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Influence of carbon concentration on the electrochemical behavior of CrCN coatings in simulated body fluid

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ABSTRACT

CrCN coatings with various carbon contents were deposited on 316 L stainless steel disks by unbalanced magnetron sputtering via adjusting carbon target current, and their relevant microstructure was characterized by Raman spectrum and X-ray photoelectron spectroscopy, respectively. The influence of carbon content on the electrochemical properties of CrCN coatings in simulated body fluid (SBF) was investigated using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests. It turned out that the CrCN-coated 316 L disks performed better electrochemical properties than uncoated 316 L disk. All CrCN coatings contained a-CN_x, but the bonding structure converted from N–C bonds to N═C bonds as carbon content increased. As a result, the CrCN coatings (52.6–75.0 at.% C) with N═C bonds were prone to be easily degraded by breakage of π bond. In contrast, the CrCN coatings (15.4 at.% C) with N–C bond alone exhibited relatively higher charge transfer resistance (R_{ct}), and was able to prolong the longevity of prosthesis.

1. Introduction

On account of cheap price, free of magnetism and excellent ductility, prosthesis made of 316 L stainless steel has accounted for a major portion in surgical prosthesis market [1,2]. Nevertheless, 316 L stainless steel still confronted unsatisfactory service life resulting from local corrosion, fretting fatigue and formation of fibrous tissue in physiological environment [3–7], which led to about 10% of hip arthroplasties being substituted after 10–15 years [8–10]. In order to prolong the longevity of femoral head prosthesis made of 316 L stainless steel, some advanced compound coatings such as metal or non-metal incorporated a-C and TiCN coatings [11–16] have been applied to modify its surface characteristics. Recently, CrCN coatings have been paid more attention due to lower internal stress, higher hardness and superior tribological property [17,18]. Meanwhile, their electrochemical behavior has been investigated in different environments. Yi et al. [19] pointed out that CrCN coatings exhibited better protection effect than CrN coatings when immersed in 0.5 M H_2SO_4 and 5 ppm HF solution. Similarly, Merl et al. [20] manifested that carbon incorporation could enhance the inhibition ability of CrCN coatings on SS304 in 0.5 M NaCl solution, whereas the opposite result on K340 in 0.5% NaCl solution was reported by Kaciulis et al. [21]. It is worth noting that the carbon concentration of CrCN coatings in Ref. [20] has not been reported, while that of CrCN coatings in Ref. [21] varied in the range of 55.4 at.% to 65 at.%. Thus, the totally contradictory results in Refs. [20,21] might be caused by the different carbon concentrations. In other words, the electrochemical properties of CrCN coatings were strongly dependent on carbon concentration. However, the influence of carbon concentration on the electrochemical properties of CrCN coatings in SBF has not yet been investigated systematically.

In here, the CrCN coatings with varied carbon concentrations (15.4–75.0 at.%) were deposited on 316 L steel disks using unbalanced magnetron sputtering via adjusting the carbon target current. The electrochemical characteristics of CrCN coatings in SBF were investigated using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests, and then the influence of carbon concentration on the electrochemical characteristics of CrCN coatings in SBF was outlined.

2. Experiment details

2.1. Fabrication of CrCN coatings

316 L disks with composition in Table 1 were selected as substrates (Ø30 × 4 mm), and polished to a roughness (R_a) of 30 nm by a

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Table 1
Specific chemical composition of 316 L stainless steel.

Composition	C	Si	Mn	P	S	Ni	Cr	Mo	Fe
Mass fraction (wt.%)	0.02	0.65	1.70	0.03	0.01	12.0	17.5	2.5	Balanced

Table 2
Deposition parameters of CrN and CrCN coatings.

Parameter	Figure	Thickness
Chamber pressure	0.23 Pa	–
Temperature	Room temperature	–
Bias voltage	−60 V	–
Rotating speed of holder	10 rpm	–
Current of chromium target	8 A	–
Current of graphite target	0 A CrN	1.00 μm
	1 A CrCN(1)	1.04 μm
	2 A CrCN(2)	1.74 μm
	3 A CrCN(3)	2.19 μm

metallographic polishing machine (UNIPOL-820). After being ultrasonically cleaned in ethanol and deionized water, they were fixed on the holder inside a chamber. Before deposition, Ar^+ plasma at a bias voltage of −450 V was applied to intensively clean and activate 316 L disks for 30 min. Under an atmosphere of Ar and N_2 gases, CrCN coatings were fabricated by sputtering chromium and graphite targets simultaneously (UDP-650, Teer Coatings Limited, UK). In this case, a pure Cr adhesive layer (about 0.2 μm) was deposited beforehand to enhance adhesive strength, and the detailed deposition parameters are listed in Table 2. In next section, the CrCN coatings deposited at the graphite target currents of 1A, 2A and 3A would be denoted as CrCN(1), CrCN(2) and CrCN(3) coatings, while pure CrN coating was also deposited for comparison.

2.2. Microstructure characterization of CrCN coatings

The morphology and thickness of CrCN coatings were observed and measured using a field emission scanning electron microscope (FE-SEM) (Philips FEG-XL30), while bonding structure and composition were characterized via Raman spectroscopy (InVia 2000, Renishaw) and X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220-iXL Al Kα), respectively. The excitation wavelength of Raman spectroscopy was 514 nm with exposure time of 10 s, and the power of the excitation was 2.60 mW with a spot diameter of 1 μm. As regards XPS, the spectra were deconvoluted with XPS PEAK 4.1 software with the reference energy of 284.8 eV for C_{1s} peak. Then, the corresponding N_{1s} spectrum was fitted under a Shirley background type, and the ratio of Lorentzian to Gaussian was 20%. Besides, the electrical resistivities of CrCN-coated and uncoated 316 L disks were measured by a four point probe technique (KDY-1, KunDe Technology Co., Ltd.).

2.3. Electrochemical tests of CrCN coatings

A standard three-electrode electrochemical cell was used, which consisted of a saturated calomel reference electrode (SCE), a platinum wire counter electrode and working electrodes of specimens. At first, open circuit potential (OCP) was recorded immediately since the immersion of specimen in SBF. When OCP measurement had been done for 1 h, electrochemical impedance spectroscopy (EIS) was conducted at OCP with an AC excitation of 10 mV from 1 mHz to 100 kHz. The duration of each EIS measurement lasted for about 2.5 h, and the EIS measurement was repeated for three times by using a new sample in fresh solution to ensure the reliability of the data.

Table 4
Element concentrations detected by XPS and electrical resistivities measured by four point probe technique for different samples.

Samples	Cr (at.%)	C (at.%)	N (at.%)	Electrical resistivity ($\Omega\cdot mm^2/m$)
316 L	–	–	–	0.71
CrN	60.1	0.00	39.9	0.66
CrCN(1)	64.2	15.4	20.4	0.75
CrCN(2)	23.1	52.6	24.3	0.94
CrCN(3)	9.5	75.0	15.5	0.82

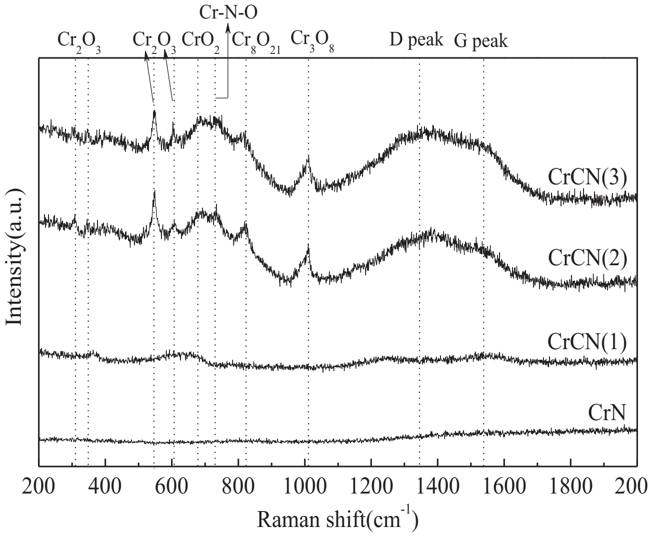

Fig. 1. Raman spectra of CrCN coatings deposited at different graphite target currents.

$$C = -\frac{i}{\omega Z''} = -\frac{i}{2\pi f Z''}. \tag{1}$$

Then, interfacial capacitance C was obtained using Eq. (1), where Z'' is the imaginary part of impedance, and f is the AC frequency in Hertz [22]. Subsequently, potentiodynamic polarization test was carried out by polarizing specimens in anodic direction from −0.8 V to 0.8 V with a sweep rate at 20 mV/min, and each polarization test lasted for about 1.4 h. All the above-mentioned measurements were carried out at room temperature in simulated body fluid (SBF) with pH 7.4, of which the detailed formula is listed in Table 3 [23]. After measurement, EIS data were fitted according to equivalent circuit via ZsimpWin software. Besides, corrosion potential (E_{corr}) and corrosion current density (j_{corr}) were deduced from the Tafel plot via extrapolation method.

$$R_p = \frac{\beta_a \beta_c}{2.303 j_{corr}(\beta_a + \beta_c)} \tag{2}$$

Then polarization resistance (R_p) was obtained using Stern–Geary Eq. (2) [24,25], where the β_a and β_c are the Tafel anodic and cathodic slopes.

Table 3
Formula of simulated body fluid.

Compound	NaCl	$NaHCO_3$	KCl	$K_2HPO_4\cdot 3H_2O$	$MgCl_2\cdot 6H_2O$	$CaCl_2$	Na_2SO_4	$(CH_2OH)_3CNH_2$
Concentration (g/L)	7.996	0.35	0.22	0.228	0.305	0.278	0.071	6.057