Effect of *p*H on the Behaviour of Some Titanium Alloys with Biphasic Structure

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In this paper, the thermal and plastic deformation treatments were applied to Ti6Al4V alloy and its behaviour in Ringer 2 solution of different pH values (2.49; 6.9; 8.91), simulating the hardest conditions that can appear in human body, on the life time of an implant (10-20 years or more) was studied. The behaviour of the untreated Ti6Al4V ELI alloy and its five types of thermal-mechanical treated alloys was estimated from the corrosion rates, ion release, variation in time (500 hours) of the open circuit potentials E_{oc} and of the potential gradients $\Delta E_{oc}(pH)$ due to the pH non-uniformity of Ringer 2 solution. Very low corrosion rates in the "perfect stable" or "very stable" range were determined. Ion release revealed very low values under permitted limits, therefore much reduced citotoxic effects. The open circuit potentials were ennobled at the beginning, then slowly decreased, tending to about constant values, showing the existence of the passive films on the studied material surfaces and of some dissolution, repassivation and absorption processes and their tendency to become stable. Open circuit potential values are more electropositive than those of titanium, so, more stable, more resistant films due to the both passivation effects of the alloying elements and the stability effect induced by the thermo -mechanical treatments. Potential gradients due to the pH nonuniformity of the Ringer solution have low values that can not generate galvanic corrosion (for 500 exposure hours).

Keywords: monitoring of open circuit potentials; Ringer 2 solution of different pH values; passive films

Titanium alloys with $\alpha + \beta$ biphasic structure are used as implants due to of their very good mechanical resistance ductility and better resistance than the α or β mono-phase titanium alloys [1-5]. The most used biphase titanium alloy in implantology is Ti6Al4V alloy that has a very good corrosion resistance in human fluids, due to the passive film that is formed on its surface and acts like a barrier against the dissolution of the alloy [6-8]. It was demonstrated that this passive layer contains titanium dioxide TiO_2 and small quantities of titanium suboxides TiO and Ti_2O_3 in its internal part and in its external parts contains aluminium and vanadium oxides [9-14]; aluminium was detected in higher quantity (26%) in the passive layer and vanadium in less quantity [1%].

Though the passive film formed on the surface of Ti6Al4V alloy is very compact and resistant, however, ions of the component elements were detected in the sorrounding tissues and can have adverse effects [15,16]. Titanium has a low effect producing the discoloration of the adjacent tissues [17-19]. Aluminium is adsobed in the intenstine tract and in blood [20]. Vanadium can altere the kinetics of the ensimatic activity associated with inflamatory processes [21].

The increase of the Ti6Al4V alloy performances can be obtained by thermal and thermo-mechanical treatments which will omogenise the structure and will produce a micro-structure with small, uniform, without inclusion gains etc., that is favourable both for the improvement of the mechanical properties and for the increase of the corrosion resistance in biofluids [22,23].

In this paper, the thermal and plastic deformation treatments were applied for Ti6Al4V ELI alloy and its behaviour in Ringer 2 solution of different *p*H values (2.49; 6.98; 8.91), simulating the extreme conditions which can appear in human body on the service life of an implant (10-20 years or more) was studied.

Experimental part

Titanium and Ti6Al4V ELI alloy were obtained by vacuum melting. Their composition was presented in a previous paper [23].

For Ti6Al4V ELI alloy, different thermal and high temperature plastic deformation treatments were applied and five different types of alloys were obtained: Ti6Al4V-I, Ti6Al4V-II, Ti6Al4V-III, Ti6Al4V-IV, Ti6Al4V-V.

The application way of the thermal treatments and plastic deformation and the preparation of the working electrodes were described in a previous work [23].

The corrosion resistance of the five types of thermo-mechanical treated Ti6Al4V alloys was determined by linear polarisation technique. Using the VoltaLab 80 equipment, Tafel curves were registered for a potential range of ±300 mV arround the corrosion potential and the following electrochemical characteristics [23] were determined: polarisation resistance R_p, corrosion current density i_{corr}, corrosion rate V_{corr} (mm/year) and the total quantity of the ions released in solution (ng/cm²).

Also, the open circuit potentials were monitored for 500 h with a Hullett-Pakard multimeter. The conditions of *p*H non-uniformity were simulated using Ringer 2 solution of different *p*H values (2.49; 6.9;8.01).

The different values of *p*H on the surface of an implant conduct to different values of the open circuit potentials, to potential diferences (potential gradients ΔE_{oc}) that could generate galvanic cells, that could increase the corrosion rate.

The following potential gradients in function of Ringer 2 solution *p*H, $\Delta E_{oc}(pH)$ were calculated and monitored:

$$\Delta E_{oc1}(pH) = E_{oc}^{pH=2.49} - E_{oc}^{pH=6.9} \quad (1)$$

$$\Delta E_{oc2}(pH) = E_{oc}^{pH=2.49} - E_{oc}^{pH=8.91} \quad (2)$$

$$\Delta E_{oc3}(pH) = E_{oc}^{pH=6.9} - E_{oc}^{pH=8.91} \quad (3)$$

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All experimental measurements were carried out in Ringer 2 solution of pH = 2.49 (obtained by HCl addition), pH = 6.9 (normal pH) and pH = 8.91 (by KOH addition). The composition of Ringer 2 solution (g/L) was: NaCl – 6.8; KCl – 0.4; $CaCl_2$ – 0.2; $MgSO_4.7H_2O$ – 0.2048; $NaH_2PO_4.H_2O$ – 0.1438; $NaHCO_3$ – 1.1; glucoză - 1.

The temperature was kept at $37^0 \pm 1^0$C.

Results and discussions

The behaviour of titanium, Ti6Al4V ELI alloy and of the five types of thermo-mechanical treated alloys was appreciated from their corrosion rates, ion release, variation in time (500 h) of the open circuit potentials, E_{oc} and of the potential gradients ΔE_{oc}(pH) due to the pH non-uniformity of Ringer 2 solution.

The behaviour of Ti6Al4V alloys in Ringer 2 solution of pH = 2.49

Corrosion rates (table 1) are very low positioning the Ti6Al4V alloys in the resistance class „very stable" and „stable" for II and III types. If the alloys of II and III types would function for 20 years in the extreme conditions of pH = 2.49, would corrode with about 0.3 mm respectively 0.2 mm per total; so, the implants from these alloys would resist very well. But these parameters of acidity cannot possibly persist for such a long period; it resulted that these metal losses can not be teached in the service life of 20 years of an implant.

The studied biomaterials can be arranged according to their corrosion resistance in the following sequence:

Ti6Al4V ELI > Ti6Al4V – V > Ti6Al4V – I > Ti > Ti6Al4V – IV > Ti6Al4V –III > Ti6Al4V –II

The total quantity of ions released in Ringer 2 solution of pH = 2.49 (table 1) is very low. It can be concluded that the cytotoxic effects are negligible.

Titanium and its ternary Ti6Al4V untreated and thermo-mechanically treated alloys exposed in Ringer 2 solution of pH = 2.49 presented values of *the open circuit potentials* (fig. 1) that, at the begining ennobled and then, slowly decreasing, tending to about constant values, showing the existance of the passive films on these alloy surfaces and dissolution, repassivation and absorption processes on these films and the tendency of the films to stabilise [24-26]. The untreated and thermo-mechanically treated Ti6Al4V alloys revealed more electropositive values of the open circuit potentials than the titanium, namely more stable, more resistant films, due to the passive effects of the alloying elements and due to the stability effects induced by the thermo-mechanical treatments.

The local corrosion was not detected and the monitoring of the biomaterial behaviour will continue for long term.

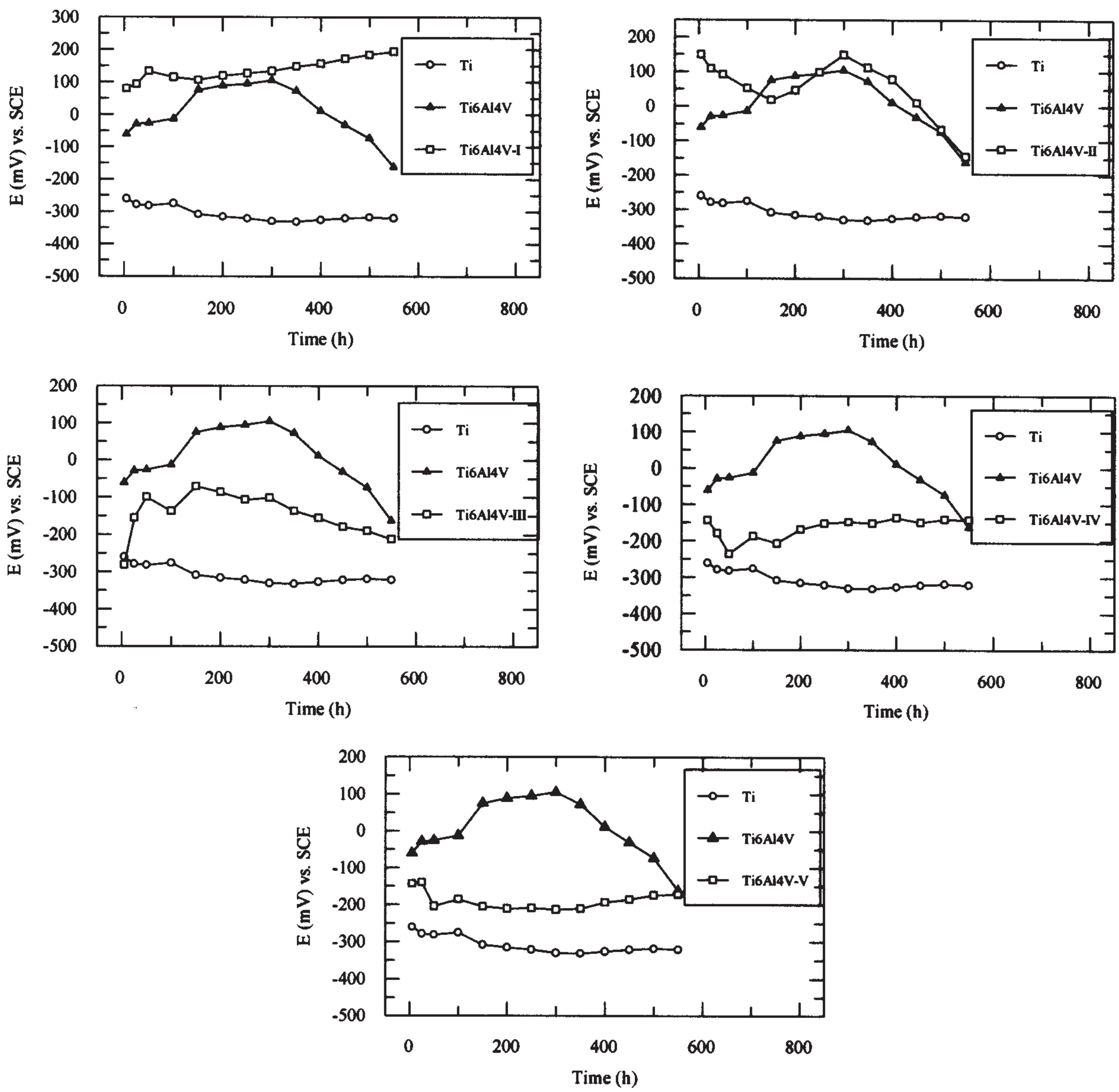
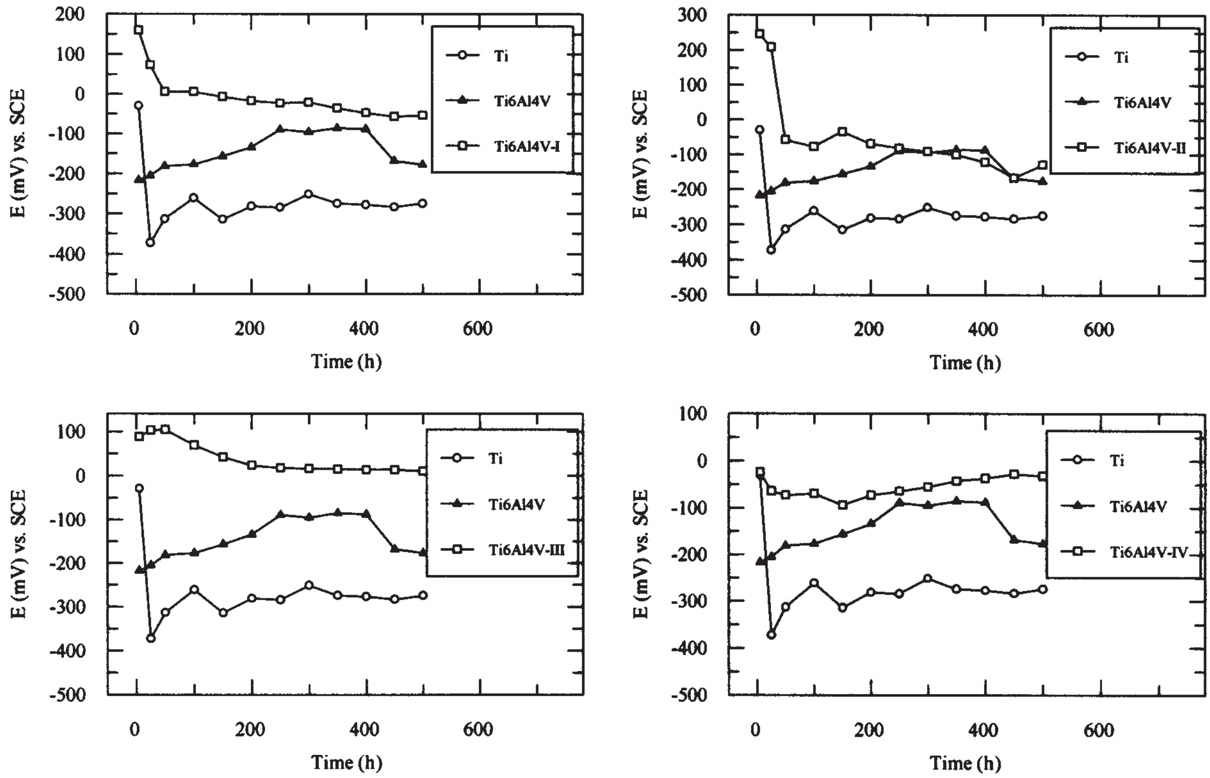


Fig. 1. Variation in time of open circuit potentials in Ringer 2 solution of pH = 2.49, at 37^{0}C

Table 1
CORROSION RATES AND CYTOTOXIC EFFECTS OF TI6AL4V ALLOYS IN RINGER 2 SOLUTION OF *p*H = 2.49, AT 37°C

Material	R_p (kΩ.cm²)	i_{corr} (μA/cm²)	V_{corr} (mm/an)	Resistance class	Ion release (ng/cm²)	Cyto-toxicity
Ti	11.35	0.75	8.63×10^{-3}	Very Stable	876.81	< limit
Ti6Al4V ELI	59.74	0.09	1.07×10^{-3}	Very Stable	108.71	< limit
Ti6Al4V - I	47.92	0.37	4.20×10^{-3}	Very Stable	426.72	< limit
Ti6Al4V – II	8.05	1.33	1.54×10^{-2}	Stable	1564.64	< limit
Ti6Al4V –III	8.10	1.02	1.18×10^{-2}	Stable	1198.88	< limit
Ti6Al4V –IV	12.63	0.77	8.91×10^{-3}	Very Stable	905.26	< limit
Ti6Al4V – V	22.45	0.25	2.89×10^{-3}	Very Stable	293.62	< limit



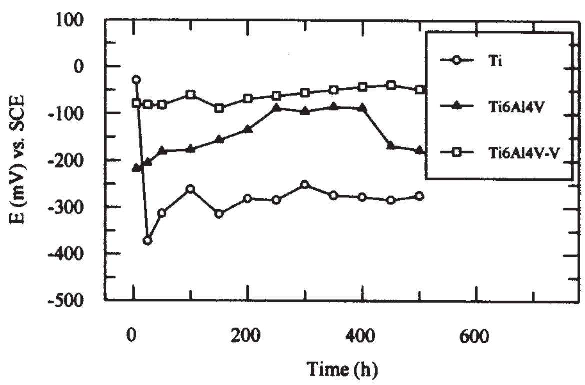


Fig. 2. Variation in time of open circuit potentials in Ringer 2 solution of *p*H = 6,9, at 37°C

The behaviour of Ti6Al4V alloys in Ringer 2 solution of pH = 6.9

The most electropositive values *the open circuit potentials* in Ringer 2 solution of neutral *p*H appeared for thermo-mechanically treated alloys (fig. 2) showing the beneficial effect of the application of these treatments. It can be apreciated and in this case that the passive films are more stable and evidently more resistant.

No change of the surface that is covered by a yelow film, without defects were observed; also, no local corrosion appeared.

The monitoring of the open circuit potenntial values will continue for long time periods (1-3 years) taking into account the fact that the bioalloys will be used as implant for 10-20 years.

The behaviour of Ti6Al4V alloys in Ringer 2 solution of pH = 8.91

Very low *corrosion rates* (table 2) were determined, all alloys being „perfect stable" and „very stable", excepting titanium that is „stable"; the order regarding the corrosion resistance in Ringer 2 solution of *p*H = 8.91 is the following:

Ti6Al4V ELI > Ti6Al4V-III > Ti6Al4V -IV > Ti6Al4V -V > Ti6Al4V -II > Ti

Also, *"ion release"* relevealed very low values, so, very reduced cytotoxic effects.

Material	R_p (kΩ.cm^2)	i_{corr} (μA/cm^2)	V_{corr} (mm/an)	Resistance class	Ion release (ng/cm^2)	Cyto-toxicity
Ti	13.91	1.19	13.76x10^{-3}	Stable	1.398.02	< limit
Ti6Al4V ELI	1.42	0.02	0.14 x10^{-3}	Perfect Stable	13.98	< limit
Ti6Al4V – II	10.95	0.56	6.47 x10^{-3}	Very Stable	657.35	< limit
Ti6Al4V –III	1200	0.04	0.40 x10^{-3}	Perfect Stable	38.40	< limit
Ti6Al4V –IV	227.8	0.07	0.79 x10^{-3}	Perfect Stable	12.64	< limit
Ti6Al4V – V	345.8	0.12	1.40 x10^{-3}	Very Stable	22.40	< limit

Table 2
CORROSION RATES AND CYTOTOXIC EFFECTS OF TI6AL4V ALLOYS IN RINGER 2 SOLUTION OF *p*H = 8.91, AT 37^{0}C

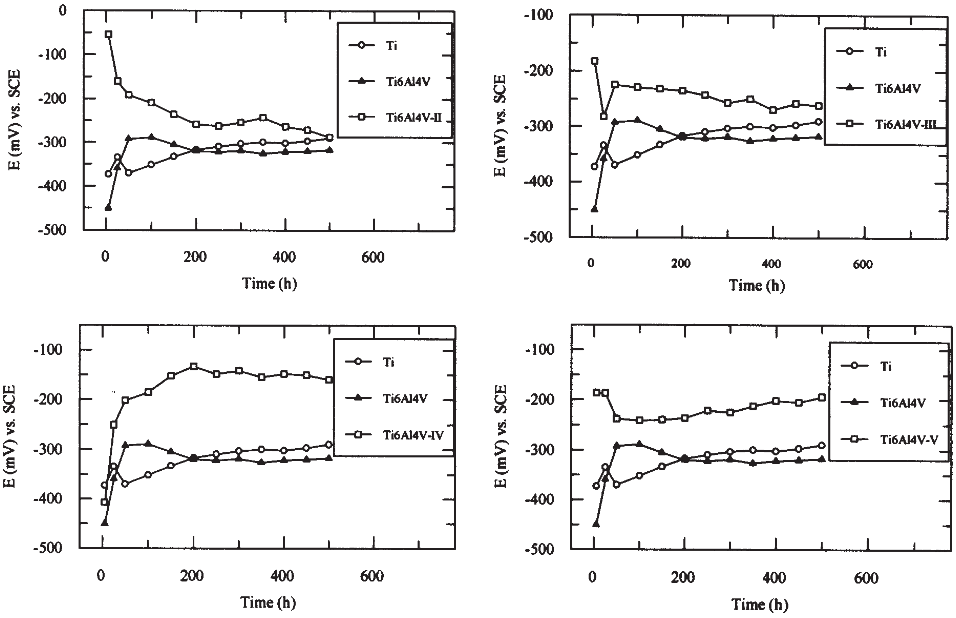


Fig. 3. Variation in time of open circuit potentials in Ringer 2 solution of *p*H = 8.91, at 37^{0}C

Table 3
POTENTIAL GRADIENTS ΔE_{oc}(pH) FOR TI6A14V ALLOYS IN RINGER 2, SOLUTION AT 37^{0}C

Biomaterial	Time (h)	ΔE_{oc1} (V)	ΔE_{oc2} (V)	ΔE_{oc3} (V)
Ti	100	-0.014	+0.076	+0.091
	200	-0.027	+0.001	+0.035
	500	-0.044	-0.028	+0.016
Ti6Al4V	100	+0.164	+0.276	+0.465
	200	+0.222	+0.408	+0.453
	500	+0.250	+0.244	+0.494
Ti6Al4V - I	100	+0.190	-	-
	200	+0.136	-	-
	500	+0.238	-	-
Ti6Al4V – II	100	+0.130	+0.262	+0.132
	200	+0.115	+0.305	+0.190
	500	+0.063	+0.337	+0.159
Ti6Al4V – III	100	-0.206	+0.092	+0.298
	200	-0.109	+0.149	+0.258
	500	-0.199	+0.072	+0.271
Ti6Al4V – IV	100	-0.118	-0.002	+0.113
	200	-0.096	-0.035	+0.061
	500	-0.108	+0.020	+0.128
Ti6Al4V - V	100	-0.125	+0.036	+0.181
	200	-0.148	+0.016	+0.168
	500	-0.124	+0.020	+0.156

The values of E_{oc} potentials (in alkaline Ringer 2 solution) for thermo-mechanically treated Ti6Al4V alloys (fig. 3) are more electropositive than the untreated alloy and the alloying base. This behaviour shows that the passive films formed on the surface of the thermo-mechanically, treated alloys are for comparison more stable, more safe and more resistant than those formed on the surface of the alloys. Moreover, their tendency to reach stable, constant values is observed, so, the stabilisation and stability of the film is improved in time, a good behaviour in future can be foreseen . No local corrosion was observed. The monitoring of the open circuit potential values will continue for medium and long term.

The effect of pH values on the potential gradients

The untreated and thermo-mechanically treated Ti6Al4V alloys preseted (Table 3) the values of the potential gradients ΔE_{oc} (*p*H), due to the non-uniformities of the Ringer 2 solution *p*H that vary from 0.001 V to 0.494 V (in absolute value), low values [27,28] that can not generate galvanic corrosion (for 500 experimental hours). The highest values resulted for the un-treated alloy and the alloys of II and III types. However, these potential gradients change with the exposure time and for long term (10-20 years in the case of implants) is very hard to prognose the behaviour of these bioalloys. So, it is necessary to continue the monitoring of the open circuit potential values in time and in function of *p*H and of the potential gradients.

Conclusions

The values of the open circuit potentials for thermo-mechanical treated Ti6Al4V alloys are constantly more electropozitive than of the untreated alloy and of the alloying base, titanium. This behaviour shows that the passive films formed on the surface of the thermo-mechanical treated bioalloys are more stable, more safe and more resistant than those formed on the surface of the comparison biomaterials. Their tendency to reach stable constant values is observed, so, the stabilisation and stability of the films is improved in time and a good behaviour can be prognosed in the following period. No local corrosion appeared

Corrosion rates are very low in the „very stable" and „stable" domain.

The total quantity of ions released in Ringer 2 solution is low. It can be concluded that the cytotoxic effects are negligible.

The untreated and thermo-mechanically treated alloys presented low values of the potential gradients due to the non-uniformities of Ringer solution *p*H, that can not generate the local corrosion (for 500 experimental h).

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