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Surface treatment on an implant cobalt alloy for high biocompatibility and wear resistance

S. Spriano [a,*], E. Vernè [a], M.G. Faga [b], S. Bugliosi [b], G. Maina [c]

[a] *Dipartimento di Scienza dei Materiali ed Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy*
[b] *Istituto di Scienza e Tecnologia dei Materiali Ceramici, Consiglio Nazionale delle Ricerche, Strada delle Cacce 73, 10135 Torino, Italy*
[c] *Dipartimento di Traumatologia, Ortopedia e Medicina del Lavoro, Università di Torino, Via Zuretti 29, 10126 Torino, Italy*

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Abstract

Total hip prostheses are implanted to younger and more active patients, so the open problem is to create implants which will enhance the implant survivorship and will offer greater longevity. From this point of view, metal-on-metal arthroprostheses are well performing. The volume of periprosthetic inflammatory tissues appears to be less than with metal-on-UHMPWE, however osteolysis often occurs and it is known that the levels of metal ions in the blood and urine are elevated in patients with metal-on-metal bearing. The aim of this research activity was the synthesis and characterization of surface modified cobalt alloys, in order to obtain a biocompatible material presenting at the same time good wear performances, low metal ion release and low toxicity.

The surface chemical composition of an implant cobalt alloy (Biodur) was modified, producing relevant tantalum enrichment. Tantalum was chosen because of its low toxicity and high corrosion resistance. The chemical composition, morphology, roughness, crystallographic structure and wettability of the surface, as well as the interface of the modified layer with the substrate, were characterized. The mechanical behavior of the modified materials was investigated by scratch and pin-on-disc wear tests. The metal ion release of the modified surfaces was measured by in vitro experiments after wear tests.

Keywords: Cobalt alloy; Arthroprosthesis; Metal ion release; Tantalum; Surface modification

1. Introduction

As indications for total hip prostheses (THA) have begun to include younger patients, the main demand is for implants that will offer greater longevity. This is related to the quest for better bearing surfaces that will enhance the implant survivorship. The first generation metal-on-metal implants were the Wiles, McKee-Farrar, Muller and Ring prosthesis (1960). Early failure often occurred with these implants, secondary to aseptic loosening. At the same time a dark colouring of periprosthetic tissues was detected in some patients (metallosis), due to metallic ions diffusion. As a consequence, these prostheses were no longer commercialized for many years. However, the implants that survived have lasted more than two decades and are still functioning well in some patients. The idea of an all-metal joint was taken up again in the mid 1980s and led to the development of the so-called second-generation metal articulation, with improved alloy microstructure, surface finishing and manufacturing tolerances. The overall amount of wear was reduced to a fraction of the rates observed with metal–polyethylene or ceramic–polyethylene combinations. A number of clinical studies have described the successful use of these second generation metal–metal THA, which were found to be reliable and provide an excellent outcome. In any case, individual cases of metallosis have been reported in some cases. Metal particles (20–100 nm) have been shown to be disseminated throughout the body and have been found in the lymph nodes, liver, spleen, and bone marrow. The levels

* Corresponding author. Tel.: +39 011 5644711; fax: +39 011 5644699.
E-mail address: silvia.spriano@polito.it (S. Spriano).

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of metal ions, in the blood and urine, are elevated in patients with metal-on-metal bearing. The toxicity and carcinogenesis risks of these trace metal have not been established [1]. In the past, some ceramic coatings were proposed, in literature, as wear resistant and metal ion release barrier for metal arthroprosthesis. They were obtained by different vapour deposition techniques (PVD, ion implantation, sputtering) and they consisted of hard, smooth films of diamond-like carbon [2,3] or nitrides (TiN [4], CrN [5,6], AlN [7]). Nowadays they have not found commercial applications in the field of THP, in spite of their quite low wear coefficients. The main problem is related to their ceramic nature and brittle interface with the metallic substrate.

In this paper is presented the study of a surface modification of a cobalt alloy able to produce an outer layer with proper wear resistance, low metal release and a strong interface with the substrate. An interesting aspect is that it doesn't deal with a deposited coating and ceramic phases are not involved. Tantalum was selected as surface modifier element, due to its high biocompatibility and excellent corrosion resistance. In fact, Ta is an elemental metal that has recently gained interest for a variety of orthopaedic applications. For example, trabecular Ta constructs have been shown to be excellent scaffolds for bone ingrowth and mechanical attachment [8]. Scaffold made of 99 wt.% pure tantalum and 1 wt.% of glass carbon are nowadays implanted as acetabular caps or scaffolds for bone reconstruction.

2. Experimental

Pure cobalt (99.95 Alfa Aesar) and a cobalt micro-melt alloy (Biodur CCM Plus, Carpenter Technology Corporation) were used as substrates. The Biodur alloy is commonly used in metal-on-metal prosthesis (Metasul–Zimmer). The alloy composition is: C 0.24 wt.%, Cr 29.5 wt.%, Ni 0.2 wt.%, Mo 6.4 wt.%, Co 61.80 wt.%. It was received and used in the un-annealed condition. The surface modification treatment consists of a thermal treatment in molten salts. It was performed under argon flux, by setting a linear heating up to 800–1000 °C and then an isothermal heating for 1–2 h. The sample acronymus used in the following report as first the kind of substrate (Co for pure cobalt or Alloy for Biodur alloy), then the time used during the isothermal treatment (60–90–120 min) and as last the temperature of the isothermal treatment. So the acronymus "Alloy-60-1000" means that the Biodur alloy substrate was treated for 60 min at 1000 °C. The samples were as first mirror polished and weighted, then they were put in graphite crucibles filled with a solid salt mixture containing NaCl 47 wt.%, K_2TaF_7 52 wt.% and Ta 1 wt.%. The salt mixture composition was selected according to [9] where a similar treatment on Ni alloys was proposed. After heat treatment the samples were weighted in order to evaluate the eventual weight increment due to the surface modification. The surface and the interface morphology were observed by scanning electron microscopy (SEM, Leica Stereoscan). Quantitative surface analysis was performed by energy dispersion spectroscopy (EDS). The crystallographic structure of the materials was investigated by X-ray diffraction analysis (XRD, X'Pert Philips diffractometer, Cu Kα incident radiation). Contact angle measurements were carried out by using distilled water or dilute bovine serum (LEITZ optical stage microscope equipped with LEICA camera). The same dilute bovine serum was used also as lubricant during wear tests. It consists of a solution of 75 vol.% of distilled water and of a 25 vol.% of calf bovine serum. Na_3N was added as antibacterial agent in the ratio of 1 g/l. Roughness and wear track's volume measurements were performed by using a Rank Taylor Hobson surface profiling instrument. Friction coefficient measurements were performed both by using pin on disc and ball on disc tests. In the first case, pin–disc couples consisted of the same material (treated cobalt substrates or untreated ones as reference), while alumina balls (6 mm diameter) were used for ball on disc tests. The applied load was in the range 0.7–4.8 MPa. The sliding rate was of 10 cm/s. A sliding distance sufficient to obtain a constant friction coefficient value was run in each case. Wear tests were performed by using a load of 5 or 7 N and an alumina ball 6 mm in diameter. The sliding rate and distance were 10 cm/s and 785 m (25,000 revolutions). The contact pressure in the case of ball on disc tests was calculated according to the Hertz's theory and in the case of alumina–Biodur contact it was found to be 1.3 GPa by applying 5 N and 1.7 GPa by applying 7 N. The track height and area were registered by means of a prophilometer after every measurement. The abrasive wear rates were calculated as the worn volume divided for the load and sliding distance product (mm^3/N m). All the friction and wear measurements were performed at 37 °C by using dilute bovine serum as lubricant. A CSEM high temperature tribometer was employed. Samples were observed by means of SEM/EDS after all the tribological tests. Scratch tests were performed both by performing several scratch lines at different loads (starting from 2.5 up to 70 N) with a Rockwell C indenter and by using a CSM Revetest® scratch-testing equipment. It employs a diamond-stylus scratch method and detects acoustic emission, frictional force and penetration depth. The maximum employed load was 100 N. Metal ion release measurements were performed by analyses of the dilute bovine serum employed during wear tests and containing metal debris. An atomic absorption spectrophotometer (GFAA-ICP technique) was used to evaluate metal ions concentration in the withdrawn solution, focusing on cobalt and chromium content.

3. Results and discussion

The main interest in this work is related to the surface modification of the Biodur alloy, because of its arthroprosthesis application. The aim of the modification is to enhance its biocompatibility and to lower release of toxic metal ions. In any case, a preliminary investigation was performed on