Polarographic and kinetic parameters of the Schiff base

	PLP: nex		PL: nex	
	8.5 <ph<11.3< th=""><th>pH>11.3</th><th>pH<10.4</th><th>pH>10.4</th></ph<11.3<>	pH>11.3	pH<10.4	pH>10.4
$\frac{\partial E_{1/2}}{\partial pH}$ /mV	-60	-90	-58	-88
$\frac{\partial E_{P}}{\partial pH}$ /mV	-	-	-54	-83
$\partial E/\partial \log \frac{i}{iL-i} /mV$	-29	-29	-29	-29
∂E ∂logi /mV	-28.2	-	-29	-29
$\frac{\partial \log i}{\partial \log c_{_{\rm H}}}$	2.2	_	2.1	3.0
<pre>∂log i ∂log c_s</pre>	-	_	-	0.9

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THE EFFECT OF TA ION IMPLANTATION ON THE AQUEOUS CORROSION RESISTANCE OF M50 BEARING STEEL

C.M. Rangel, M.H. Simplício, A.C. Consiglieri LNETI - Departamento de Tecnologia de Materiais, Paço do Lumiar, 22 - 1699 LISBOA CODEX, PORTUGAL

Corrosion of the localized type of steel bearings used in gas turbine engines has been found to be a serious problem. This is mainly due to the accumulation of salt-spray condensates in the engine lubricant, probably, during non-working periods.

A large percentage of bearings can be removed from service due to corrosion problems and even minor corrosion pitting of the receways has been proven to reduce life significantly.

The present work reports on results regarding corrosion resistance of ionically implanted substrates of M50 steel with Ta. Implantation with other ions is being implemented.

Measurements on non implanted samples were made on M50 steel disks supplied by RHP Bearings Ltd. Nominal composition is given elsewhere^[1].

Potentiostatic determination of breakdown potentials (Eb) together with examination of surface morphology by Scanning Electron Microscopy were also conducted.

Experimental details are given elsewere^[1].

Implanted surface with Ta at nominal concentrations from 5×10^{16} ions.cm⁻² to 4×10^{17} ions.cm⁻² were studied using the same techniques as for the base metal (see Fig.1).

An overall view of the effect of implantation is better analyzed when studying the peak current as a function of the scan rate in a log-log plane. The relationship is found to be linear (Fig. 2) with no significant difference between doses in the range from 5×10^{16} to 2×10^{17} ions.cm⁻² probably due to sputtering and saturation^[2,3]. A kinetic analysis is the subject of further publication.

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Fig.1 - Cyclic voltammograms to M50 steel implanted with a nominal dose of 5×10^{16} ions.cm⁻² Ta in 0.5M NaHCO₃ + 0.05M Na₂CO₃ + 0.5M NaCl solutions at several scan rates.



- Fig.2 Unidirectional voltammograms for M50 steel in 0.5M NaHCO₃ + 0.05M Na₂CO₃ + 0.5M NaCl solutions for the Ta implanted samples and base metal, at 20mV.s⁻¹(a).
 - The peak current as a function of sweep rate for Ta implanted samples and base metal (b).

Potentiostatic determination of breakdown potentials (Eb) were also conducted. Typical step by step polarization run from - $\emptyset.9V(SCE)$ up to the breakdown potential were performed. Table 1 shows the ennoblement of Eb values as a result of Ta implantation eventhough the implanted doses, as indicated by RBS analysis (4), did not exceed $5x10^{16}$ ions.cm⁻².

In the long term tests, in open circuit conditions, the ocurrence of crevice was noticeable at the interface between the implanted and non-implanted surfaces. This was suggested by the fluctuations in potential recorded against a saturated calomel electrode^[4]. Examination of the morphology of attack, in the crevice areas, was also performed.

Results obtained in free crevice samples indicated more noble open circuit potentials, with differences up to 0.250V(SCE). Best corrosion resistance was indicated for $1x10^{17}$ ions.cm⁻² Ta, data in agreement with breakdown potentials.

[Ta]*	Eb	
ions.cm ⁻²	mV(SCE)	
$ \begin{array}{c} 0 \\ 5 \\ x \\ 1017 \\ 1 \\ x \\ 1017 \\ 2 \\ x \\ 1017 \\ 4 \\ x \\ 1017 \\ \end{array} $	- 225 + 350 + 475 + 400 + 375	

TABLE 3 - Breakdown potential for Ta implanted substrates and base metal.

* nominal concentrations

CONCLUDING REMARKS

- The effect of implantation of tantalum on M50 steel produces a decrease in the anodic current density as a result of a metastable solid solution of Ta in Fe which performs better than the base metal in terms of corrosion resistance. This is probably due to the passivating effect produced by the formation of a Ta₂O₅ film during exposure and/or polarization.

- Depth profiles obtained by RBS confirmed that the retained dose did not exceed 5×10^{16} ions.cm⁻². Flat topped and skewed distribution profiles (RBS) were obtained and regarded as indicative of sputtering and saturation doses^[4].
- Breakdown and dissolution of Fe-Ta surface alloy layers is localized with preferential dissolution of iron. This is suggested as a result of EDAX analysis in active and passive adjacent zones, in a crevice, where the amount of detected Ta was not significantly different.
- A potential displacement of about 0.5V in the noble direction scale was found as a result of implantation.

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CORROSION PRODUCTS OF LOW ALLOY STEEL UNDER WET-DRY CYCLING CONDITIONS

J. Dávalos, J.F. Marco, M. Gracia, and J.R. Gancedo

Instituto de Química Física "Rocasolano" CSIC, C/ Serrano 119, 28006 Madrid, Spain

Summary

The corrosion products formed on weathering steel and pure iron exposed to a wet-dry cycled SO_2 -atmosphere have been studied by means of reflection (CEMS) and transmission Mössbauer spectroscopy and X-ray diffraction. After 48 days of exposure, rusts of both materials exhibit different morphologies. FeSO₃:3H₂O, FeSO₄:nH₂O and amorphous ferric oxyhydroxides (probably ferrihydrite and/or a-FeOOH of small particle size) are the constituents of both materials are related with the concentration of Fe²⁺ species and the crystallinity and/or particle size of ferric oxyhydroxides. The presence of Fe²⁺ species in 48 day-old rusts is attributed to the effect of the wet-dry cycling conditions.

1. Introduction

The daily change from wet to dry atmosphere, the so-called wet-dry cycle, affects the atmospheric rusting of ferrous materials [1-3]. In this work, the differences between the products formed on pure iron and low alloy steel, both exposed to simulated wet-dry cycles under artificially SO_2 -polluted atmospheres, are shown. Mössbauer spectroscopy and X-ray diffraction were the main techniques employed for the analysis of products.

2. Experimental

Samples were polished (Al₂O₃, 0.3 μ m) discs of weathering steel (ASTM A-508 gr A) and commercial iron (Comeca, St. Cyr, France, <0.15% Cu; 0.1% C+P+Mn+Si) exposed at 25°C during 48 days to an SO₂-polluted (0.008% by vol.) atmosphere, whose relative humidity (RH) was sequentially maintained 6h at 98% RH and 18h at 15% RH. The artificially SO₂-polluted atmosphere was prepared as described in [4].

Mössbauer spectra of rusts were taken by CEMS using a home made parallel plate avalanche counter [5] and by transmission after rust descaling. A closed-cycle Helium cryogenic generator (Air Products) was employed during the recording of transmission spectra at 78 and 14 K.

X-ray diffractograms of the rusts were taken "in situ", prior to rust descaling, in a Philips PW 1730/10 diffractometer using the Cu K_{α} line.