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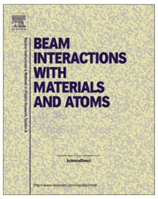

Use of combination of accelerator-based ion-beam analysis techniques to the investigation of the corrosion behavior of CoCrMo alloy

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ABSTRACT

Nuclear Reaction Analysis – NRA in combination with d-RBS (E_d: 1.35 MeV) was applied in order to investigate the corrosion behavior of CoCrMo alloy. The corrosion resistance of the alloy was compared to that of modified CoCrMo samples by several techniques as plasma nitriding and oxidizing at moderate temperature (~400 °C). Electrochemical techniques in simulated body fluid 0.9% NaCl (37 °C) were applied in order to accelerate the corrosion process. The nitrogen depth distribution before and after the corrosion was determined using the $^{14}N(d,\alpha)^{12}C$ and the $^{14}N(d,p)^{15}N$ nuclear reactions whereas the oxygen by the $^{16}O(d,p)^{17}O$. The surface morphology and microstructure was investigated using microscopy techniques. It was found that surface treatments produce thick nitrided layers (5–6 μm) consisting of a supersaturated nitrogen solution (nitrogen concentration is ~30 at.%) in the matrix (expanded phase γ_N) and a thin oxygen solution (0.3 μm). The samples subjected to plasma nitridation and oxidation exhibited the lowest deterioration and better resistance to corrosion compared to the single nitrided or single oxidized and the untreated material. This could be attributed to the modified surface region with the high nitrogen content and the presence of oxygen.

1. Introduction

CoCrMo alloys, due to their excellent mechanical properties and corrosion resistance have been widely used in orthopaedic prosthesis. However, their wear and corrosion stability are of great concern during the last years [1–3]. Literature studies showed that the released of metal ions (e.g. Co, Cr, Mo) may interact with the neural system, influence bone mineralization or be carcinogenic [4–7]. The long term durability of the implants relies on the control of their corrosion resistance and wear behavior. Therefore, the increase of their lifetime through development of a corrosion- and wear-resistant biocompatible surface layer is of special importance.

Recent studies indicated that plasma nitriding (PN) and plasma-based ion implantation (PBII) at moderate temperatures (~400 °C) can considerably improve the wear and fatigue resistance of metallic alloys with austenitic structure (e.g. steels, Ni-based alloys, CoCr alloys with a face cubic centred FCC γ_N phase). Such nitriding leads to the formation of thick nitrided layers (of few μm after few hours of treatment), consisting of a supersaturated nitrogen solution in the a γ_N matrix, usually called expanded S-phase or a γ_N [7–10]. These techniques are "3D" processes allowing a workpiece of complex shape to be treated from all sides. The treatments were also shown to improve the tribological and corrosion properties of the modified material surfaces.

The objective of this work was the investigation of the effect of plasma assisted nitriding or oxidizing on the corrosion and mechanical properties of CoCrMo alloy for biomedical applications using a combination of accelerator-based ion-beam analysis techniques.

2. Experimental details

2.1. Samples preparation

The investigated alloy was a commercial medical grade CoCrMo substrate (ISO 5832-12) with composition Cr (27.66 wt.%), Mo (5.60 wt.%), Al (0.01 wt.%), Ti (0.01 wt.%), C (0.048 wt.%), Zr (0.01 wt.%), Fe (0.08 wt.%) and Co (ca. 65 wt.%).

Three sets of samples were prepared in a R.F. plasma assisted thermal treatment reactor previously described [11,12]. The first set (CoCrMo + N) was nitrided at 395 °C for 150 min, in 8 Pa of

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Table 1
Chemical composition of the investigated CoCrMo samples.

Sample	Treatment	*T* (°C)	Thickness (μm)	Co (wt.%)	Cr (wt.%)	Mo (wt.%)	O (wt.%)	N (wt.%)
CoCrMo + N	Nitridation	395	4.6	40	20	6	–	34
CoCrMo + O	Oxidation	400	0.3	54	20	2	34	–
CoCrMo+ N+O	Nitridation+ Oxidation	395 and 400	6.0	40	20	2	15	23

N_2 (60 vol.%) and H_2 (40 vol.%), with R.F. power of 700 W. The second set (CoCrMo + O) was oxidized at 400 °C, for 120 min, in 8 Pa of O_2, with R.F. power of 700 W. The third set (CoCrMo + N + O) is composed of initially nitrided samples (like the first set) being oxidized afterward like the second set.

2.2. Samples characterization

The structure, the composition and the surface morphology of the materials were investigated by X-ray Diffraction (XRD), Glow Discharge Optical Emission Spectroscopy (GDOES), X-ray Photoelectron Spectroscopy (XPS). Micro-hardness and wear tests were also performed to study the modifications of the mechanical and wear resistance (results to be published).

The thickness and the chemical composition of the modified layers of the materials were investigated, prior and after the corrosion tests, by Rutherford Backscattering Spectrometry (RBS) and Nuclear Reaction Analysis (NRA) using 1.35 MeV deuteron beams at the 5.5 MV Tandem Accelerator of the NCSR Demokritos (Athens, Greece). For the determination of the nitrogen and oxygen content of the samples the $^{14}N(d,p)^{15}N$, $^{14}N(d,\alpha)^{12}C$ and $^{16}O(d,p)^{17}O$ nuclear reactions were utilized [13]. The beam spot size was $1.5 \times 1.5\ mm^2$ and the overall uncertainty of the determination was estimated to be ca. 5%. The analysis of the RBS and NRA data was performed by the SIMNRA code [14,15] as well as for the simulation of nitrogen, oxygen and carbon the cross section data of S. Pellegrino, A. Gurbich and M. Kokkoris were taken into account respectively [16–19].

Examinations of the samples by SEM/EDS were performed using a JEOL JSM 840A electron microscope equipped with an energy – dispersive X-ray (EDS) INCA micro-analytical system (accelerating voltage 20 kV, probe current 45 nA and counting time 60 s, with ZAF correction being provided on-line). The samples were coated before the examination with carbon, using a JEOL JEE-4X vacuum evaporator.

2.3. Corrosion tests

The investigation of the corrosion behavior of the samples was performed in an argon aerated NaCl 0.9% solution by means of potentiodynamic and cyclic voltammetric techniques according to ASTM Designation G5-82 [20]. The tests were undertaken at room temperature in an AUTOLAB Potentio–Galvanostat (ECO CHEMIE, Netherlands) interfaced with a computer and recorder. A conventional three-electrode cell (EG&G PARR model) was used for all measurements. The cell was equipped with a saturated calomel reference electrode, a graphite auxiliary electrode and a holder leaving only the one side of the specimen exposed to the corroding medium. In all cases the electrolyte volume was 800 ml and the sample surface which was in contact with the testing solution 1 cm^2. The open circuit potential or corrosion potential E_{corr} was recorded after 30 min stabilization whereas rapid (50 V/h) and slow scan rates (0.6 V/h) were used. The potential investigated region was $-1000/E_{corr}/+1250$ mV.

3. Results

Table 1 gives the average chemical composition and the thickness of the main modified zone obtained by RBS and NRA using

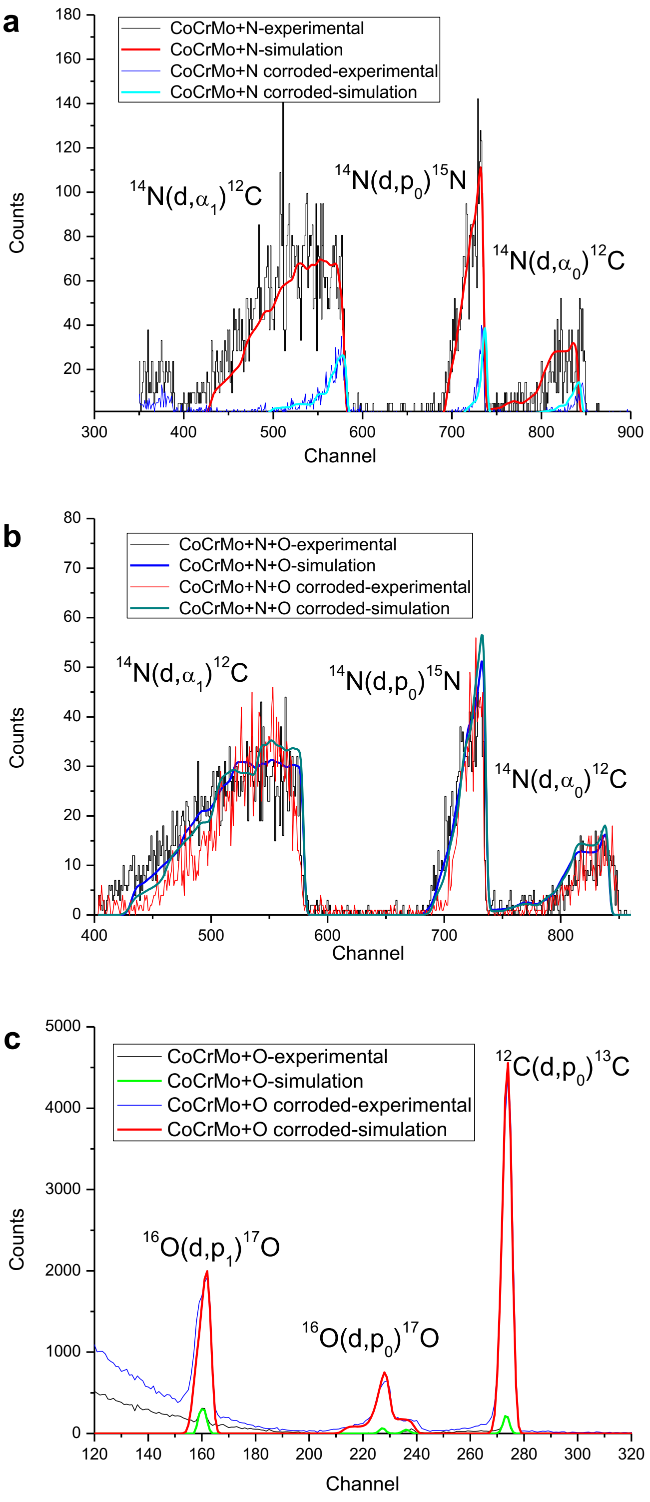

Fig. 1. (a and b) Nitrogen determination, (c) oxygen and carbon determination, by NRA before and after the corrosion investigation.