

Characterization of Tribocorrosion Behaviour of CoCr Alloy by Electrochemical Techniques in Several Corrosive Media

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(Received December 20, 2017; Revised April 19, 2018; Accepted April 20, 2018)

Substitution of hip and knee joints by CoCr alloys is in great demand due to their high wear resistance and good biocompatibility. Understanding of tribocorrosion in joint replacements requires study of variables such as coefficient of friction and the choice of a proper corrosive medium in wear-corrosion tests carried out in the lab. The objective of this study was to characterize tribocorrosion behaviour of CoCr alloy with low (LCCoCr) and high carbon (HCCoCr) contents in several corrosive media: NaCl, Phosphate Buffer Solution (PBS), and PBS with hyaluronic acid (PBS-HA). Tribocorrosion tests were carried out on a pin-on-disk tribometer with an integrated electrochemical cell. A normal load of 5N was applied on the alumina ball counterpart at a rotation rate of 120 rpm. Coefficient of friction (COF) was measured and tribocorrosion behaviour was characterized by in situ application of electrochemical techniques. HCCoCr alloy immersed in PBS-HA showed the best tribocorrosion behaviour with the lowest COF. In this case, in situ measurement of corrosion potential and the impedance data under wear corrosion process showed an active state while passive film was continuously destroyed without possibility of regeneration.

Keywords: CoCr alloy, Tribocorrosion, Hyaluronic acid, Electrochemical techniques, Joint

1. Introduction

In recent years, total hip replacement by metallic biomaterials because of a loss of mobility has become an important concern in human health [1]. The most widespread clinical practice for hip substitution involves the polyethylene/metal joint replacement. However, excessive wear of polyethylene causes the production of particles that are believed to be the major cause of the progressive bone loss (osteolysis) [3] and subsequent loosening of the prosthesis [4]. This problem has strongly driven the research through the study of tribocorrosion of metal against other materials such as metal, alumina or modified surfaces [5]. Among all the mechanical properties needed in permanent biomaterials, CoCr alloys are widely used in such cases where high wear resistance is required, such as in joints. In the specific case of trying to simulate the real case of joints, wear-corrosion tests must be considered. The study of parameters like the coefficient

of friction in wear-corrosion tests is essential in order to make a first screening of the wear-corrosion behaviour of the material and the value of this parameter depends on the chosen electrolyte. The selection of the physiological media used in wear-corrosion tests has always stimulated controversy in the literature. Efforts are being focused on the adaptation of the physiological medium to the in vitro situation by approximating of the artificial biological medium to the real physiological medium. Considering the chemical composition of the synovial fluid, several researchers have used media that simulate this fluid as electrolyte in their tribocorrosion tests. One of the main compounds included in synovial fluid is the hyaluronic acid, an organic acid that acts as a perfect lubricant in the joints of the human body significantly reducing the friction [6-8]. Hyaluronic acid appears in a concentration of 0.3% in synovial fluids and these fluids can be simulated by preparing a phosphate buffer solution (PBS) with 0.3% hyaluronic acid as an electrolyte medium in wear-corrosion tests.

The interaction of the physiological fluids with the bear-

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Table 1 Chemical composition (wt%) of the CoCr alloys used in the study

CoCr alloys	C	Co	Cr	Mo	Ni	S	P	Al (ppm)	W	Mn	Fe	Si	N (ppm)	Ti
HC	0.25	Bal.	28.0	5.35	0.41	0.003	0.003	0.02	<0.05	0.40	0.16	0.78	69	0.01
LC	0.03	Bal.	27.2	5.52	0.01	0.004	0.004	0.005	0.01	0.66	0.02	0.68	0.17	0.005

ing surfaces of hip implants is of great importance in the investigation of artificial joint lubrication, although this research area has so far been little explored. The use of the different media in the wear corrosion tests permits the evaluation of the contribution of the different compounds to the formation of the tribochemical layers [9,10]. The objective of this work is the study of the tribocorrosion behaviour of CoCr alloys by the measurement of the friction coefficient and the application of electrochemical techniques in several corrosive media. In this work, the tribocorrosion behaviour of the CoCr alloy with low (LCCoCr) and high carbon (HCCoCr) content was studied in several corrosive media from the simplest, 0.9% NaCl solution with a chloride content comparable to the physiological solution, through named physiological media including phosphates, PBS, to the most complex, by adding hyaluronic acid to PBS.

2. Experimental Methods

Table 1 shows the chemical compositions of the two types of CoCr alloys containing high (HC) and low carbon content (LC).

The sample preparation consisted of grinding on SiC paper from mesh 600 to mesh 1200, successively followed by mechanical polishing with 6 and 1 μm diamond paste, ultrasonic cleaning in ethanol and air drying.

The microstructure was observed after acid etching in 92 mL of HCl, 5 mL of H₂SO₄ and 3 mL of HNO₃, for 45 seconds. The microstructures of both HC and LC CoCr alloys were evaluated with an optical microscope.

The wear-corrosion behaviour was evaluated in the following corrosive media:

- NaCl 0.9% – M1
- NaCl 0.9%, Na₂HPO₄ 0.91 mM, CaCl₂ 1.8 mM (PBS) – M2
- NaCl 0.9%, Na₂HPO₄ 0.91 mM, CaCl₂ 1.8 mM (PBS) + 0.3% Hyaluronic acid – M3

Hyaluronic acid has been chosen because it is the main responsible for the good lubricant properties of the synovial fluid and whose effect on the metal surfaces is of great interest [11].

Wear-corrosion experiments were carried out on a

pin-on-disk tribometer with an integrated electrochemical cell (3-electrode cell) where the CoCr disks (HC and LC) function as working electrodes with a ring-shaped Pt wire as counter electrode and an Ag/AgCl electrode as the reference. Before the tests, the specimen surfaces were ground with sandpaper up to 1200 grit and final polishing with diamond paste of 1 μm . The counterpart (pin) was an alumina, Al₂O₃, ball of 6 mm in diameter. The CoCr disks and their counterpart were washed with double distilled water and cleaned in an ultrasonic ethanol bath for 10 min. The alumina ball was placed in a plastic pin holder and fixed on the load cell. A normal load of 5N was applied on the counterpart. The frictional force was measured by means of a piezo-electric force transducer. The motion of CoCr working electrodes was provided by a rotating motor at a rotation rate of 120 rpm.

After mounting the specimen and the counterpart on the tribometer, the selected solution was poured into the electrochemical cell and the temperature was set and maintained at 37 ± 1 °C. The test procedure was carried out using the following steps: 1) immersion of the CoCr disk in the electrolyte and measurement of the corrosion potential; 2) sliding test with or without electrochemical measurements (corrosion potential and electrochemical impedance spectroscopy); 3) after the sliding is finished, the measurement of the evolution of the corrosion potential; 4) and finally, potential maps by Scanning Kelvin Probe (SKP) of the CoCr samples at 95% relative humidity, after the tribocorrosion tests.

The electrochemical experiments were conducted in the three-electrode cell described above connected to a Gamry Instrument Potentiostat/Galvanostat (Reference 600). At immersion, the CoCr working electrodes were measured and stabilized at the open circuit potential for 20 min. Then, the electrochemical impedance spectroscopy (EIS) experiments were performed at the corrosion potential by applying a sinusoidal wave of 10 mV in amplitude in a frequency range from 10⁵ Hz to 10⁻³ Hz spaced logarithmically (five per decade). In addition, single sweep potentiodynamic polarization curves were performed, without wear, at 10 mV/min from the corrosion potential up to a limit current value of 10⁻³ A or 1.5 V versus E_{corr}. At this point, reverse scan was drawn until it reached the

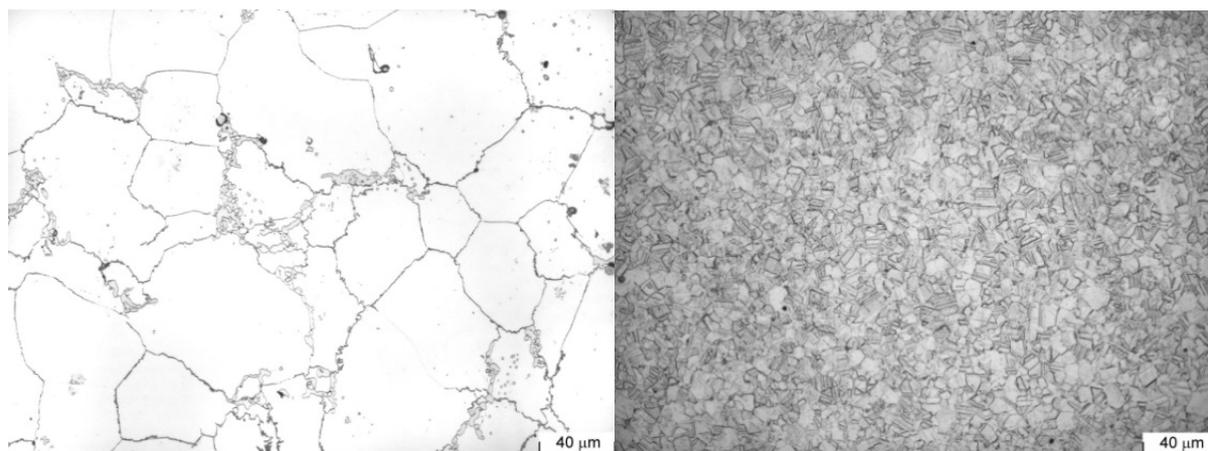


Fig. 1 Optical micrographs of high carbon HC (left) and low carbon LC (right) CoCr alloys.

Table 2 Parameters obtained from anodic polarization curves of Fig. 2

Media	E_{corr} mV _{vs SCE}	I_{pas} (A)	E_b mV _{vs SCE}	E_p mV _{vs SCE}	$E_b - E_{corr}$ (mV)	$E_p - E_{corr}$ (mV)
M1 HC	208	2.4E-08	774	840	566	632
M2 HC	-38	2.3E-08	495	720	533	758
M3 HC	78	5.4E-08	589	704	511	626
M3 LC	-125	1.4E-07	570	763	695	888

I_{pas} = passive current; E_b = breakdown potential; E_p = protection potential

repassivation potential. The passivation currents (I_p) and breakdown potentials (E_b) were determined. All experiments were carried out in triplicate under aerated conditions.

The potential maps of the testing areas after the wear-corrosion tests were recorded by Scanning Kelvin Probe (SKP). The technical specifications of the home made SKP used are reported in [12,13]. This non-contact technique permitted the determination of potential maps related to the surface reactivity, through the work function. For this purpose, the Kelvin probe tip, which was a Ni-Cr wire of 50 μ m diameter, was calibrated with a saturated Cu/CuSO₄ electrode. Areas of 5 x 5 mm² were scanned at 25 °C and 95% relative humidity, obtaining potential values relative to the standard hydrogen electrode.

3. Results and Discussion

Fig. 1 shows the microstructure of the high carbon (HC) and low carbon (LC) CoCr alloys. On the left hand photograph, it is possible to observe the precipitates of carbides, which are the responsible for the increase in the hardness of the alloy up to 366 HV.

The susceptibility to pitting corrosion of the HCCoCr

in the three corrosive media and LCCoCr in PBS-HA (M3) appears in Fig. 2. The most relevant data obtained from the anodic polarization curves of Fig. 2 are shown in Table 2, where I_{pas} is the passive current, E_b is the breakdown potential that is the potential at which the passive layer is broken, and E_p is the protection potential

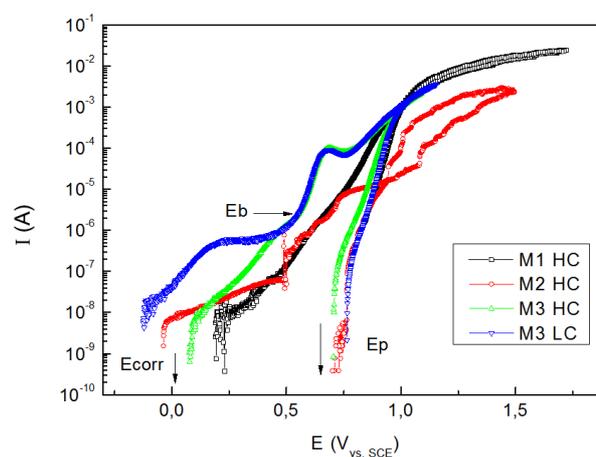


Fig. 2 Anodic polarization curves of CoCr with high carbon (HC) in 0.9% NaCl (M1), PBS (M2) and PBS + Hyaluronic acid (M3), and low carbon (LC) in M3.

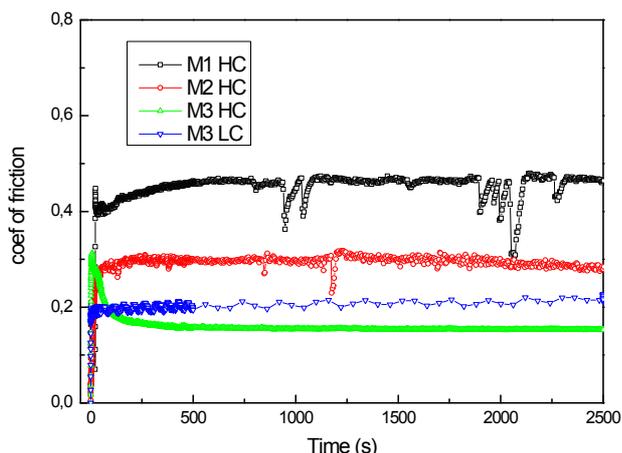


Fig. 3 Coefficient of friction of high (HC) and low carbon (LC) CoCr alloy during wear-corrosion in different corrosive media: 0.9% NaCl (M1), PBS (M2) and PBS + Hyaluronic acid (M3). Couple CoCr/Al₂O₃.

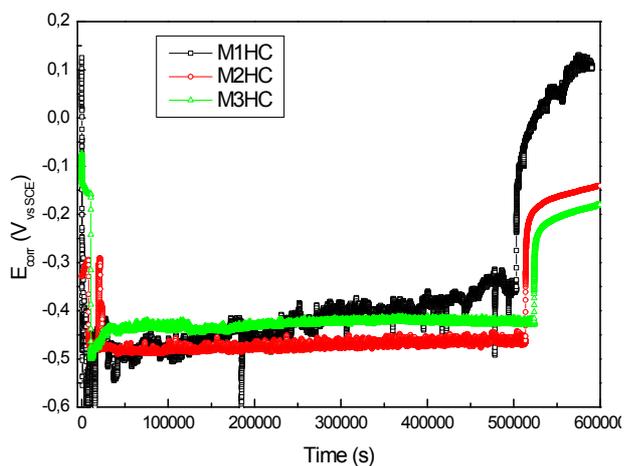


Fig. 4 Evolution of corrosion potential of high carbon (HC) CoCr alloy: before, during and after wear-corrosion test in 0.9% NaCl (M1), PBS (M2) and PBS + Hyaluronic acid (M3). Couple: CoCr /Al₂O₃.

or the potential where the repassivation is again reached. The difference between E_b and E_{corr} is the polarization that the passive layer resists before pitting is produced. The highest difference between E_b and E_{corr} is obtained for LCCoCr, in the most complex medium (M3) indicating the lowest susceptibility to pitting corrosion as well as the highest capacity for repassivation ($E_p - E_{corr} = 888$ mV). This is in agreement with other results published in the literature [14] where it has been reported that the presence of chromium carbides (Cr₂₁Mo₂C₆) in CoCr alloy with high carbon content increases the hardness but impairs the corrosion resistance due to the chromium impoverishment in the matrix. This is the reason why the CoCr alloy with low carbon content immersed in PBS-HA has a lower

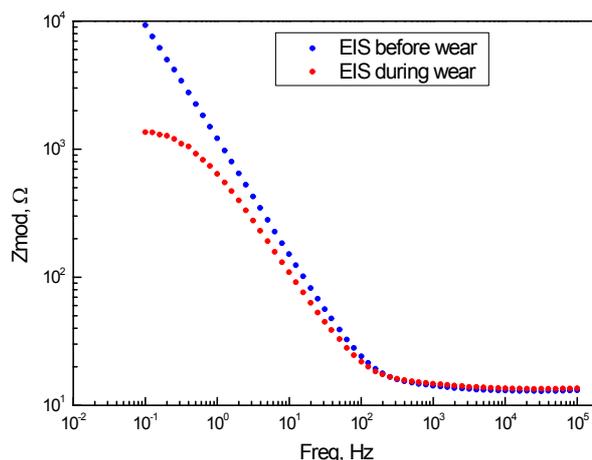


Fig. 5 Bode diagram of impedance modulus versus frequency of the high carbon (HC) CoCr alloy before and during wear corrosion tests in PBS+ hyaluronic acid solution (M3).

susceptibility to pitting corrosion.

Fig. 3 shows the evolution of the coefficient of friction of the HC CoCr alloy in the three corrosive media (0.9% NaCl-M1, PBS-M2, and PBS+ HA-M3), and LC CoCr alloy in M3, for comparative purposes. As can be seen, the coefficient of friction (COF) remains more or less constant over time. Minor fluctuations occur in the values of the COF obtained for LC and HC CoCr alloy in M3. The presence of CaCl₂ and Na₂HPO₄ in M2 protects the surface reducing the friction, compared to the COF obtained in M1 (only NaCl in its composition). The CoCr alloy immersed in hyaluronic media (M3) displays the lowest COF, in both high (HC) and low (LC) carbon content. The fact that the coefficient of friction of the CoCr/alumina couple immersed in PBS-HA is lower than in NaCl confirms the better lubricant properties of hyaluronic acid.

The electrochemical reactions between the CoCr surfaces and the corrosive media under wear are stimulated if the surfaces suffer a continuous sliding between them. The measurement of the corrosion potential of the HC CoCr alloy before, during and after sliding in 0.9% NaCl (M1), PBS (M2) and PBS + Hyaluronic acid (M3) is shown in Fig. 4. Before sliding, the corrosion potential at the equilibrium state is around -0.25 V_{vs. Ag/AgCl}. When sliding starts, the corrosion potential sharply decreases until -0.500 V_{vs. Ag/AgCl}. The sliding causes the breakdown of the passive film and an active state of the surfaces is formed. The continuous wear activates mechano-chemical reactions that continuously promote the formation and removal of chemical/electrochemical reaction products. Throughout the test, the corrosion potential of the HC CoCr alloy is more stable in the medium containing hya-

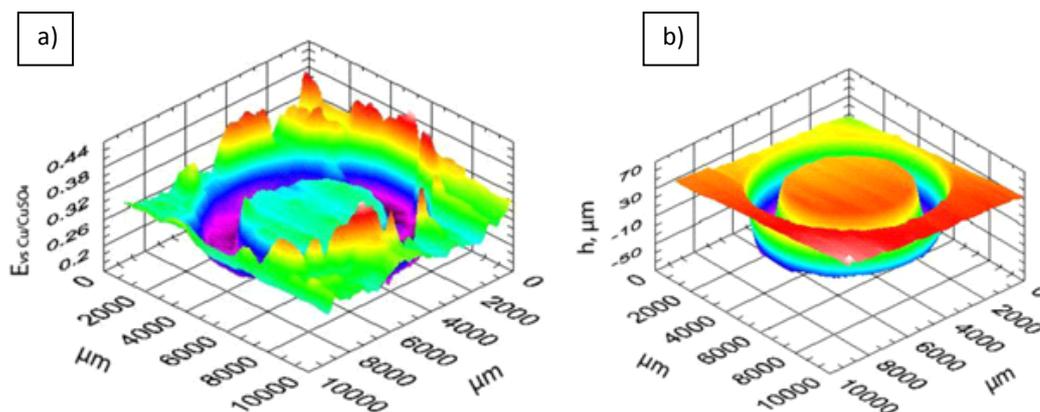


Fig. 6 a) Potential map at Relative Humidity > 95% and, b) topography of the HC CoCr surface after wear corrosion test.

luronic acid (M3) than in 0.9% NaCl (M1). This provides evidence that hyaluronic acid exerts some protection to the surface from the mechanical damage caused by the wear process. This behaviour has been previously seen in other corrosive media containing proteins (foetal bovine serum, albumin) [15]. The adsorption of proteins into the metal surfaces serving as solid lubricants [16]. Then, this adsorption layer under wear helps to generate thin layers known as tribochemical films in metal on metal tribo-corrosion processes [17].

Fig. 5 shows the Bode diagram of the impedance modulus versus frequency of the HC CoCr alloy in PBS + hyaluronic acid (M3) before and during wear-corrosion tests. There can be seen the decrease in the impedance modulus at the lowest frequency by more than one order of magnitude during wear corrosion. The mechanical action of wear destroys the passive film producing active areas that are not passivated until the sliding is finished. Fig. 6 shows the potential map and topography registered by SKP of the HCCoCr surface after wear corrosion in PBS-HA. The track area is perfectly distinguished because the potential in this area is 100 mV lower (blue color) than in the surface without wear. The new passive film has probably a different chemical composition in these areas.

4. Conclusions

The susceptibility to pitting corrosion of LCCoCr alloy is lower and its capacity to repassivate is higher than in HCCoCr alloy in PBS-HA.

The hyaluronic acid in PBS reduces the coefficient of friction of CoCr alloy with both high and low carbon content.

Both the corrosion potential as well as the impedance modulus show an active state of the CoCr surface in the wear corrosion tests in PBS-HA that impair the repassivation of the passive film.

CoCr alloy with high carbon content immersed in PBS with hyaluronic acid shows the best tribocorrosion behaviour.

Acknowledgments

Financial support received through the MAT2015-67750-C3-1 and MAT2011-29152-C02-01 projects from the Ministerio de Economía y Competitividad (MINECO/FEDER) from Spain.

References

1. S. R. Knight, R. Aujla, and S. P. Biswas, *Orthop. Rev.*, **3**, e16 (2011).
2. U. Holzwarth and G. Cotogno *JRC Scientific and Policy Reports*, European Union, European Commission, Luxembourg (2012).
3. J. J. Jacobs, K. A. Roebuck, M. Archibeck, N. J. Hallab, and T. T. Glant, *Clin. Orthop. Relat. R.*, **393**, 71 (2001).
4. P. F. Doorn, P. A. Campbell, and H. C. Amstutz, *Clin. Orthop. Relat. R.*, **329**, S206 (1996).
5. D. Bitar and J. Parvizi, *World J. Orthop.*, **6**, 172 (2015).
6. J. DesJardins, A. Aurora, S. L. Tanner, T. B. Pace, K. B. Acampora, and M. LaBerge, *Proc. Inst. Mech. Eng. H.*, **220**, 609 (2006).
7. S. Uesaka, K. Miyazaki, and H. Ito, *Mod. Rheumatol.*, **14**, 470 (2004).
8. B. A. Hills and B. D. Butler, *Ann. Rheum. Dis.*, **43**, 641 (1984).
9. M. A. Wimmer, A. Fischer, R. Buscher, R. Pourzal, C. Sprecher, R. Hauert, and J. J. Jacobs, *J. Orthop. Res.*, **28**, 436 (2010).
10. S. S. Brown and I. C. Clarke, *Tribol. T.*, **49**, 72 (2006).
11. M. R. C. Marques, R. Loebenberg, and M. Almukainzi.

- Dissolut. Technol.*, **31**, 15 (2011).
12. G. S. Frankel, M. Stratmann, M. Rohwerder, A. Michalik, B. Maier, B. J. Dora, and M. Wicinski, *Corros. Sci.*, **49**, 2021 (2007).
 13. C. Zea, J. Alcántara, R. Barranco-García, J. Simancas, M. Morcillo, and D. de la Fuente, *J. Coat. Technol. Res.*, **14**, 841 (2017).
 14. S. Hiromoto, E. Onodera, A. Chiba, K. Asami, and T. Hanawa, *Biomaterials*, **26**, 4912 (2005).
 15. R. A. Gil and A. Igual Muñoz, *J. Mech. Behav. Biomed. Mater.*, **4**, 2090 (2011).
 16. Y. Yan, A. Neville, D. Dowson, S. Williams, and J. Fisher. *Proc. Inst. Mech. Eng. J.*, **224**, 997 (2010).
 17. M. A. Wimmer, A. Fischer, R. Buscher, R. Pourzal, C. Sprecher, R. Hauert, and J. J. Jacobs, *J. Orthop. Res.*, **28**, 436 (2010).