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CORROSION RESISTANCE MODELING OF A NEW TITANIUM ALLOY IN ACID ENVIRONMENTS

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Corrosion resistance modeling of a new ternary titanium Ti-0.5Mo-1Ni alloy (in casting or forging state) in comparison with the base metal in ortho- and meta- phosphoric acid solutions of various concentrations and temperatures was studied. The potentiostatic and potentiodynamic polarisation measurements were carried out in order to determine the main electrochemical parameters. The linear polarisation method was used to obtain the corrosion current densities and corrosion rates. Electrochemical impedance spectroscopy was also applied and equivalent electric circuits were fitted with the experimental data.

INTRODUCTION

Though is very resistant in many aggressive environments, the titanium[1] presents a low corrosion resistance in concentrated acidic solutions at high temperatures. In order to optimize the titanium behaviour in these conditions, the efficient method is its alloying.[2-17]

It was found that the molybdenum[18-21] has a beneficial influence, conferring higher corrosion stability. The increase of the corrosion resistance takes place due to both a considerable inhibition of the anodic dissolution reactions and some increase in the thermodynamic stability.

Nickel[22,23] as alloying component can have effect on the anodic dissolution of the titanium because, in the active dissolution potential range of the titanium, the nickel is under the control of the cathodic process. But, the nickel has a low solubility ($< 0.5\%$) in αTi phase and an average solubility (12%) in βTi phase.

However, the stable structures of Ti alloy can be obtained by special thermal treatments.[24-27] So, for the alloying with molybdenum the baking and slow cooling should be used, whereas the alloying with nickel was used for hardening and forging.

It was obviously that both molybdenum and nickel can contribute to the consolidation of the protective film (consisting in a TiO_2 resistant oxide) on the Ti-Mo-Ni alloy surface with their passivating oxides, involving changes of the defect number, and so, of the film conductivity, and, consequently, of the corrosion rate.[28-31]

It results that, the simultaneous alloying of the titanium with molybdenum and nickel is beneficial.

The modeling of corrosion resistance of Ti-0.5Mo-1Ni alloy in comparison with the base metal in ortho- and meta-phosphoric acid solutions at different concentrations and temperatures was studied in the present paper. The investigated samples were provided by the Institute for Non-Ferrous and Rare Metals, Bucharest, Romania, that has obtained this new Ti-0.5Mo-1Ni alloy, which was stabilized by forging.

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EXPERIMENTAL

The titanium and Ti-Mo-Ni alloy were obtained by vacuum melting.

The composition of the alloy is: 1.04%Ni, 0.53%Mo, 0.11%O, 0.0065%N, 0.055%Cl, < 0.002%Mg, < 0.05%Al, < 0.005%Mn, < 0.005%P, < 0.005%Zn, < 0.01%Cr, < 0.05%Si, < 0.025%Sn, balance Ti. The alloy sample has a + ß bi-phase structure.

The corrosion behaviour of this alloy was studied in comparison with a titanium sample of composition: 0.0095%Fe, 0.05%O, 0.0045%N, 0.035%Cl, < 0.0025%Mg, < 0.05%Al, < 0.005%Mn, < 0.005%P, < 0.005%Sn, < 0.01%Cr, < 0.05%Si, < 0.02%Sn, balance Ti.

Before experiments, the cylindrical electrodes were abraded with emery paper, fixed in a Stern-Makrides mount system, rinsed with tap and distilled water, degreased in boiling benzene and dried.

The experiments were performed in three solutions: 30% orthophosphoric acid – H_3PO_4 and 10% and 30% metaphosphoric acid – $(HPO_3)_n$. The solution temperature was kept at 23^0, 50^0, $75^0 \pm 1^0$C.

The potentiostatic and potentiodynamic polarization measurements were carried out in order to determine the main electrochemical parameters: the corrosion potential E_{corr}, the critical passivation potential E_{cr}, the passivation potential E_p, the passive potential range ΔE_p, the transpassive potential E_T, the critical passivation current density i_{cr}, and the dissolution current density in the passive range, *i.e.*, passive current density i_p. The linear polarization procedure was used to obtain the corrosion current density $i_{corr} = k(di/dE)_{Ecorr}$ from Stern formula, considering k=26.8 mV. The potentiostatic polarization measurements started from –0.8 V to +4.0V (vs. SCE) using a 50 mV step at every 2 min.; the potentiodynamic cyclic polarization was performed starting from –0.8 V to +2.0 V using a scan rate of 2 mV/sec.; the linear polarization were applied for ±10 mV around the corrosion potential. The electrochemical set-up consisted in a potentiostat (PAR Model 173), a XY recorder (Endim 62002) and a universal impulse generator (AT).

Electrochemical impedance spectroscopy (EIS) was applied to obtain Bode spectra at three electrode potentials: E_{corr}, E_{cr}, E_p. Single sine wave measurements at frequencies between 0.1 Hz and 100 kHz were performed at these potentials (7 frequencies per decade using a 5 mV amplitude of the sinusoidal voltage). The EIS spectra were interpreted using the non-linear least square fitting procedure.[32] The electrochemical set-up consisted in an EG&PAR 273A potentiostat connected with a PAR 5210 lock-in amplifier controlled by EG&G 6398 impedance measurement software.

The electrochemical glass cell was provided with a central compartment for the electrode assembly. Two equidistant platinum plates were counter electrodes and a Luggin probe was connected with a saturated calomel reference electrode (SCE).

RESULT AND DISCUSSION

1. Corrosion resistance in orthophosphoric acid

The corrosion potentials of the ternary alloy Ti-0.5Mo-1Ni (casting or forging) are nobler than of the base metal due to the beneficial effects of the alloying elements. On the anodic polarisation curves of the titanium and ternary alloy appear an active-passive potential range and two peaks for the critical passivation current density (i_{cr1} and i_{cr2}); we noticed that for the ternary alloy, the first peak is lower than the first peak of the base metal (Fig. 1 and 2). Correspondingly, two values of the critical passivation potential (E_{cr1} and E_{cr2}) can be observed, which are nobler for alloy than for titanium (Table 1). This behavior can be explained[21, 26] by initial formation (at the first critical passivation potential) of either titanium trioxide, Ti_2O_3, or pentoxide, Ti_2O_5. At the second critical passivation potential, these oxides are converted to the compact and protective titanium dioxide, TiO_2.

The extent of passive potential range for Ti-0.5Mo-1Ni alloy is smaller than for pure titanium because transpassive potentials of molibdenum and nickel are low and their influence appears to be important.

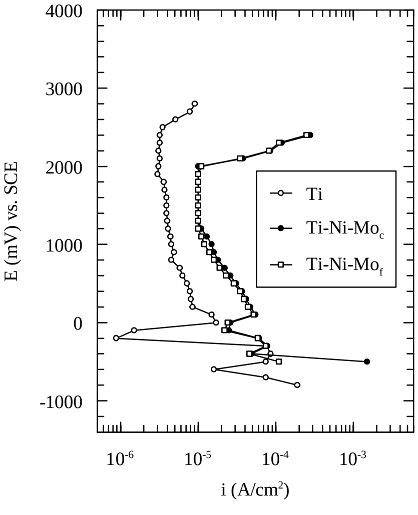

Fig. 1 – Polarization curves for Ti and Ti-0.5Mo-1Ni alloy in 30% H_3PO_4 solution at 25^0C: c – casting sample; f – forging sample

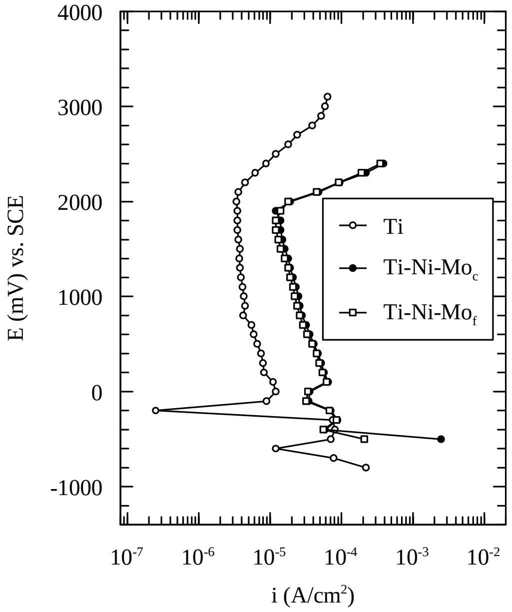

Fig. 2 – Polarization curves for Ti and Ti-0.5Mo-1Ni alloy in 30% H_3PO_4 solution at 75^0C: c – casting sample; f – forging sample

As Figures 1 and 2 show, the passive current density for ternary alloy is higher than of the pure titanium, because the molybdenum dissolves transpassive in this potential range. Also, an incorporation in the passive film of the molybdenum oxide, MoO_3, or nickel oxide, Ni_3O_4, can take place,[17, 25, 29] these oxides increasing the ionic conductivity of the film and the dissolution rate, too.

Impedance spectra, in Bode plots, clearly show the existance of more time constants (Fig. 3) for both Ti and its ternary alloy in casting or forging state. These time constants corespond with three physical processes: one process for charge transfer reactions at E_{corr}; the second process characterised by a phase angle closed to – 90^0 is typical for passive film (curve ? and ?) and the third process with a phase angle about – $60^0 \div -70^0$ (curve ?) suggests some diffusion processes through the passive layer.

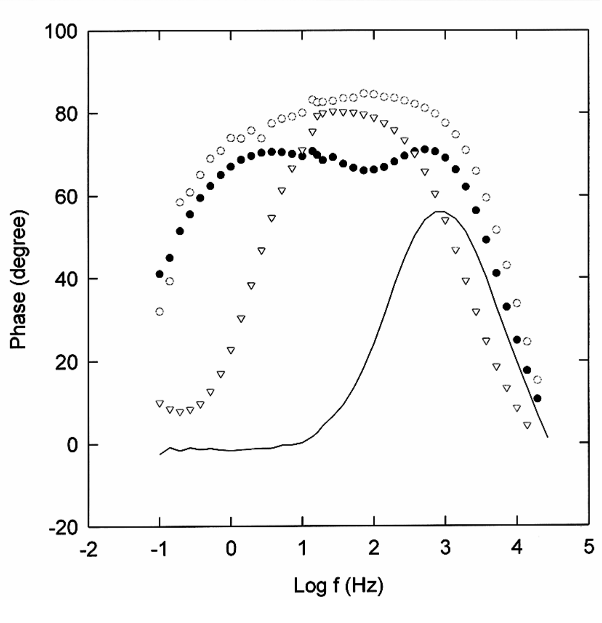

Fig. 3 – Bode plots for Ti in 30% H_3PO_4 solution (75^0C) at three electrode potentials: ? E_{corr}; ∇ E_{cr1}; ? E_{cr2}; ? E_p

Analysis of these spectra was done comparing experimental data with simulated data and selecting a minimal sistematically deviation. It resulted an electric equivalent circuit with three time constants (Fig. 4): a constant for charge transfer reactions represented by a resistance (R_1) and a constant phase element (CPE) in parallel; another constant for passive layer visualised by the double layer capacitance (C_{dl}) and passive film resistance (R_p); the third constant is due to the ionic diffusion through the protective film and is represented as a resistance (R_2) and a Warburg element (W) in parallel.

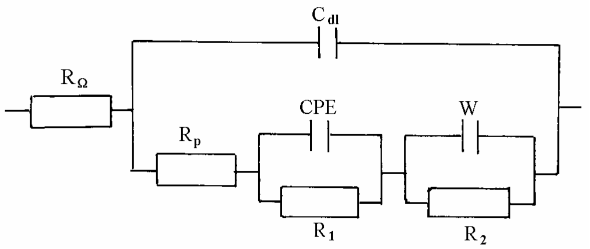

Fig. 4 – Three time constants equivalent circuit

2. Corrosion resistance in metaphosphoric acid

It is known that the metaphosphoric acid has a lower acidity than orthophosphoric acid.

2.1. Diluted metaphosphoric acid

In diluted, 10% metaphosphoric acid (Fig. 5), both titanium and its ternary alloy present self-passivation.

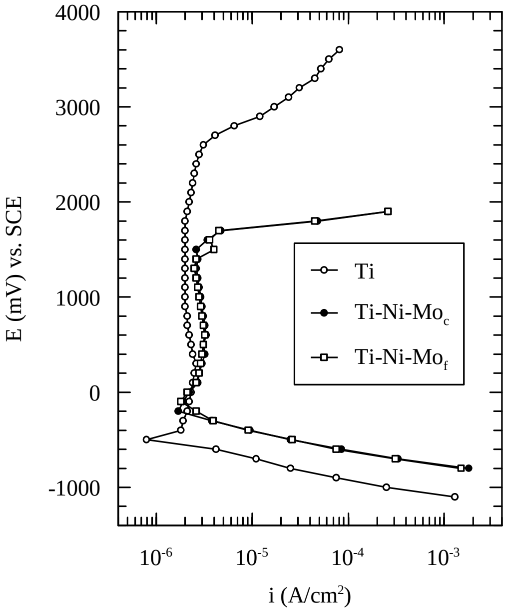

Fig. 5 – Polarization curves for Ti and Ti-0.5Mo-1Ni alloy in 10% $(HPO_3)_n$ solution at 75^{0}C: c – casting sample; f – forging sample

The open circuit potentials (corrosion potentials) of Ti-0.5Mo-1Ni alloy are more electropositive than of titanium due to the same favorable influence of the alloying components. The passive current densities do not differ, having very close values (Table 1).

Table 1

Main electrochemical parameters for Ti and its ternary alloy in casting and forging states

Media	Parameter	Ti		Ti-0.5Mo-1Ni$_c$		Ti-0.5Mo-1Ni$_f$	
		25^{0}C	75^{0}C	25^{0}C	75^{0}C	25^{0}C	75^{0}C
30% H_3PO_4	E_{corr} (mV)	-600	-650	-400	-350	-400	-350
	E_{cr} (mV)	-300 +50	-400 +100	-250 +50	-300 +100	-250 +50	-300 +100
	E_p (mV)	+200	+250	+100	+150	+100	+150
	E_T (mV)	+2400	+2200	+2000	+1900	+2000	+1900
	i_{cr} (μA/cm^2)	98 21	99 20	85 60	95 70	68 58	78 62
	i_p (μA/cm^2)	4.2	4.5	12	14	9.8	10

Table 1 (continues)

Table 1 (continued)

10% $(HPO_3)_n$	E_{corr} (mV)	-500	-550	-150	-200	-100	-150
	E_{cr} (mV)	-	-	-	-	-	-
	E_p (mV)	-350	-400	-100	-150	-100	-150
	E_T (mV)	+2700	+2600	+1700	+1600	+1800	+1700
	i_{cr} ($\mu A/cm^2$)	-	-	-	-	-	-
	i_p ($\mu A/cm^2$)	1.9	2.1	2.2	2.8	2.1	2.5
30% $(HPO_3)_n$	E_{corr} (mV)	-650	-700	-150	-200	-100	-150
	E_{cr} (mV)	-350	-400	+200	+250	+150	+150
	E_p (mV)	-100	-50	+250	+250	+150	+200
	E_T (mV)	+2400	+2200	+1800	+1400	+2000	+1800
	i_{cr} ($\mu A/cm^2$)	210	350	11	19	10	12
	i_p ($\mu A/cm^2$)	5.2	6	6.2	7	5.5	6.8

Bode spectra (Fig. 6) show the existence of two physical processes and were represented by a two time constants equivalent circuit (fig. 7): one constant for double layer capacity (C_{dl}) and passive film resistance (R_p) and another constant for the diffusion processes illustrated by a Warburg element (W) and a resistance (R_1).

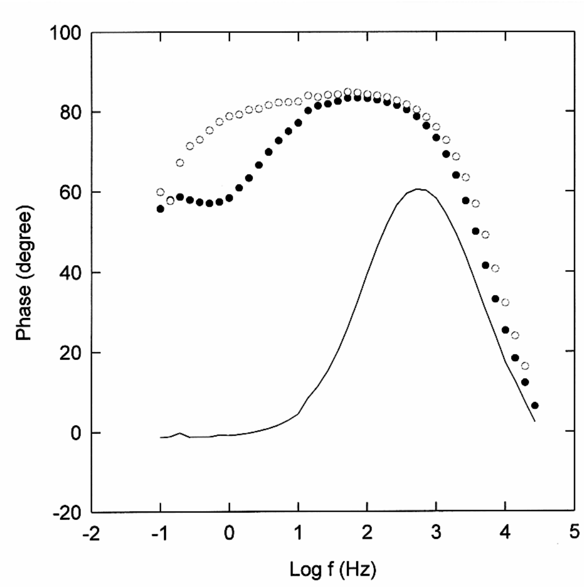

Fig. 6 – Bode plots for Ti-0.5Mo-1Ni$_c$ in 10% $(HPO_3)_n$ solution (75^{0}C) at three electrode potentials: ? E_{corr}; ? E_{cr}; ? E_p

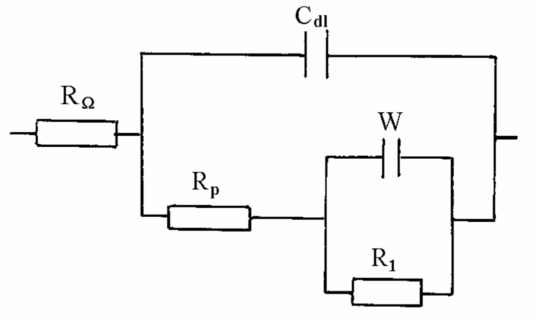

Fig. 7 – Two time constants equivalent circuit

2.2. Concentrated metaphosphoric acid

In concentrated, 30% metaphosphoric acid, the anodic curves for titanium (Fig. 8) present an active dissolution potential range with a high critical passivation current density. For ternary alloy (Fig. 8), the corrosion potential is more electropositive and the critical passivation current density is lower than for pure titanium, because of the positive effect of the alloying elements. In the transpassive region, the unfavorable influence of the alloying additions is shown by the more active transpassive potentials (Table 1).

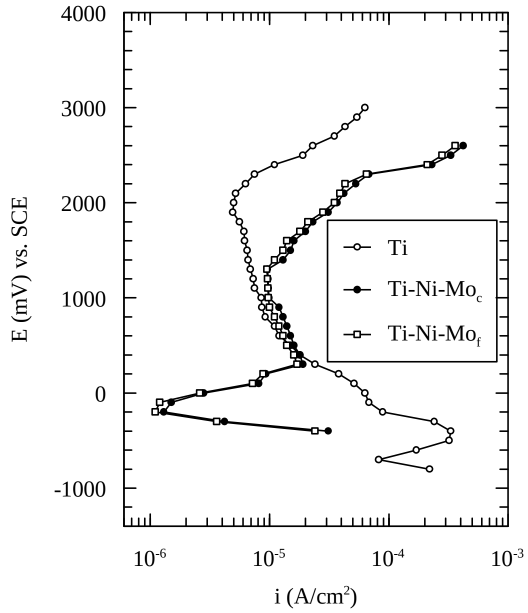

Fig. 8 – Polarization curves for Ti and Ti-0.5Mo-1Ni alloy in 30% $(HPO_3)_n$ solution at 75^0C: c – casting sample; f – forging sample.

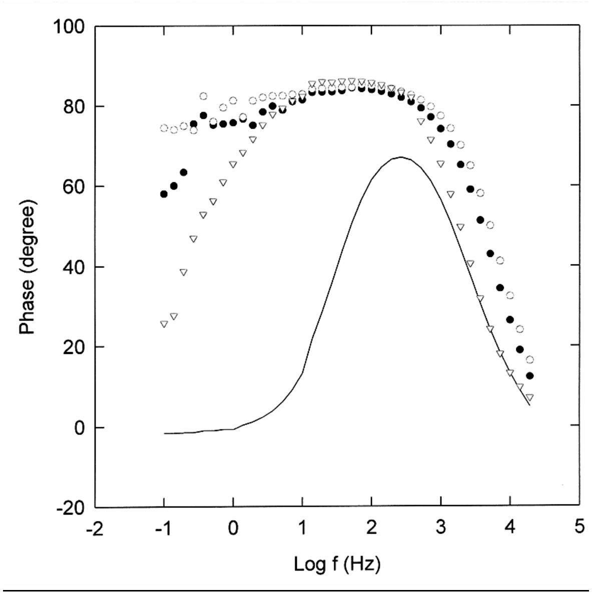

Fig. 9 – Bode plots for Ti-0.5Mo-1Ni$_f$ in 30% $(HPO_3)_n$ solution (75^0C) at three electrode potentials: ? E_{corr}; ∇ E_{cr1}; ? E_{cr2}; ? E_p

From data resulted by impedance measurements, the occurring of three processes may be suggested (Fig. 9): charge transfer, passive layer formation, and diffusion through this film. By simulating with the three-time constants equivalent circuit, the theoretical data were well fitted with experimental data (Fig. 4).

3. Corrosion rates

The corrosion rates determined by linear polarization revealed that the ternary alloy Ti-0.5Mo-1Ni (in casting and forging states) is more resistant than the base metals; the forging alloy has a better stability than the casting alloy (Table 2).

Table 2
Corrosion rates (V) for Ti and its Ti-0.5Mo-1Ni ternary alloy

Corrosion media	Temperature (^{0}C)	V (mm/yr.)		
		Ti	Ti-o.5Mo-1Ni$_c$	Ti-o.5Mo-1Ni$_f$
30% H_3PO_4	25	4.00×10^{-2}	2.70×10^{-2}	1.20×10^{-2}
	50	3.40×10^{-1}	1.90×10^{-1}	1.50×10^{-1}
	75	1.27	1.15	1.05
10% $(HPO_3)_n$	25	2.23×10^{-3}	1.60×10^{-3}	1.20×10^{-3}
	50	9.50×10^{-3}	4.20×10^{-3}	1.30×10^{-3}
	75	1.88×10^{-1}	2.20×10^{-3}	2.10×10^{-3}
30% $(HPO_3)_n$	25	3.30×10^{-3}	2.50×10^{-3}	1.90×10^{-3}
	50	1.49×10^{-1}	4.20×10^{-2}	1.20×10^{-2}
	75	5.30×10^{-1}	5.70×10^{-2}	3.50×10^{-2}

CONCLUSIONS

The modeling of corrosion behaviour of titanium and its ternary Ti-0.5Mo-1Ni alloy led us to pointed out the following conclusions.

In ortophosphoric acid solutions both titanium and its ternary alloy present active-passive transition with two peaks for the critical passivation potential and current density, corresponding with the formation of titanium trioxide or pentoxide at the first critical potential and of the compact protective titanium dioxide at the second critical potential. These critical passivation potentials are more positive for alloy than for pure titanium, due to the beneficial effects of the alloying elements. The passive potential range for alloy has a smaller extent and passive current density is higher than that of titanium, because of the transpassive dissolution of molybdenum and nickel. The Bode spectra show three physical processes on the surface of the titanium and its alloy resulting by an electric equivalent circuit with three time constants.

In diluted metaphosphoric acid, which has low acidity, the titanium and its ternary alloy present self-passivation behaviour. In this medium, the corrosion potentials of alloy are also more electropositive than for pure titanium, because of the positive influence of the alloying components. The Bode spectra show the existence of two physical processes that were modeled by a two time constants equivalent circuit.

In concentrated metaphosphoric acid, the sample of pure titanium presents an active-dissolution potential range with a high critical passivation current density, whereas in the case of Ti-0.5Mo-1Ni ternary alloy, the corrosion potential is more electropositive and critical passivation current density is lower, as a consequence of the alloying. A difference occurs in the data from impedance measurements, where a three time constants equivalent circuit was fitted.

In all tested corrosive media, the corrosion rates revealed that the ternary alloy is more resistant than pure titanium and by comparing the two forms, the forging alloy has a better stability than the casting alloy.

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