .001 amp/cm^2 or until the pitting potential was reached.

Electrochemical impedance spectroscopy (EIS)
Electrochemical impedance spectroscopy was also performed on the specimens in all the solutions used in this study. The conditions for this technique were: ΔE = 10 mV, the frequencies scanned were from 10,000 Hz to .001 Hz. All measurements were run until the open circuit potential was stable.

3. RESULTS

Synthetic sea water

The open circuit potential of the stainless steels became anodic during the first three days. After one months, it can be observed (Fig. 1) that the potentials of 316L and 316L + Sn remained anodic whereas those of 316L + Cu and 316L + As returned to the cathodic potentials.

Regarding the polarization curves, the results obtained from the second part of the scanning, which correspond to the anodic polarization curves, demonstrated that during the test period, passivity was improved and pitting potential was more noble for all stainless steels except for the 316L + As which did not show a good passive behavior since its passive current was higher than the other stainless steels and its passive region was not as large as that found for the other stainless steels.

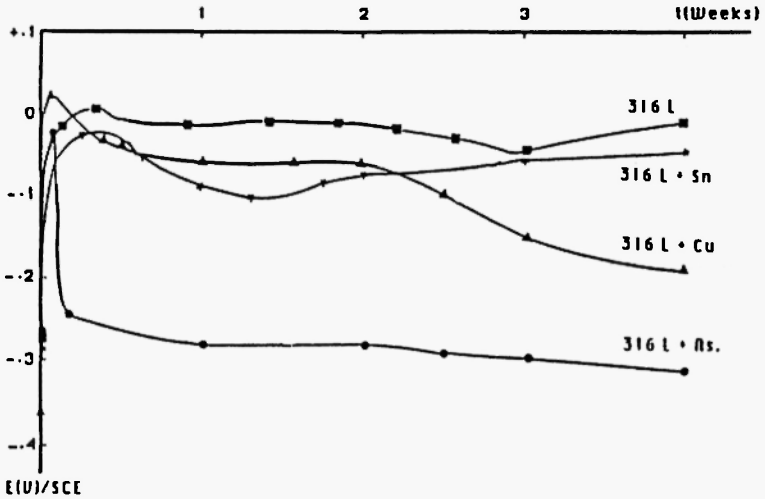

Fig. 1: Open circuit potentials of SS in synthetic sea water.

Inoculated synthetic sea water

Only the 316L and 316L + As were studied in this solution. It can be observed (Fig. 2) that the open circuit potential of 316L became more noble in the solution without bacteria while, in the solution containing bacteria, its open circuit potential went to the cathodic potentials.

The 316L + As stainless steel showed contrasting behavior. In synthetic sea water with bacteria, the open circuit potential went to the cathodic potentials while in the solution without bacteria, the open circuit potential became more anodic (Fig. 3). This curve also showed some irregularities as peaks.

Natural sea water

In natural sea water, the stainless steel potentials monitored against time were done in a laboratory sea water loop with a 0.5 m/sec water flow at room temperature. During the first three days the stainless steel potentials became cathodic. After seven days they returned to the original potential and remained stable for two weeks, after which the potential shifted to noble potentials until they reached the pitting potential, except the 316L + Sn which did not reach the pitting potential after the same exposure time (Fig. 4).

The cathodic polarization curves showed a depolarization after one month of exposure (Fig. 5). However, all the anodic curves showed a polari-

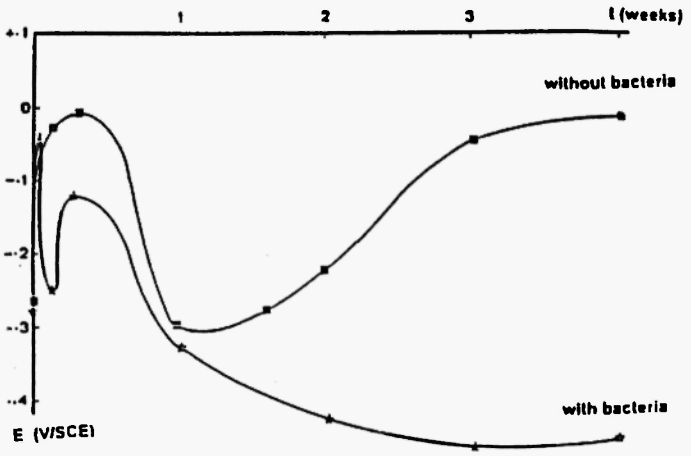

Fig. 2: 316L in synthetic sea water.

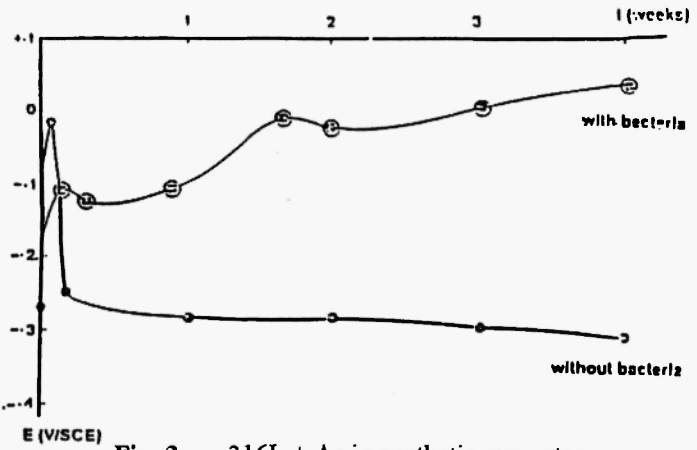

Fig. 3: 316L + As in synthetic sea water.

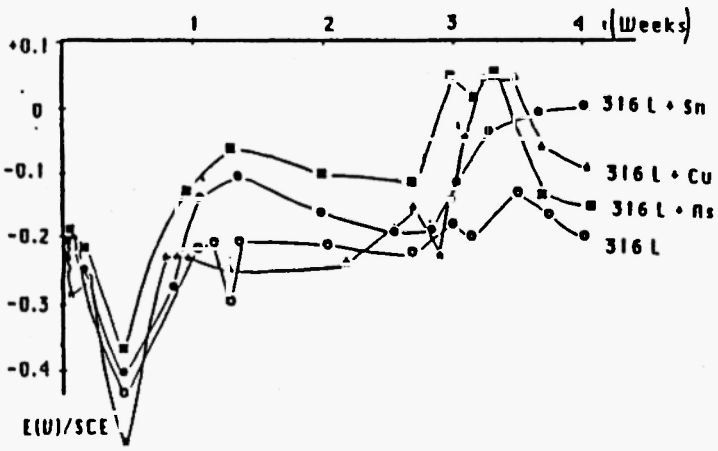

Fig. 4: Open circuit potentials of SS in sea water.

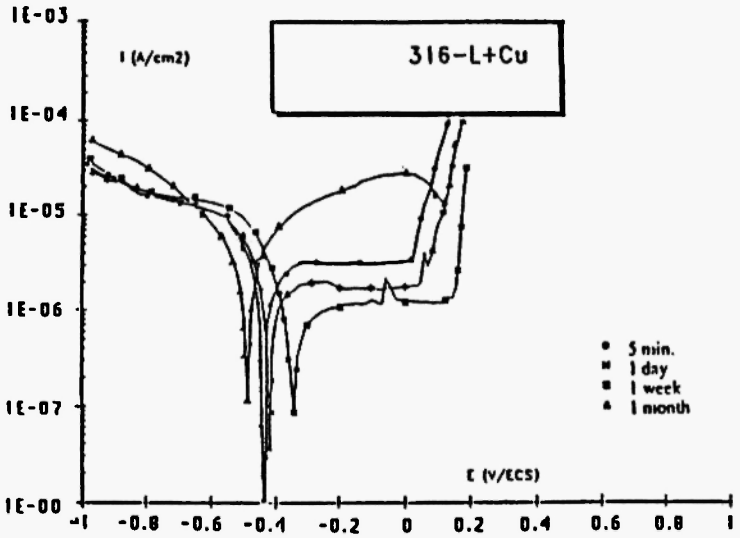

Fig. 5: 316L + Cu in natural sea water for 5 minutes to 1 hour.

zation during the first week since the passive currents decreased, the passive region increased and the pitting potential became more noble. After one month, anodic depolarizations were observed for all the steels except the 316L + Sn which resisted the depolarization better than the others.

EIS measurements were also performed during the time of exposure. Only capacitive behaviors were observed on the stainless steels. Charge transfer resistance was obtained from EIS and, from these results, a general depolarization can be shown in terms of a decrease in resistance. Table 1 shows the charge transfer resistance values. It should be stated that only 316L + Sn did not show any depolarization during that specific time, a finding that is very consistent with the other results obtained in this solution.

Table 1

Charge transfer resistance of stainless steels in sea water (in KΩ)

Immersion time Stainless steel	1 day	1 week	1 month
316L	430	294	29
316L + Cu	148	383	25
316L + Sn	345	152	356
316L + As	75	375	13

Autoclaved and inoculated sea water

The open circuit potentials of the stainless steels showed a very defined behavior. During the first three weeks, the steels were in the presence of *Vibrio vulgaris* (aerobic bacteria) and the open circuit potentials had a constant behavior. The potentials remained between –180 mV/SCE and –350 mV/SCE (Fig. 6). The open circuit potential of 316L went to the anodic potentials during the first week, after which the potential joined the values of the other potentials and remained there until the second inoculation. It can also be seen that the 316L + Sn open circuit potential showed a more noble potential compared to the other stainless steels. After the second inoculation, all the open circuit potentials went to the more cathodic potentials. At the end of the experiment the 316L + Sn and 316L + Cu open circuit potentials were more anodic than the others while the 316L + As potential was the more cathodic.

The cathodic polarization curves showed a polarization after the second inoculation on 316L + Cu and 316L + As (Fig. 7). This phenomenon is less marked on 316L and 316L + SN. This polarization is also found in anodic polarization curves of 316L + Cu and slightly on 316L + As. However, a certain depolarization was observed on 316L and 316L + Sn.

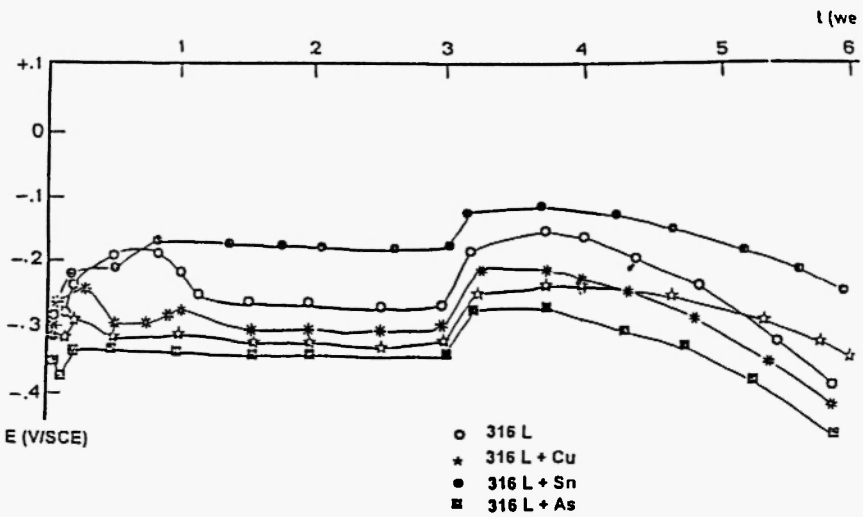

Fig. 6: Open circuit potentials of the stainless steels in filtered and autoclaved sea water.

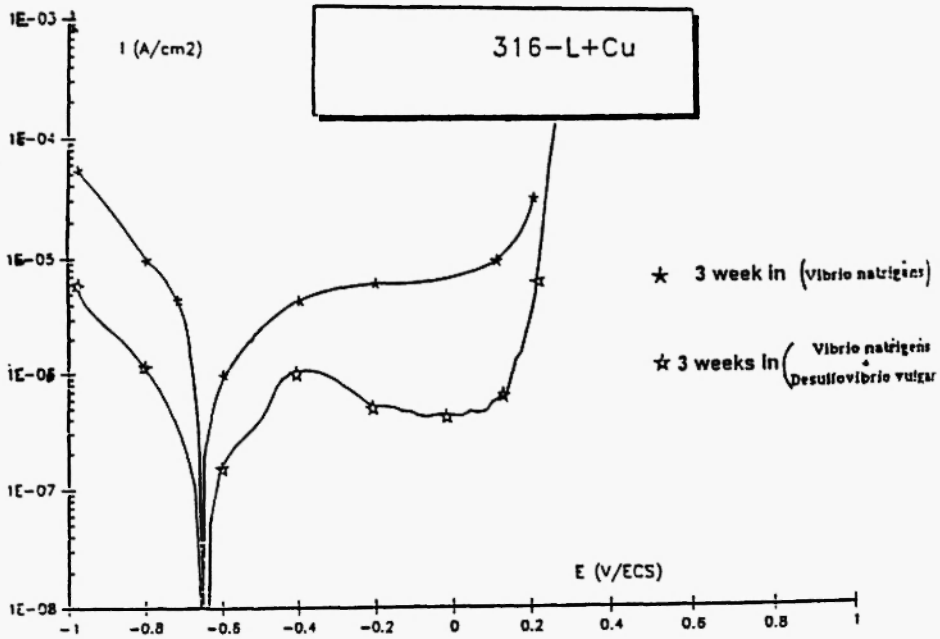

Fig. 7: 316L + Cu in filtered and autoclaved sea water.

4. DISCUSSION

According to the results of this work, it can be seen that bacteria did have an effect on the electrochemical behavior of the stainless steels studied. The absence of bacteria in synthetic sea water promoted a good passive film formation, except for 316L + As which showed poor passive behavior. However, in inoculated synthetic sea water, the 316L and 316L + As behaviors were the opposite. Bacteria seemed to deteriorate passive properties of 316L (Fig. 2). The absence of a toxic element in the stainless steel passive layer left the steel unprotected against microbial attack. Microscopic observations (not shown in this paper) demonstrated that bacterial colonization on 316L SS was larger than on 316L + As. This could be due to the fact that an arsenic enriched passive layer /4/ had a toxic effect on bacteria, thus decreasing the risk of MIC. Scanning electron microscopic observations also showed that 316L + As was less colonized than 316L.

In natural sea water, the results are in very good agreement with the literature /5/. The establishment of the biofilm during the first weeks made

them more corrosion resistant, probably due to the presence of extracellular exopolymers that may have acted as inhibitors during that specific time. On the other hand, anaerobic bacteria may not have been active before the third week (Fig. 4), but after the biofilm is well formed, anaerobic bacteria can be active and then they can initiate corrosion. According to the open circuit measurements (Fig. 4), three steps can be observed: 1. The biofilm formation; 2. the ennoblement of the open circuit potentials, and 3. The reaching of pitting potential. From the polarization curves it can be seen that during the first weeks both passive and cathodic current decreased, but after one month both cathodic and anodic depolarizations occurred. These depolarizations were also observed with EIS measurements. Table 1 shows these values. It should be stated that these depolarizations were only observed in natural sea water and not in other solutions, where contrary behavior was found.

In filtered and autoclaved sea water, the stainless steel behavior was different from that of natural sea water. Both cathodic and anodic polarizations were found on 316L + Cu and 316L + As. After the first inoculation, the open circuit potentials remained stable; this could correspond to the biofilm formation and it would be consistent with the open circuit potential obtained in natural sea water (Fig. 6). This is also consistent with the literature in the sense that, in sea water, aerobic bacteria settle first and produce exopolymers in order to stick definitely to the surface.

The polarization observed in this solution is less evident on 316L and 316L + Sn. However, it can be seen again that 316L and 316L + Sn form a group with similar properties and 316L + Cu and 316L + As form a group with other properties. In this solution and under these conditions, Cu seems to have an effect on bacteria, a good corrosion resistance having been maintained during the experiment.

On the other hand, from the polarizations observed as well as from the charge transfer resistance values, one can conclude that the biofilm formed by aerobic bacteria showed protective properties and, for the duration of the experiment, anaerobic bacteria did not produce severe corrosion.

5. CONCLUSIONS

The conclusions reached are as follows:

a. Severe corrosion was found on the specimens immersed in natural sea water compared to those immersed in the solutions intended to reproduce it.

b. Different results were obtained in the solution containing bacteria compared to synthetic sea water without bacteria. Bacteria play an important role in marine corrosion that cannot be neglected when using synthetic sea water.

c. 316L + Sn showed the best corrosion resistance in all the four solutions used in this study. The passive layer was enriched with Sn. This element had a toxic effect against bacteria in sea water.

d. There could be a risk when using results obtained in solutions intended to reproduce natural sea water to predict the behavior of stainless steel in real sea water. Under different conditions, biofilm formation and bacteria relationships as well as microbial metabolisms may change, and therefore the mechanisms of attack could also be different.

6. REFERENCES

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