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Reduced tribocorrosion of CoCr alloys in simulated body fluid after nitrogen insertion

J. Lutz [a,b,*], S. Mändl [b]

[a] Translational Centre for Regenerative Medicine, Universität Leipzig, Leipzig, Germany
[b] Leibniz-Institut für Oberflächenmodifizierung, Leipzig, Germany

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ABSTRACT

Tribological studies in air and simulated body fluid (SBF) after surface modification by nitrogen plasma immersion ion implantation of medical CoCr alloys were compared. The PIII treatment temperatures were varied between 390 and 570 °C. Subsequent wear measurements in air exhibit reduced wear rates for the PIII treated specimens. In SBF, a minimum wear rate was observed for a process temperature near 400 °C. For higher PIII temperatures, fretting corrosion leads to an elevated cobalt ion release. Apparently a weakened chemical bonding of cobalt as well as chromium immobilization caused by the nitrogen insertion and a subsequent reduction of passivating oxide layer causes the selective high Co ion release for samples with high process temperatures. A compromise for the PIII treatment temperature must be found as the minimum particle release rate does not correspond to the minimum Co ion release rate.

1. Introduction

CoCr alloys are considered to be a biocompatible material with a wide range of applications including prosthetic replacements as well as cardiovascular uses [1]. Although they exhibit excellent mechanical properties and a satisfactory biocompatibility, implant failures and high revision rates of 5–10% lead to a considerable interest to improve and to optimise the surface properties of these alloys. Several influencing factors have to be considered to understand the interplay between implant surface and human tissue which can manifest themselves, e.g., in the release of toxic ions due to corrosive failure, wear particles, micro- and nanotopography of the surface and its bioactivity [2–4]. Often some of these mechanisms interact with each other and lead to a complex tissue-implant response.

There are various surface treatment methods which may improve the biocompatibility of biomaterials and lead to longer lifetimes by optimising the surface properties. One group of processes encompasses surface functionalizations with energetic ions. However, only few publications exist about surface modifications to improve the biocompatibility of CoCr alloy: Conventional beamline nitrogen ion implantation [5], plasma surface alloying [6] and high intensity plasma ion nitriding [7] have been reported. These experiments using nitrogen or oxygen, as well as experiments with plasma immersion ion implantation (PIII) [8–11] result in an increase of the surface hardness and a reduction of wear rate. In the case of nitrogen insertion, the formation of an expanded austenitic structure at lower process temperatures and the precipitation of chromium nitrides at process temperatures above 400 °C is observed. Few investigations about metal ion release after such ion implantation can be found in the literature: Öztürk et al. [12] report on elevated metal release during immersion tests after nitrogen implantation, which was attributed to a strongly increased surface roughness. Additionally, one publication about improved tribological properties in sodium chloride solution exists [6] the interplay between wear and corrosion together has not been addressed in detail yet. The focus of the majority of the experiments was either to study wear mechanisms or the corrosion behaviour independent from alternative influences.

This work investigates the wear mechanisms in physiological solution in comparing them with the wear behaviour under dry conditions after plasma immersion ion implantation. The aim is to reflect the situation of implants in medical environment.

2. Experiment

Flat discs of commercially available wrought CoCr alloy SY21med (ISO 5832-4; 28 wt.% Cr, 5 wt.% Mo, 1 wt.%. Ni, balance Co) were cut from rods and polished to a mirror-like finish. The base material consists of an fcc lattice with all alloying elements in solid solution and typical grain sizes between 10–20 µm.

Nitrogen plasma immersion ion implantation was performed in a vacuum chamber with a base pressure of 10^{-6} Pa. An electron cyclotron resonance (ECR) plasma source operating at a power of 150 W generated a nitrogen plasma with an electron temperature of 1.3 eV and a plasma density of 1.6×10^{10} cm^{-3} as determined from Langmuir probe measurements [13]. At a nitrogen gas flow rate of 150 sccm the resulting pressure during the experiments was 0.53 Pa. The experiments were carried out in applying negative high voltage pulses of 10 kV and a pulse length of 15 µs to the substrate holder for

* Corresponding author. Translational Centre for Regenerative Medicine, Universität Leipzig, Leipzig, Germany.
E-mail address: jlutz@trm.uni-leipzig.de (J. Lutz).

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two hours. The process temperature was varied between 390 and 570 °C by changing the pulse frequency from 0.7 to 3.0 kHz.

Wear tests of the nitrided samples were performed using an oscillating ball-on-disc configuration with an alumina ball of a diameter of 4.8 mm and the following parameters: load 1 N, speed 5 cm/s, radius of circular wear tracks 5 mm, number of cycles 20,000. The experiments were made in air and in simulated body fluid (SBF). SBF was prepared according to Kokubo et al. [14]containing 142.0 mM Na^+, 5.0 mM K^+, 1.5 mM Mg^{2+}, 2.5 mM Ca^{2+}, 147.8 mM Cl^-, 4.2 mM HCO^{3-}, 1.0 mM $HPO_4^{2-}$and 0.5 mM SO_4^{2-}.

Analysis of the samples' morphology was done with scanning electron microscopy (SEM), their chemical composition was analysed with energy-dispersive X-ray analysis (EDX). In order to investigate the roughness of the nitrided samples and the wear volume a laser profilometer was used. Additionally, to determine the corrosion behaviour in SBF the electrolyte was analysed with inductively coupled plasma glow discharge spectroscopy (ICP).

3. Results and discussion

The layer and phase formation have been already studied in detail before [8–10]. Therefore, the results are only summarized here. In all samples, a fast thermally activated diffusion with resulting layer thicknesses up to 5 µm, depending on the process conditions is observed. The nitrogen content just below the surface of the nitrided samples is between 20 and 30 at.%. X-ray diffraction measurements reveal the formation of an expanded austenitic structure at temperatures below 400 °C and precipitation of chromium nitrides at higher temperatures.

The development of the RMS (root mean square) surface roughness is plotted against the process temperature in Fig. 1. Since the temperature is directly correlated with the pulse frequency the higher temperatures belong to high ion doses (8.6×10^{18} ions/cm^2) whereas low temperatures are related to lower ones (3.2×10^{18} ions/cm^2), despite identical process times. Therefore the increasing roughness with increasing ion dose is due to the elevated number of ions which lead to sputtering of the surface [15].

The investigation of the wear tracks in air after the end of the experiment using SEM revealed a mixture of adhesion, abrasion and plastic deformation for all specimens with much milder wear behaviour for the PIII treated ones. Selected wear tracks are shown in Fig. 2. Two groups of particles depending on the surface treatment can be distinguished: spherical particles with a diameter of about 50 nm (sometimes agglomerated to particles with a diameter of up to 1 µm) and needle shaped particles with a length of less than 1.5 µm.

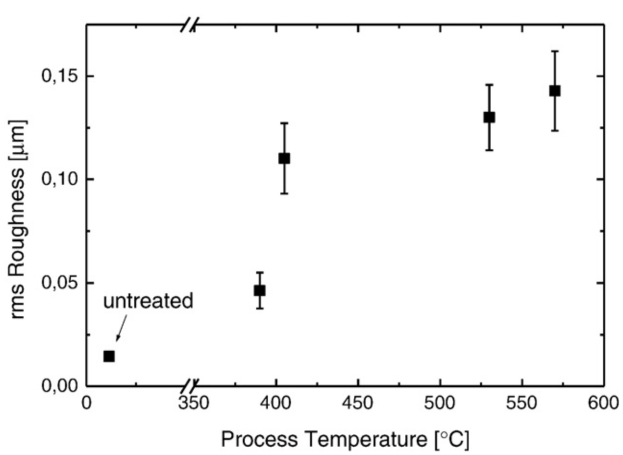

Fig. 1. RMS roughness of CoCr after nitrogen implantation at different process temperatures.

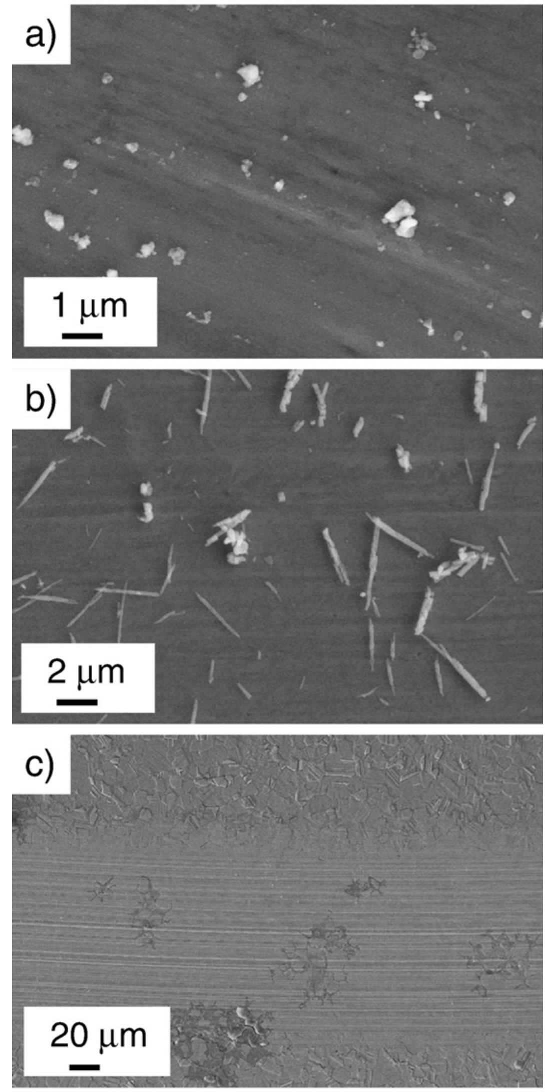

Fig. 2. SEM micrographs of the wear tracks in air of the untreated specimen (a), the specimen nitrided at 390 °C (b) and the wear track in SBF of the specimen nitrided at 570 °C (c).

Whereas the spherical particles are predominant in the wear tracks of untreated CoCr (Fig. 2a) and nitrided CoCr at high temperature (Fig. 2c, however, not visible in this magnification) the needle shaped particles characterise the specimens nitrided at low temperatures (Fig. 2b). As shown by EDX measurements they both have an increased oxygen content in comparison with the surrounding surface. The occurrence of nanosized spherical and needle shaped wear particles of untreated cobalt-based alloys has been already reported in literature. According to the work of Büscher et al. [16] the spherical particles result from torn off nanocrystals while the needle shaped are generated by fractured ε-martensite. Apparently, the occurrence of ε-martensite in our samples is highly correlated with the occurrence of the expanded austenite lattice after nitrogen insertion at moderate temperatures, whereas the CrN precipitates observed at higher temperatures do not modify the underlying wear process. Thus, an intentional aging with a transformation of the initial fcc lattice can be excluded, while differences in the stacking fault energy for the base material and the expanded austenite structure may explain the modified particle formation [17].

The wear tracks of the untreated and the low temperature sample which were investigated in SBF are quite similar to those in air and are not presented in this paper for space. However, after PIII treatment at