Hydrothermal synthesis of Ag-ZrO₂/r-GO coating on CoCrMo substrate L.J. Zhao ^{a,b}, W. Zai ^{a,b}, M.H. Wong ^a, H.C. Man ^{a,*}

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Abstract

A simple hydrothermal method was used to synthesize silver-doped zirconia-reduced graphite oxide (Ag-ZrO₂/r-GO) composite coating on CoCrMo, an alloy commonly used in artificial hip joints. The Ag-ZrO₂/r-GO coating is mainly intended to extend the service life of artificial hip joints via a rational coating design, which consists of three components, namely, a ceramic component ZrO₂, a friction reducing component r-GO, and an antibacterial agent Ag. After hydrothermal treatment in Zr(SO₄)₂·4H₂O solution containing GO at 200 °C for 24 h, ZrO₂/r-GO coating of about 12.5 µm thick was formed on CoCrMo substrate. Ag was incorporated subsequently by soaking in AgNO₃ solution and calcination was carried out to improve the adhesion of the coating on CoCrMo substrate.

Keywords: Hydrothermal method; Ag-ZrO₂/r-GO; CoCrMo implant

1. Introduction

CoCrMo alloy is the most popular femoral head material in artificial hip joint by virtue of its good mechanical properties combined with good corrosion resistance in body fluid [1]. The femoral head is ball-shaped and fits into a cup lined with UHMWPE (ultrahigh-molecular-weight polyethylene) to form a ball-and-socket joint. Thus the femoral head and the liner are in constant contact and under abrasive wear. Due to constant abrasion and other types of mechanical stress, the average life of artificial hip joints is limited to about 15 years. Pre-mature failure and complications arising from various causes are not uncommon. Surface treatment of CoCrMo to reduce friction and wear in the CoCrMo-UHMWPE pair is an effective means to extend the service life of artificial hip joints. Various coating techniques to enhance the wear resistance of CoCrMo have been reported in the literature [2-6]. The present study attempts to employ a new route, via simple hydrothermal treatment, to coat silver-doped zirconia-reduced graphite oxide (Ag-ZrO₂/r-GO) on CoCrMo substrate. The ZrO_2 in the coating is expected to increase the hardness and hence the wear resistance of CoCrMo, while the addition of GO would reduce the wear of UHMWPE and Ag is incorporated in the coating as an antibacterial agent. In this short paper, only the synthesis and characterization of the coating will be reported. Detailed study on the wear performance and antibacterial function will be reported in future studies.

2. Materials and method

CoCrMo plates (30 x 15 x 3 mm) with chemical composition of Co-28Cr-6Mo (wt.%) according to ISO 5832-12:2007(E) for implants were used as substrate. The CoCrMo plates were grinded successively with SiC papers from 320 to 2000 grit and then ultrasonically cleaned in an ethanol bath and rinsed using distilled water. 0.01 g of GO (diameter of 10-50 µm and thickness of 3.4-8 nm) and 0.004 g of glucose were dispersed in 65 mL of distilled water and sonicated for 70 minutes, and then 15 mL of Zr(SO₄)₂·4H₂O solution was added. Subsequently, the solution mixture and CoCrMo plate were put in an autoclave and hydrothermally treated at 200 °C for 24 h. To increase the thickness of the coating, the hydrothermal process was repeated once more. After that, the sample was washed with distilled water and dried at room temperature. The hydrothermally treated sample was then soaked in AgNO₃ solution at room temperature for 12 hours, followed by calcination in N2 atmosphere at 600 °C for 2 hours. The synthesis route is schematically summarized in Fig. 1.



Fig. 1. Schematic illustration for the synthesis of Ag-ZrO₂/r-GO coating on CoCrMo.

The morphology and structure of the Ag-ZrO₂/r-GO coating were characterized by

scanning electron microscopy, and X-ray diffractometry, FTIR spectroscopy and

Raman spectroscopy at an excitation wavelength of 647 nm.

3. Results and discussion

Under hydrothermal condition ZrO2 was firmed according to

$$Zr(SO_4)_2 4H_2O = ZrO_2 + 2H_2SO_4 + 2H_2O$$

In the hydrothermal process, glucose was added as it provided abundant –OH radicals, which enhanced the interaction between GO and ZrO₂ since Zr⁴⁺ ions could then easily anchor covalently to GO through the surface functional groups of GO [11]. During the hydrothermal process, GO was transformed into r-GO due to deoxidation. Finally, ZrO₂/r-GO grew on the surface of CoCrMo during the hydrothermal process. Ag⁺ ions were adsorbed on the ZrO₂/r-GO when the coated sample was soaked in AgNO₃ solution at 0.01 mol L⁻¹. By calcination at 600 °C for 2 h, the adhesion between Ag-ZrO₂/r-GO and CoCrMo was also improved.

To verify the presence of ZrO_2 and r-GO on CoCrMo substrate, Raman studies were performed, with results shown in Fig. 2(a). The peaks between 500-1200 cm⁻¹ are mainly due to the presence of ZrO_2 [16]. The Raman peaks at 1354 and 1593 cm⁻¹ are attributed to the defect-induced D band arising from the double-resonance excitation of phonons close to the K-point in the Brillouin zone and the G band arising from the optical E_{2g} phonons at the Brillouin zone center, respectively, indicating the presence of r-GO.



Fig. 2. (a) Raman spectrum and (b) FT-IR spectra of Ag-ZrO₂/r-GO

The FT-IR spectra in Fig. 2(b) further support the presence of ZrO_2 and r-GO in the Ag-ZrO₂/r-GO coating by comparing with the FT-IR spectra of ZrO_2 and GO. The peaks below 700 cm⁻¹ are associated with the characteristic peaks of ZrO_2 [17]. The peaks at 1739 and 1403 cm⁻¹ belong to the oxygen-containing functional groups derived from r-GO [18], while the shifting and the decreasing intensity are due to the reduction of GO to r-GO. The surface morphology of the Ag-ZrO₂/r-GO coated is shown in the SEM micrograph in 3(a).



Fig. 3 Ag-ZrO₂/r-GO on CoCrMo: (a) SEM image of surface, (b) cross-section and (c) EDS spectra.

Evenly distributed cracks are present on the surface. These cracks would provide room for temporarily storing wear debris, which would otherwise act as a third body and accelerate wear between the CoCrMo femoral head and UHMWPE liner, leading to early failure of implant. From the tilted view of the cross section of Ag-ZrO₂/r-GO (Fig. 3(b)), it could be observed that a uniform and flat Ag-ZrO₂/r-GO coating was grown on the CoCrMo substrate, with a thickness of around 12.5 µm (SEM stage has a 45° tilt). During the calcination process, the Ag⁺ ions were reduced to Ag by carbon as evidenced by the EDS spectra in Fig. 3(c).

4. Conclusions

A simple hydrothermal method combined with calcination in N₂ atmosphere was used to coat Ag-ZrO₂/r-GO on CoCrMo substrate. An adherent Ag-ZrO₂/r-GO coating of about 12.5 μ m thick with evenly distributed cracks was formed on CoCrMo substrate. In this composite coating, ZrO₂ is expected to serve as a hard ceramic component against abrasive wear, and graphite oxide is expected to reduce the coefficient of friction. Ag is added to function as an antibacterial agent, which is important in implant applications.

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