

CHEMICAL ENGINEERING

Electrochemical Behavior of Stainless Steel Alloys Containing Mo and Ti in Sea Water

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Abstract. This study was carried out to investigate the effect of Mo and Ti on the corrosion of stainless steels in sea water. The electrochemical tests showed that adding Mo up to 4% will enhance the corrosion resistance of the steel. The free corrosion potential was shifted to more positive potentials by adding Mo, the polarization resistance (R_p) increases 10 times that of Mo free steel. The corrosion current reduced 45 times due to the addition of 4% Mo. Adding Ti to the base alloy enhance the corrosion resistance of stainless steel alloy with an optimum percentage of 2.32 Ti.

Introduction

The 18/8 (Cr,Ni) type stainless steel has been a popular corrosion resistant material used in marine conditions. These types of steel find wide application as a material of construction in desalination plants [1,2]. There are some compositional modification employed to improve the corrosion resistance, among the modification, the addition of molybdenum to improve pitting and crevice corrosion resistance, also titanium is added to reduce intergranular corrosion in welded material.

Recent studies showed that Mo-containing stainless steel are superior in their corrosion behavior to other stainless steel [3], also less susceptible to stress corrosion [4] and more resistant to pitting attack [5]. For these model alloys (see Table 1) in Gulf water, no work has been done, and therefore this work is carried out to study the electrochemical behavior of stainless steel alloys containing Mo and Ti in sea water.

Materials Preparation

Six different alloys were made. These alloys were prepared from pure elements. The alloys were prepared by melting in a high vacuum induction furnace under a vacuum of 10^{-4} to 10^{-5} torr. The surfaces approximately 1 mm thick of the cast blocks, which were either 1" square or 1" diameter in section, were machined away to remove any contaminants. The obtained ingots were forged to 10 mm thickness and hot rolled to 3 mm thickness at 1050°C. After hot rolling to 3 mm, the sheets were heated (normalized) in an evacuated quartz tube furnace for one hour at 920°C. Table 1 shows nominal composition of the studied alloys.

Table 1. Alloy composition wt %

Alloy	C	S	Cr	Ni	Mo	Ti	Fe
1	0.06	0.003	17.0	9.8	—	—	Bal.
2	0.05	0.003	16.9	10.0	1.89	—	Bal.
3	0.05	0.003	16.8	10.3	3.96	—	Bal.
4	0.02	0.002	17.2	10.2	—	1.33	Bal.
5	0.04	0.002	17.2	9.8	—	2.32	Bal.
6	0.07	0.002	17.1	9.7	—	4.13	Bal.

The specimens of one square cm cross-sectional area were cut from the steel sheet using a shaping machine.

Specimens Preparations

The standard disc specimens (1 cm²) were ground with a wet silicon carbide paper progressively from 180, 400, 600 to 1000 grade papers. They were then washed, degreased by carbon tetrachloride and stored in a desiccator.

Environment

All measurements were carried out in presence of Arabian Gulf water, without deaeration. The composition of Gulf water is shown in Table 2.

Experimental Procedure

Three electrochemical techniques were applied in this work, they are Tafel plot, polarization resistance and pitting potential beside measuring the free corrosion potential. These techniques were carried by using an automatic corrosion unit

Table 2. Characteristics of the Arabian Gulf sea water

Electrical conduction, S	69,600
TDS, ppm	43,089
Cl ⁻ , ppm	27,300
Ca ²⁺ , ppm	543
Mg ²⁺ , ppm	1,790
HCO ₃ ⁻ , ppm	115
CO ₃ ²⁻ , ppm	15.5
pH	8.14

"model" 350A, produced by Princeton Applied Research Company. The specimen is installed in the specimen holder and fully immersed in sea water. As soon as the specimen is immersed the specimen surface is electrochemically cleaned by keeping the specimen under -1V for 20 minutes, then the free corrosion potential was recorded for 30 minutes. All of the d.c techniques were carried out after free corrosion potential measurements. In polarization resistance the potential was scanned ± 25 mV with respect to the free corrosion potential starting from negative towards positive, in Tafel plot the scanning range was ± 250 mV in both techniques the scan rate is 1 mV/sec. For pitting potential tests the measurements were started from the free corrosion potential towards the positive up to the (breaking potential) pitting potential. Pitting potential measurements were carried out in 3.5% NaCl because in sea water it is too difficult to predict the pitting potential due to the limitations of the instrument used in measurements. In all measurements SCE was used as a reference electrode and two graphite electrodes as the counter electrodes.

Results and Discussion

Table 3 summarized the results obtained from the different techniques. In general adding Mo and Ti enhance the corrosion resistance of the alloy.

Table 3. Measurements results

Alloy number	Free corrosion potential volts	Polarization resistance ohms	Corrosion current nA/cm ²	Pitting potential volts
1	-0.187	7.97E5	177	0.55
2	-0.23	1.54E5	36.3	0.5
3	-0.092	1.44E6	3.9	1.2
4	-0.025	1.72E5	11.5	0.49
5	0.06	4.32E5	5	0.46
6	-0.165	3.69E6	13	0.6

Figures 1-6 show the potential change with time of different alloys in Arabian Gulf water at 25°C for 30 minutes. The changes in potentials indicate that the air-formed films on the surface of alloys are unstable in the environment under investigation. The measured potentials were shifted to more positive value due to the repair of the air-formed oxide films. There is no fluctuation in potential during the measuring period, which suggests that the rapid film break-down and repair processes are not occurring [6].

The addition of 1.9% Mo (alloy 2) shifts the free corrosion potential of the base alloy to more negative potentials, while the addition of 3.9% Mo (alloy 3) shifts the free corrosion potential to more positive value see Fig. 2.

For the Ti containing alloys, the potential change is not different from that of Mo containing alloys. Adding Ti to the alloys shifts the potential to more positive potentials the higher shifts occur with the lowest Ti content (1.33%) see Figs. 4-6.

Figures 7-12 show the polarization resistance of the different alloys in Arabian Gulf water. The base alloys show a polarization resistance of $7.97 \text{ E } 5$ (see Fig. 7), while the Mo containing alloys (alloy 3) and (alloy 2) show $1.44 \text{ E } 6$ and $1.54 \text{ E } 5$ respectively, see Figs. 8 and 9. For titanium containing alloys, the higher the titanium content (alloy 6) the greater the polarization resistance ($3.59 \text{ E } 6$) see Fig. 10 and as the titanium content decreases (alloys 5 and 4), the polarization resistance decreases, see Figs. 11 and 12. As a result of this technique, the higher the Mo, and Ti content alloys the better resistance to corrosion.

Figs. 13-18 show the Tafel plots of the alloys in Arabian Gulf Water. The cathodic reactions of all alloys are all the same (oxygen reduction), but as an electrochemical reaction it should be effected by the alloy composition (6 compositions) and surface preparation and as a consequence the Tafel slopes will not be the same. Fig. 13 shows the Tafel plot of the base alloy the corrosion current is 177 nA/cm^2 which is equivalent to 0.002 mm per year. The corrosion current was drastically decreased from (177 to 3.9) nA/cm^2 by adding 3.9% Mo to the base alloy, see Fig. 14. For the lower Mo content alloy (1.89% Mo) the corrosion current (36.3 nA/cm^2) is smaller than that of the base alloy but 10 times that of the 3.9% Mo alloy, see Fig. 15. The anodic branch of the Tafel plot of 3.9% Mo alloy is fluctuated which may be due to the formation of different molybdenum oxides.

For titanium containing alloys the corrosion currents of their alloys are smaller than that of the base alloy, see Figs. 16-18. The optimum titanium content is 2.32% (alloy 5) which gives 5 nA/cm^2 , see Fig. 16. Increasing or decreasing the titanium con-

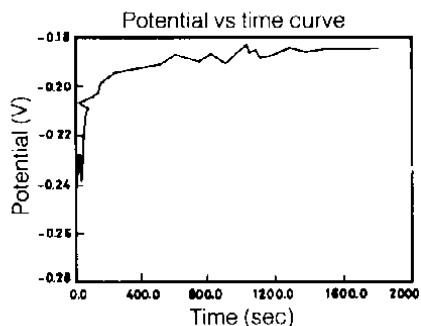


Fig. 1 Potential vs time curve of alloy 1.

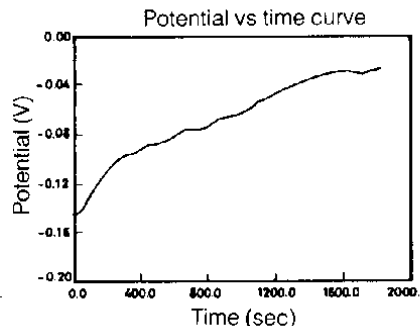


Fig. 4. Potential vs time curve of alloy 4.

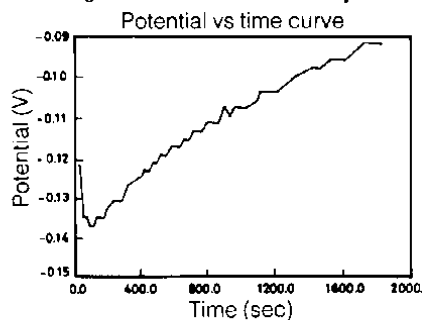


Fig. 2. Potential vs time curve of alloy 3.

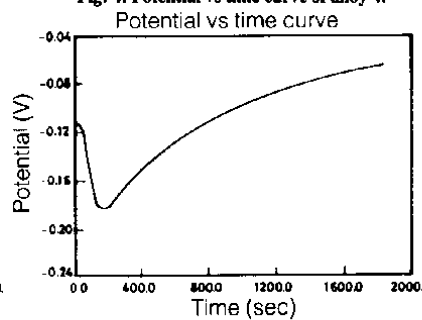


Fig. 5. Potential vs time curve of alloy 5.

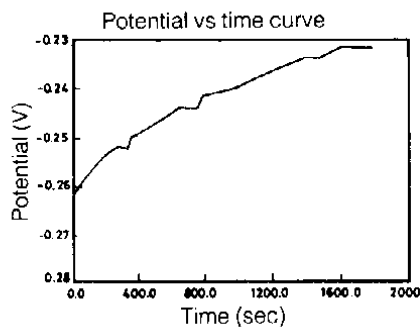


Fig. 3. Potential vs time curve of alloy 2.

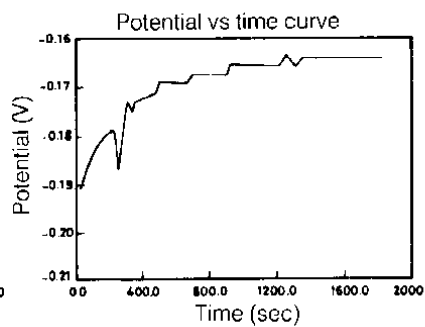


Fig. 6. Potential vs time curve of alloy 6.

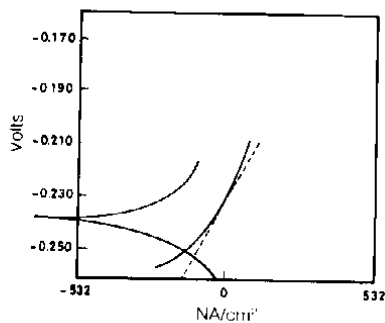


Fig. 7. Polarization resistance curve of alloy 1.

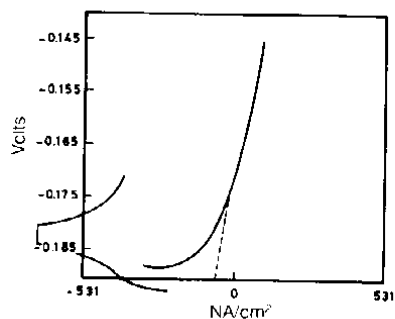


Fig. 10. Polarization resistance curve of alloy 6.

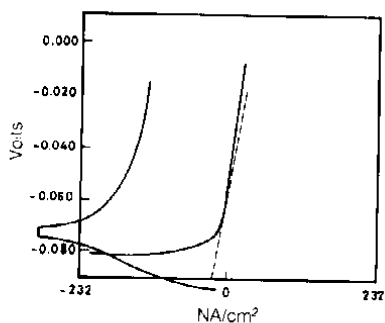


Fig. 8. Polarization resistance curve of alloy 3.

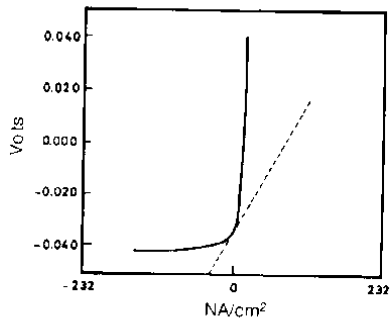


Fig. 11. Polarization resistance curve of alloy 5.

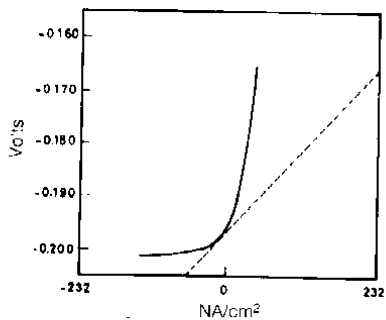


Fig. 9. Polarization resistance curve of alloy 2.

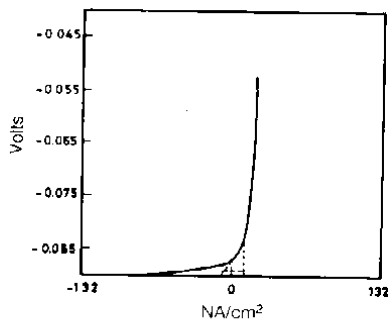


Fig. 12. Polarization resistance curve of alloy 4.

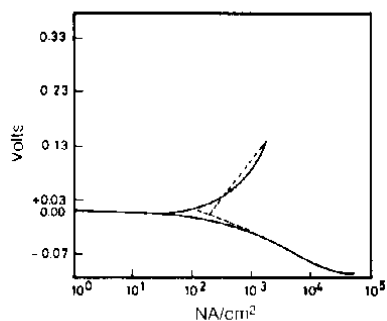


Fig. 13. TaFel plot of alloy 1.

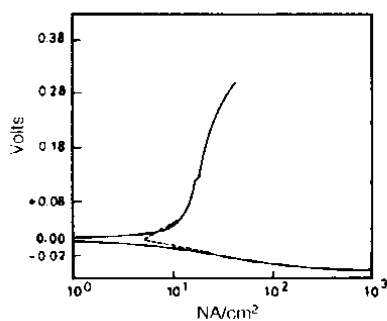


Fig. 16. TaFel plot of alloy 5.

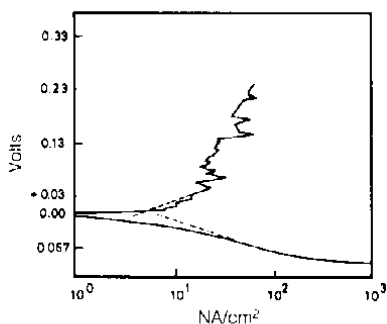


Fig. 14. TaFel plot of alloy 3.

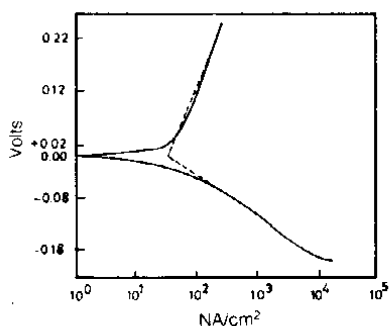


Fig. 17. TaFel plot of alloy 6.

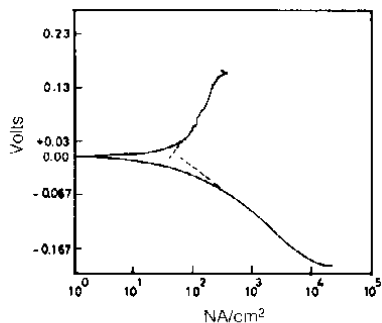


Fig. 15. TaFel plot of alloy 2.

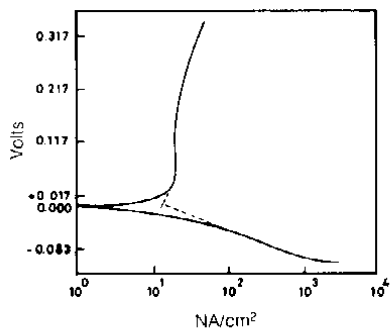


Fig. 18. TaFel plot of alloy 4.

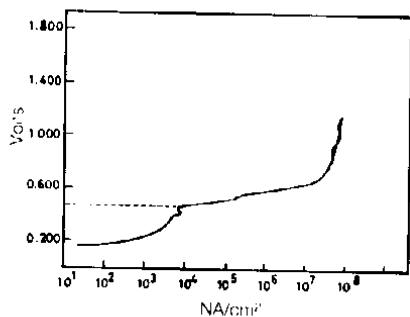


Fig. 19. Pitting potential of alloy 5.

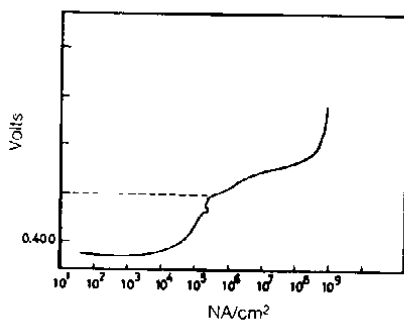


Fig. 22. Pitting potential of alloy 6.

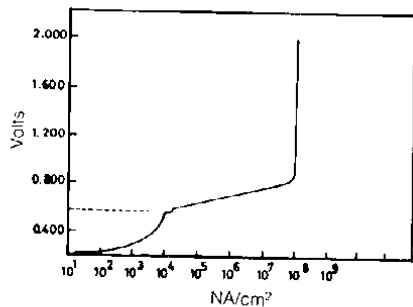


Fig. 20. Pitting potential of alloy 1.

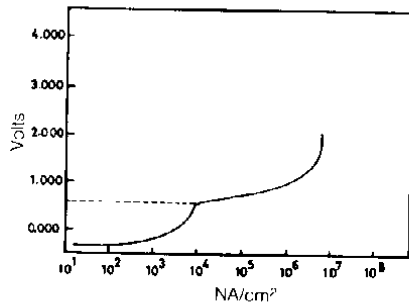


Fig. 23. Pitting potential of alloy 4.

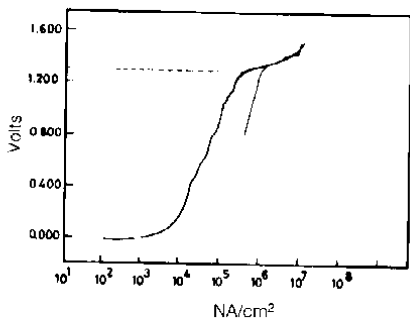


Fig. 21. Pitting potential of alloy 3.

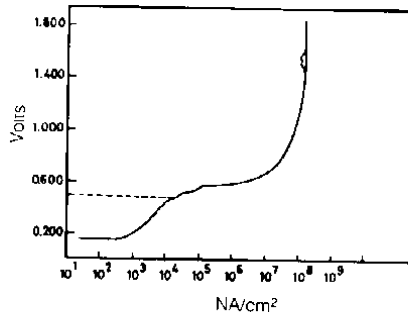


Fig. 24. Pitting potential of alloy 2.

tent (alloy 6 and 4 respectively) the corrosion current decreased compared to the base alloy but higher than alloy 5 see Figs. 17 and 18.

The pitting potentials of the alloys in 3.5% NaCl solution are shown in Figs. 19-24. From Fig. 20 the pitting potential of the base alloy (1) is 0.55 V, adding titanium to the base alloy with different percentages had no remarkable effect on the pitting potential see Figs. 19, 22, 23. The effect of molybdenum on the pitting potential of the alloy depend on the molybednum level. The lower percentage (1.89) of Mo had no effect on the pitting potential. However, doubling the Mo content to 3.98% improve the pitting potential drastically see Fig. 21, this big jump in pitting potential show the role of molybdenum in the enhancement of the pitting resistance of the alloy.

Conclusions

From the above results some conclusion can be drawn:

1. Molybednum and titanium containing stainless steel alloys showed a good resistance to general corrosion.
2. Titanium containing alloys have less immunity to pitting corrosion.
3. The improved pitting behavior of stainless steel alloys containing molybdenum as an alloying element could appreciably expand the operational possibilities of using stainless steel in marine environments.
4. It is useful to expand the range of Mo in the alloys to determine the optimum Mo content.
5. A new model of stainless steel alloys containing both Mo and Ti should be investigated.

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السلوك الكهروكيميائي لسبائك الصلب المقاوم المحتوي على المولبدنم والتيتانيوم في ماء البحر

منصور إبراهيم الهزاع

قسم الهندسة الكيميائية، كلية الهندسة، جامعة الملك سعود، ص.ب ٨٠٠،

الرياض ١١٤٢١، المملكة العربية السعودية

(استلم في ١٦/٣/١٩٩٢م؛ قبل للنشر في ١٧/٥/١٩٩٣م)

ملخص البحث. أجريت هذه الدراسة لمعرفة أثر المولبدنم والتيتانيوم على تآكل الصلب المقاوم في ماء البحر. حيث أظهرت الاختبارات الكهروكيميائية أن إضافة المولبدنم حتى ٤٪ سيحسن من مقاومة الفولاذ للتآكل.

أزيع جهد التآكل الحر في الاتجاه الموجب للجهد بإضافة المولبدنم وأيضاً تضاعفت قيمة مقاومة الاستقطاب عشر مرات بسبب هذه الإضافة. قلّ تيار التآكل بمعدّل ٤٥ ضعفاً بسبب إضافة ٤٪ من المولبدنم. إضافة التيتانيوم إلى السبيكة الأصلية حسن من مقاومتها للتآكل بتركيز أمثل يصل إلى ٣٢، ٢٪.