



Electrochemical characterization of Ti12Mo5Ta alloys in contact with saline medium

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Abstract: The electrochemical behaviours of unrecrystallized and recrystallized Ti12Mo5Ta alloys were compared with those of the unrecrystallized Ti12Mo alloy and commercial pure titanium (cp-Ti). Experiments were carried out using physiological 0.9% NaCl solution (pH 2.3) at 37 °C. Very low passive current densities (in order of 10^{-6} A/cm²) were obtained from the anodic polarization curves, indicating high resistances of all samples in acidified 0.9% NaCl solution. Scanning electron microscopy (SEM) was employed to observe the surface morphology and all sample surfaces were identically corroded, no pitting, cracks, or other defects appeared on the sample surfaces after anodic potentiodynamic polarization tests. Equivalent circuit was used for modeling the electrochemical impedance spectroscopy (EIS) data, in order to characterize the sample surface and better understand the effect of Mo and Ta addition on the cp-Ti and the effect of recrystallization. The EIS results confirm that all titanium samples exhibit passivity in physiological 0.9% NaCl solution (pH 2.3) at open circuit potential (polarization resistance is around 10^5 Ω·cm²). The corrosion resistance of these samples in physiological 0.9% NaCl solution (pH 2.3) at 37 °C is in the following order of recrystallized Ti12Mo5Ta > unrecrystallized Ti12Mo5Ta > unrecrystallized Ti12Mo > cp-Ti.

Key words: titanium alloys; recrystallization; anodic potentiodynamic curve; Ta; Mo; electrochemical behavior

1 Introduction

Titanium and titanium alloys are employed widely in biomedical applications. The Ti6Al4V alloy is used in biomedical applications because it is mechanically stronger and resists corrosion better than CoCr alloys and stainless steel [1]. However, it concerns about potential toxicity effect of V and Al [2–4]. As a result, the characterization of new Ti alloys using Ta, Zr, Mo and Sn as alloying elements has been developed [5–18]. The most promising materials for biomedical applications are the β-Ti alloys. Unfortunately, such Ti alloy systems are inadequate to cast due to their high melting points. Computer-aided design and computer-aided manufacturing (CAD/CAM) technology coupled with CNC milling unit can be an alternative to manufacture

these Ti alloys.

The stability of the β-phase in the case of titanium alloys is expressed as the sum of the weighed average of the alloying elements known as the Mo equivalent [19,20].

A value of Mo equivalent in the range of 8%–24% relates to β-metastable titanium alloys because the content of β-stabilizer is high enough to prevent any martensitic transformation in the β phase from quenching to room temperature [19,20].

Mo is considered to be instrumental in regulating the pH balance in the body, and acts as a cofactor for a certain number of enzymes in humans [21,22]. It is considered that the addition of Mo to pure Ti improves the protection characteristics of the oxide films spontaneously formed on the materials oxides [23–26].

Therefore, it was thought that Ta content might

lead to the production of TiTa alloys with even better corrosion resistance for implant application [27,28]. Ta is considered one of the best biocompatible element in human body [29,30] but has a relatively high cost.

Using the equation of Mo equivalent indicated in literature, the Mo_{eq} values of the investigated alloys are 12 for Ti12Mo and 13 for Ti12Mo5Ta, respectively.

In terms of biomaterials applications, the most inconvenient aspect is the degradation, which occurs due to the material interaction with body or physiological fluids with 1% NaCl [31,32].

In this work, the electrochemical behaviours of Ti12Mo and Ti12Mo5Ta alloys in contact with 0.9% NaCl solution (pH 2.3) were studied. The pH was chosen because the tissue adjacent to an implant under distress was considered to become acidic [33]. The pH was obtained by the addition of hydrochloric acid.

2 Experimental

2.1 Materials

The origin and nominal chemical compositions of Ti alloys studied are shown in Table 1. The Ti12Mo and Ti12Mo5Ta (mass fraction, %) alloys were synthesized under a pure Ar atmosphere by cold crucible levitation melting (CCLM) technique in a CELES induction furnace. After solidification, the alloys were annealed under $(10^{-6}-10^{-7}) \times 10^2$ Pa vacuum at 950 °C for 20 h to remove the chemical segregation due to the thermal gradient occurring during solidification and then quenched into water to retain the β microstructure. The annealed ingots were cold rolled (reduction rate of about 80%) with a laboratory scale laminator (Caltex Ursa Heavy), heat treated at 870 °C for 0.5 h under $(10^{-6}-10^{-7}) \times 10^2$ Pa vacuum and then quenched into water at room temperature to obtain a homogenous recrystallized microstructure (only for Ti12Mo5Ta alloy).

Table 1 Origin and chemical composition of samples

Sample	Composition/%	Supplier
cp-Ti	Ti: 99.9	INMR Bucharest, Romania *
Ti12Mo	Ti: 88; Mo: 12	INSA Rennes, France **
Ti12Mo5Ta	Ti: 83; Mo: 12; Ta: 5	INSA Rennes, France

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2.2 Structural characterization

The microstructure of the Ti materials was observed with a LEICA optical microscope. Before observation, the samples were mirror-polished and etched by standard metallographic techniques.

The metallographic samples were prepared

following the procedure subsequently: first polished with emery papers (180–2000 grit), then few polished with alumina suspensions intercalated with intermediate etching (68 mL glycerine, 16 mL HNO_3 , 16 mL HF), and finally mirror-polished with 0.020 μm alumina suspension followed by chemical etching (Kroll's reagent).

2.3 Electrochemical testing

Electrochemical behaviour of the Ti samples was evaluated at (37 ± 1) °C using acidified physiological 0.9% NaCl solution with an approximate pH 2.3. Because the pH variance can be associated with infection, hydrochloric acid was added into 0.9% NaCl solution to decrease the pH to accentuate corrosion.

Electrochemical measurements were performed with a potentiostat manufactured by PAR (Model PARSTAT 4000, Princeton Applied Research, NJ, USA). The instrument was controlled by a personal computer and specific software (VersaStudio, PAR, USA). The electrochemical impedance was measured before the potentiodynamic polarization test. A glass corrosion flow cell kit (C145/170, Radiometer, France) with a platinum counter-electrode and a saturated calomel reference electrode (SCE) were used to perform the electrochemical measurements [34]. All potentials referred to in this work were with respect to SCE.

The variations of the corrosion behavior for the passive film formed on the surface of the Ti samples were studied by the electrochemical impedance spectroscopy (EIS) technique. EIS measurements were performed after the Ti samples were immersed in acidified physiological 0.9% NaCl solution at (37 ± 1) °C for different time (1 d, 2 d, and 7 d). The alternating current (AC) impedance spectra for all Ti alloys were obtained with a scan frequency ranging from 100 kHz to 10 mHz with an amplitude of 10 mV.

The EIS experimental data were analyzed in terms of equivalent circuits (EC) with ZSimpWin 3.22 software. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data.

The measurement of anodic potentiodynamic polarization curves was initiated after 7 d exposure to the test solution at 37 °C. These measurements were conducted by stepping the potential at a scanning rate of 0.5 mV/s from open circuit potential to 1 V.

2.4 SEM analysis of corroded surface

In order to investigate the occurrence of the surface effects of the corrosion, some corroded surfaces were observed by SEM. To perform this, a scanning electron microscope (Tescan VEGA II LMH) was used.

2.5 XPS analysis

The microstructure of the surface films formed on the Ti12Mo and Ti12Mo5Ta alloys after the anodic potentiodynamic polarization testing in PS was analyzed by X-ray photoelectron spectrometry (XPS) with a PHI 5000 Versa Probe (Φ ULVAC-PHI, Inc., Japan/USA) instrument with monochromatized Al K_{α} radiation (1486.6 eV) as an X-ray anode at 24.4 W.

3 Results and discussion

The microstructures of the unrecrystallized two titanium alloys are almost similar (Figs. 1(a) and (b)), for Ti12Mo alloy the effect of cold rolling is more evident. By heat treatment, Ti12Mo5Ta alloy attained a recrystallized structure with polygonal β -phase grains (Fig. 1(c)) which have an average size of $(60 \pm 15) \mu\text{m}$. For comparison, Fig. 1(d) shows the microstructure of as-received cp-Ti (α equiaxed grain structure). Figure 2 shows the XRD patterns of titanium alloys. When metastable β titanium is cold plastically deformed, a α'' strain-induced transformation is possible to occur, that was shown for Ti–Mo-based alloys, too [19,20,35]. Thus, the characteristic peaks of α'' martensite are observed on XRD patterns of the unrecrystallized Ti12Mo and Ti12Mo5Ta alloys, with observation that this kind of phase transformation is more evident for Ti12Mo alloy. Also, it is worth noting that the width of peaks is larger for the cold-rolled samples. The XRD pattern of the

recrystallized Ti12Mo5Ta alloy indicates only the body-centered-cubic (BCC) β -phase that is correlated with optical micrograph of this sample.

The impedance spectroscopy results for cp-Ti, unrecrystallized Ti12Mo alloy and unrecrystallized and recrystallized Ti12Mo5Ta alloys recorded at open circuit potential at 37 °C in acidified 0.9% NaCl solution after 1 d, 2 d or 7 d immersion are shown in the Bode diagrams in Figs. 3(a)–(d).

The presence of the maxima in the Bode-phase plot is in agreement with an equivalent circuit with one time constant. The experimental data are shown as individual points, while the theoretical spectra resulting from the fits with a suitable equivalent circuit (EC) model are shown as lines. The EC (see Fig. 4) is characterized by one parallel combination terms ($R_{\text{pL}}Q_{\text{pL}}$) in series with the resistance of the solution (R_{sol}).

The parameter R_{pL} coupled with Q_{pL} describes the processes at the electrolyte–passive layer interface. This simple EC has been generally used successfully to describe the behavior of Ti alloys in different solutions [16,25,27,36]. The chi-square value (χ^2) between 5×10^{-4} and 10^{-5} points to excellent agreement between the experimental and simulated data. The values of the parameters (R_{pL} , Q_{pL}) obtained with the fitting procedure are listed in Table 2. The same values for R_{el} , $(70 \pm 5) \Omega \cdot \text{cm}^2$, are observed and not inserted in Table 2.

High values of R_{pL} (in order of $10^6 \Omega \cdot \text{cm}^2$) are observed for all the samples, confirming the formation of

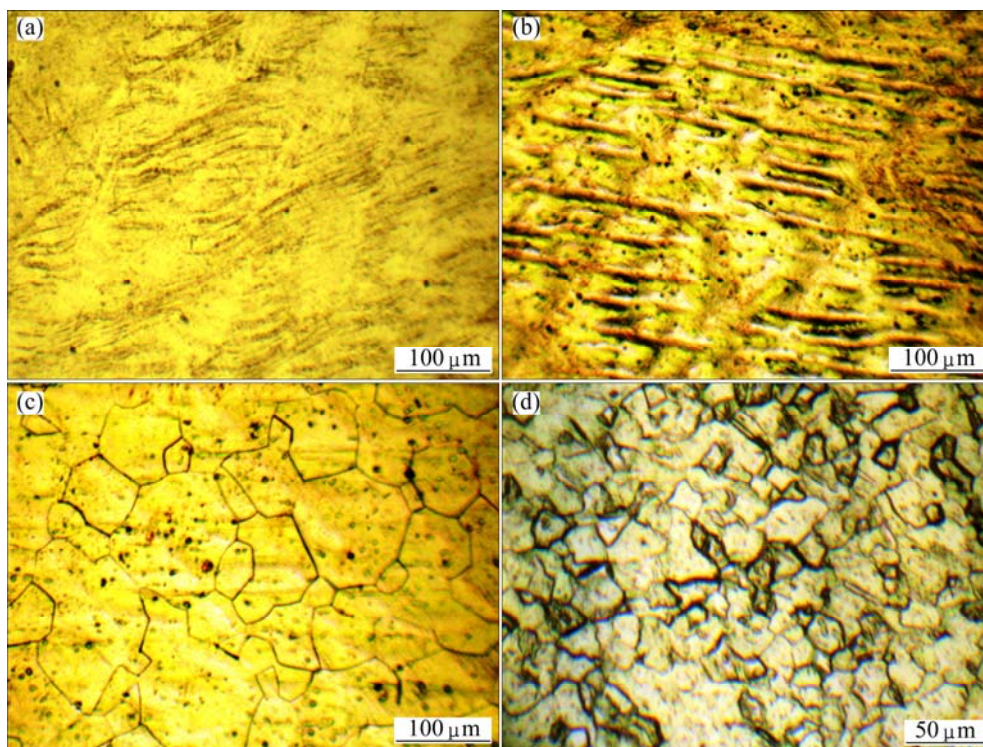


Fig. 1 Microstructures of Ti samples: (a) Unrecrystallized (cold rolled) Ti12Mo alloy; (b) Unrecrystallized Ti12Mo5Ta alloy; (c) Recrystallized Ti12Mo5Ta alloy (above β transus temperature); (d) cp-Ti

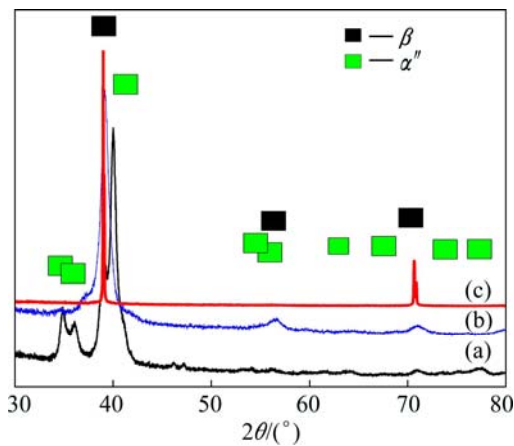


Fig. 2 XRD patterns of unrecrystallized and recrystallized TiMo and TiMoTa alloys: (a) Unrecrystallized Ti12Mo; (b) Unrecrystallized Ti12Mo5Ta; (c) Recrystallized Ti12Mo5Ta

a passive layer with high corrosion protection ability in acidified 0.9% NaCl solution. The resistance, R_{pL} , of the passive layer increases with the immersion time. These results seem to correspond to thickening of the passive film of Ti samples. The R_{pL} values observed for cp-Ti in acidified 0.9% NaCl solution are generally lower than

those found for Ti alloys in the same electrolyte. Since the corresponding values of n_1 are nearly 1, Q_{pL} can be said to behave similarly to an ideal capacitor.

Table 2 Fitting parameters obtained by fitting $R_{sol}(Q_{pL}R_{pL})$ model to experimental EIS data for Ti samples immersed in acidified 0.9% NaCl solution

Sample	Immersion time/d	$Q_{pL}/(\mu S \cdot cm^{-2} \cdot s^n)$	n_{pL}	$R_{pL}/(k\Omega \cdot cm^2)$
cp-Ti	1	8.9	0.85	810
	2	8.9	0.86	930
	7	8.7	0.89	1250
Unrecrystallized Ti12Mo alloy	1	8.7	0.86	1120
	2	8.6	0.87	1230
	7	8.3	0.90	2410
Unrecrystallized Ti12Mo5Ta alloy	1	8.6	0.85	1330
	2	8.5	0.86	1650
	7	8.1	0.92	2820
Recrystallized Ti12Mo5Ta alloy	1	8.5	0.85	1720
	2	8.4	0.88	2320
	7	7.9	0.92	3170

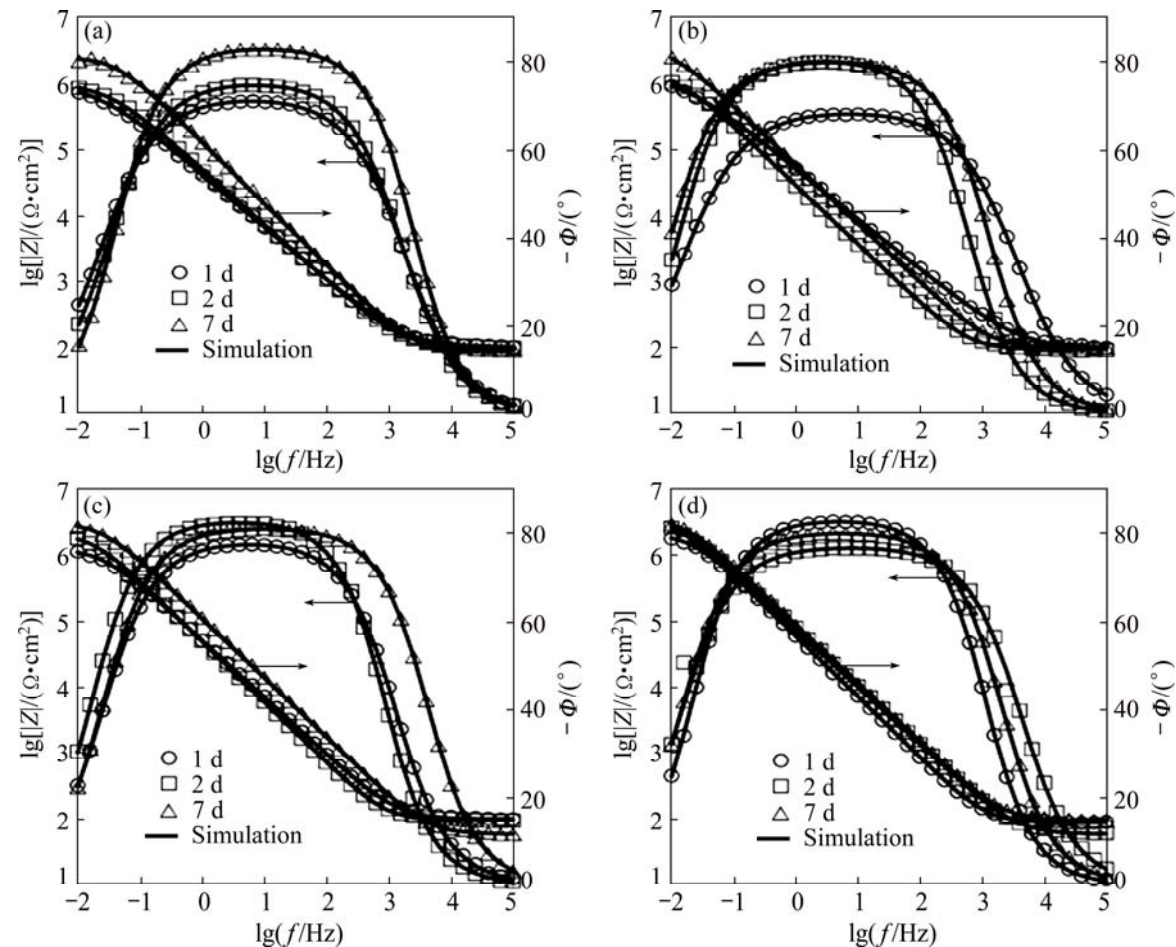


Fig. 3 Bode spectra recorded on cp-Ti (a), unrecrystallized Ti12Mo alloy (b), unrecrystallized Ti12Mo5Ta alloy (c), recrystallized Ti12Mo5Ta alloy (d) for different immersion time in acidified 0.9% NaCl solution

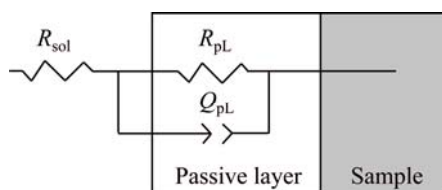


Fig. 4 Equivalent circuit (EC) used for fitting impedance data for Ti samples immersed in acidified 0.9% NaCl solution

In terms of EIS analysis, the corrosion resistance of Ti samples immersed in acidified 0.9% NaCl solution is improved with the addition of β -stabilizing elements. Probably, the addition of the β -stabilizing elements has a positive contribution in the formation of the passive oxide film. Mo has strong β -stabilizing properties on Ti alloys and small content should be sufficient to gain and stabilize a β -phase Ti alloy. The addition of Ta stabilizes probably much more β -phases and this exhibits a nobler characteristic [27,37], and improves the passivity due to the presence of Ta oxides within surface oxide layer.

The higher R_{pL} value of Ti12Mo5Ta alloy with recrystallized structure, for different immersion time in acidified 0.9% NaCl solution, indicates that this alloy possesses superior corrosion resistance compared with the unrecrystallized structure. The unrecrystallized structure possesses higher internal energy and higher density of dislocations accumulated by plastic deformation, which can result in the acceleration of corrosion [38,39]. So, the recrystallized structure improves the corrosion resistance in comparison with the unrecrystallized structure. Probably, Ti alloys with the recrystallized structure formed more compacted passive layers.

Figure 5 shows the experimental anodic potentiodynamic polarization results in acidified physiological 0.9% NaCl solution for the Ti samples. This procedure was performed in order to analyze the continuity and stability of the passive oxide film formation after anodic polarization tests.

All samples with different structures translated directly into a stable passive behavior from the “Tafel region” without exhibiting a traditional active-passive transition. It can be seen that the anodic polarization curves of Ti12Mo and Ti12Mo5Ta alloys shift to the positive (noble) direction, probably due to the positive contribution of Mo and Ta alloying elements in the formation of oxide film. Passive current densities (J_{pass}) were determined from anodic polarization curves at different potentials (0, 0.5 and 1 V). The average current densities from all different polarization curves are listed in Table 3. Very low passive current densities (in order of 10^{-6} A/cm²) were obtained from the anodic polarization curves, indicating a high resistance of all samples in acidified 0.9% NaCl solution. The lower passive current

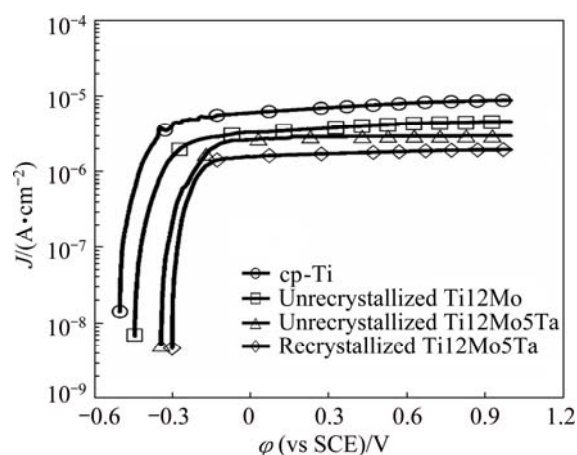


Fig. 5 Anodic potentiodynamic polarization curves for cp-Ti, Ti12Mo and Ti12Mo5Ta samples after immersion for 7 d in acidified 0.9% NaCl solution

Table 3 Passive current densities measured for cp-Ti, Ti12Mo and Ti12Mo5Ta alloys in acidified 0.9% NaCl solution

Sample	$J_{pass}/(\mu A \cdot cm^{-2})$		
	0 V	0.5 V	1 V
cp-Ti	5.4	7.4	8.3
Unrecrystallized Ti12Mo alloy	3.4	4.1	4.4
Unrecrystallized Ti12Mo5Ta alloy	2.2	2.9	2.9
Recrystallized Ti12Mo5Ta alloy	1.4	1.8	2.1

densities of Ti12Mo alloy at all potentials indicate that this alloy possesses better corrosion resistance than the cp-Ti, and the addition of Ta improves the resistance. The lower passive current densities for recrystallized Ti12Mo5Ta alloy should be attributed to the characteristics of β -recrystallized phase.

Figures 6(a)–(d) show the surface SEM images of cp-Ti, Ti12Mo and Ti12Mo5Ta alloys after anodic potentiodynamic tests in acidified 0.9% NaCl solution. During the electrochemical test in both electrolytes, the surfaces of all Ti samples have undergone a uniform oxidation process. However, all sample surfaces were identically corroded, no pitting, cracks, or other defects appeared on the sample surfaces after anodic potentiodynamic polarization tests.

Figures 7(a)–(c) show the XPS spectra of the surfaces of cp-Ti, unrecrystallized Ti12Mo and unrecrystallized Ti12Mo5Ta alloys after anodic potentiodynamic polarization in acidified 0.9% NaCl solution.

It is evident that within binding energy range between 455 and 465 eV, all spectra contain the oxygenated species of Ti [40]. For cp-Ti sample there are signals corresponding to TiO₂ (464.7 eV for Ti 2p_{1/2} and 458.8 eV for Ti 2p_{3/2}). For Ti12Mo5Ta sample there are following signals: 455 eV for Ti 2p_{3/2} corresponding

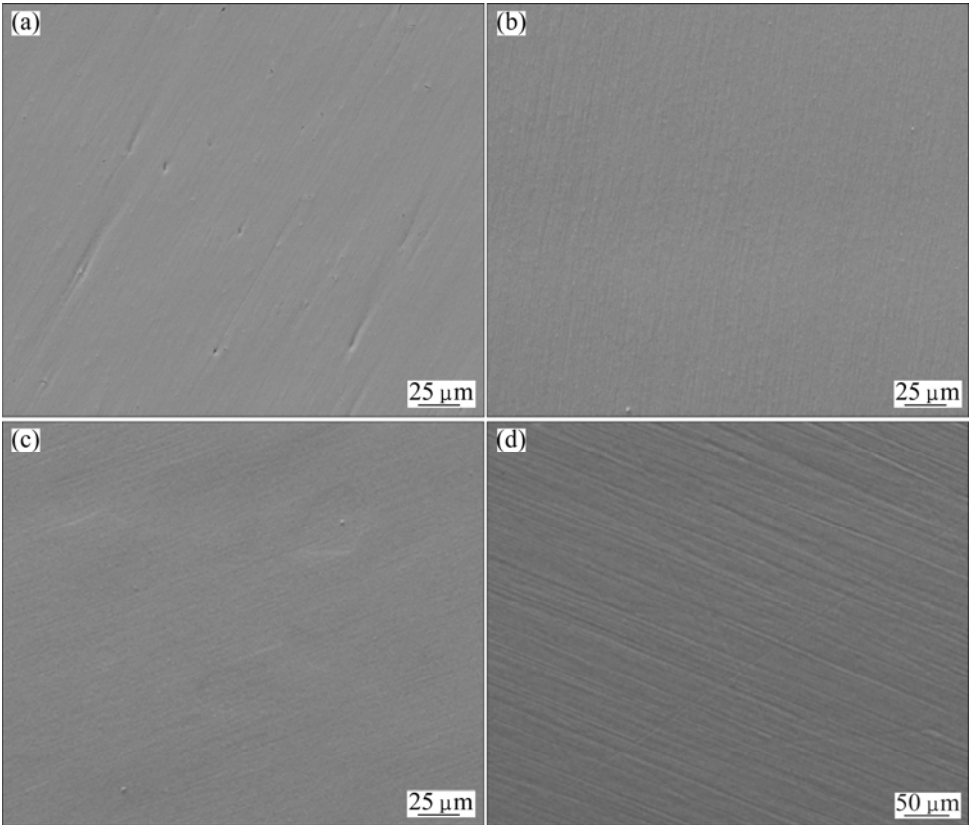


Fig. 6 SEM images showing surface of Ti samples after anodic potentiodynamic polarization in acidified 0.9% NaCl solution: (a) cp-Ti; (b) Unrecrystallized Ti12Mo alloy; (c) Recrystallized Ti12Mo5Ta alloy; (d) Unrecrystallized Ti12Mo5Ta alloy

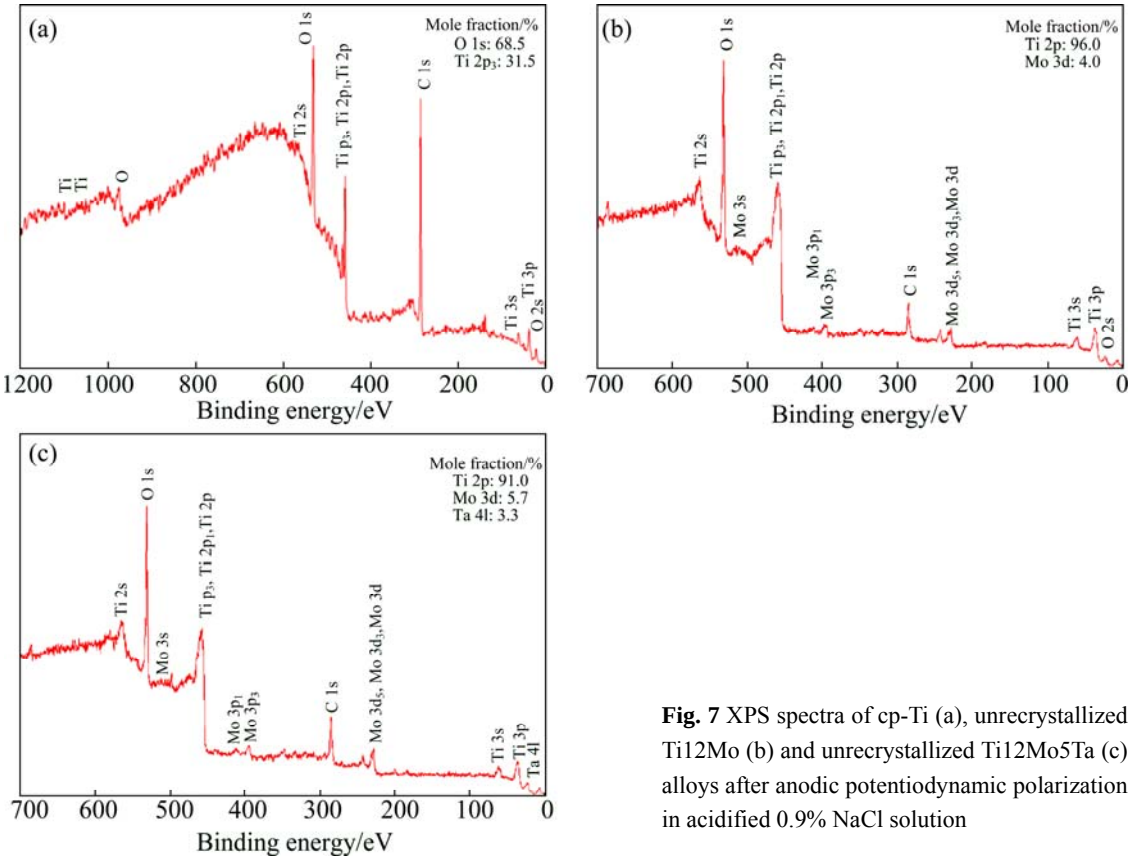


Fig. 7 XPS spectra of cp-Ti (a), unrecrystallized Ti12Mo (b) and unrecrystallized Ti12Mo5Ta (c) alloys after anodic potentiodynamic polarization in acidified 0.9% NaCl solution

to $\text{TiO}_{1.5}$ [41], 456.2 eV for Ti 2p_{3/2} corresponding Ti_2O_3 [42], 464.4 eV for Ti 2p_{1/2} and 458.3 eV for Ti 2p_{3/2} assigned to TiO_2 [43]. For Ti12Mo sample the signals that appear are attributed to $\text{TiO}_{1.5}$ (455.6 eV for Ti 2p_{3/2}) and TiO_2 (464.2 eV for Ti 2p_{1/2} and 457.8 eV for Ti 2p_{3/2}) respectively. Also, for Ti12Mo5Ta sample signals appear, which can be assigned to MoO_2 (231.4 eV for Mo 3d_{5/2}) [44] and Ta_2O_5 (26.6 eV for Ta 4f_{7/2}) [45,46]. In the case of Ti12Mo alloy signal appears corresponding to MoO_2 (231 eV for Mo 3d_{5/2}). It can be observed that when Ta is absent in last alloy, Mo remains at the same proportion. Ti is likely to form oxide in comparison with Mo. Using XPS analysis, MARDARE et al [47] found that the passive film is composed of TiO_2 and Ta_2O_5 . ZHOU and LUO [48] confirmed that the passive oxide layer formed on the surface of Ti10Mo alloy consists of a mixture of both TiO_2 and MoO_3 . Mo and Ta improve the corrosion resistance of Ti alloys. Figures 7(a)–(c) all have O1s signal at 530.9 eV, being usually attributed to metal–oxygen binding.

4 Conclusions

1) The EIS results of the samples in acidified 0.9% NaCl solution can be fitted using the model of $R_{\text{sol}}(Q_{\text{pL}}R_{\text{pL}})$. The results confirm the presence of a single barrier layer on the surface of the samples in acidified 0.9% NaCl solution.

2) A passive film is formed on all Ti samples during the anodic polarization tests carried out in acidified 0.9% NaCl solution. Its formation is accompanied by very low experimental passive current densities.

3) Passive current densities and resistance of the passive layer indicate that Mo used as alloying element improves the electrochemical corrosion behaviour of cp-Ti, and the addition of Ta improves additionally the corrosion resistance of Ti12Mo alloy in saline medium.

4) Ti12Mo5Ta with recrystallized structure has superior corrosion resistance than the same alloy with unrecrystallized structure. This improvement should be attributed to the characteristics of β -recrystallized phase.

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盐水介质中 Ti12Mo5Ta 合金的电化学特性

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摘 要: 比较了未再结晶和再结晶 Ti12Mo5Ta 合金、未再结晶 Ti12Mo 合金和工业用纯钛 (cp-Ti) 在 0.9%生理盐水 (pH 2.3) 中 37 °C 下的电化学行为。从阳极极化曲线中得到了极低的钝化电流密度(10^{-6} A/cm²), 这表明所有样品在酸性 0.9% NaCl 溶液中具有高的耐蚀性能。采用扫描电子显微镜(SEM)观察样品的表面形貌, 发现所有样品表面受到了相同的腐蚀, 而且经阳极动电位极化测试后的样品表面没有出现点蚀、裂纹或其它缺陷。使用等效电路模拟电化学阻抗谱(EIS)数据, 以表征样品表面且更好地理解 Mo 和 Ta 的添加对 cp-Ti 及再结晶的影响。EIS 结果证实, 在开路电位下, 所有样品在 0.9% NaCl 溶液(pH 2.3)中产生钝化(极化电阻约为 $10^5 \Omega \cdot \text{cm}^2$)。在 37 °C 时, 样品在 0.9% NaCl 溶液中(pH 2.3)的耐蚀性顺序为: 再结晶 Ti12Mo5Ta>未再结晶 Ti12Mo5Ta>未再结晶 Ti12Mo>cp-Ti。

关键词: 钛合金; 再结晶; 阳极动电位曲线; Ta; Mo; 电化学行为

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