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Co-ZrO_2 electrodeposited composite coatings exhibiting improved micro hardness and corrosion behavior in simulating body fluid solution

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ABSTRACT

The aim of this work was the deposition of zirconium oxide bioceramic particles in cobalt matrix within the research work aimed at obtaining metal matrix composite coatings (MMC) under direct current and the evaluation of their protective properties. The cobalt/zirconia micro structured composite coating containing bioceramic of ZrO_2 dispersed phase was prepared using direct current (DC) electrodeposition method. The surface morphology, cross section and anti-corrosion property in SBF solution of the obtained Co/ZrO_2 composite films, are characterized using optical microscopy, scanning electron microscopy (SEM) together with energy dispersive spectroscopy (EDS) system, atomic force microscopy (AFM), ultrahigh-micro-topography, linear polarization and electrochemical impedance spectroscopy (EIS) techniques. The results indicate that, ZrO_2 particles are uniformly dispersed into Co matrix and influence the surface microtopography, microhardness and corrosion behavior of composite coatings obtained. Coating thickness increases with increased current density as well as the surface roughness and microhardness. At the same time, the results obtained by polarization curves and EIS methods show that, when compared with the traditional polycrystalline Co film, the obtained Co/ZrO_2 composite film exhibits the enhanced corrosion resistance in SBF solution.

1. Introduction

In recent years much attention has been focused on the research and development of metal matrix composite coatings (MMC) because such materials offer outstanding mechanical and multifunctional properties. These composite coatings possess enhanced properties such as wear, corrosion and oxidation resistance, dispersion hardening or self-lubrication relative to pure metal, so that they can protect the metal substrates more effectively against severe environments during operation [1] better electro catalytic activity [2–10]. The MMC can be produced through a number of routes including metal processing, powder metallurgy, electrodeposition techniques, etc. [11]. MMC can be prepared by electrodeposition technique by the co-deposition of fine ceramic or polymer particles in a metal matrix from electrolytic baths. Electrodeposition is a low-temperature process to manufacture composite coatings in a single step without secondary treatment. Composite electroplating is a method of co-depositing insoluble dispersed particles of metallic or non-metallic compounds with metals or alloy in a plating bath, to improve the material coating properties such as corrosion resistance, lubrication, hardness or wear-resistance [13,12,11,10]. One of the constant goals of the composite coatings is the production of coatings with enhanced properties such as higher micro hardness, corrosion resistance and wear resistance. The coatings of this nature are being widely used for surface protection of various metal articles for industrial and biomedical users. There are reports on the incorporation of nanosized SiC, ZrO_2, Al_2O_3, TiO_2, La_2O_3 and CeO_2 in the nickel matrix forming composites [3,5,12–19]. The incorporated inert particles have played an important role in either enhancing the corrosion resistance or the wear resistance, many works being done on the Ni matrix. There are reports on the synthesis and properties of Ni–Al_2O_3 and Ni–ZrO_2 composite coatings [5,6,13]. However, to the best of our knowledge there are no reports on the synthesis and properties of Co composite coatings containing an oxide powder like ZrO_2. Among the oxide ceramics, the silicon carbide, alumina and mixed alumina–zirconia systems are by far the most useful ceramics to prepare composite coatings. Because of their excellent mechanical properties, including strength, toughness and wear resistance, as well as the thermal and chemical stability, the alumina and zirconia composite coatings have been widely used in the engineering and biomedical fields for materials such as structural ceramics, thermal barrier coatings and total hip replacement [20]. The structure and properties of the final composites are strongly dependent on the properties of the initial precursors and composite powders, such as their homogeneity, particle size distribution and

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Table 1
Operating parameters for pure Co and Co/ZrO_2 composite electroplatings.

Deposition parameters	Amount
$CoSO_4 \cdot 7H_2O$	300 g/L
$CoCl_2 \cdot 6H_2O$	50 g/L
H_3BO_3	30 g/L
pH	4.5
ZrO_2	0–50 g/L
Temperature	20–25 °C
Current density 10 mA/cm^2	23–96 mA/cm^2
Stirring speed	300 r.p.m.
Electroplating time	30–60 min

phase purity. When organized well, the benefits of the individual components play a synergistic role in the final properties of the composite coatings obtained [21–28]. Metals are generally chosen for their inert qualities whereas ceramics may offer bioactivity, resorption as biomaterials or hardness, wear-corrosion resistance as hard facing materials for industrial use. Cobalt is a used material for protection of steel against corrosion, and it is more corrosion resistant than steel in most natural atmospheres. Zirconium oxide (zirconia), ZrO_2, is considered nowadays as one of the most important ceramic materials in modern technology. It has a wide range of industrial applications because of the excellent combination of high flexural strength and good fracture toughness, together with its stability at high temperature and its optimal dielectric constant of around 20. It is used for metal coatings, as a refractory material in insulation, abrasives, enamels and glazes, as support material for catalysis and, due to its ion conductivity, it is also applied in gas sensors, oxygen pumps for partial pressure regulation and high temperature fuel cells. Further, ZrO_2 is one of the most radiation-resistant ceramics currently known and therefore has a particular importance in the nuclear industry. Combining the cobalt as metal matrix with zirconium oxide as dispersed phase the resulting composite coating could give some interesting properties with possibilities to use them as biomaterials or wear–corrosion resistant coatings. Moreover there are very few references in the literature regarding the electrodeposition of ceramic particles in the cobalt matrix [29,30]; many of studies are done on electrodeposited nickel matrix [13–19,22–28].

In the present work, efforts have been made to the synthesis and characterization of surface modified cobalt with ZrO_2 micro sized ceramic particles (mean diameter 5 μm, with a size dispersion between less than 1 μm and 10 μm), in order to obtain a coating as biocompatible material or industrial use presenting at the same time good corrosion and micro hardness performances. In the literature, there are very limited studies in the dispersion of inert particles in the cobalt matrix and its influence on the overall properties.

2. Experimental

2.1. Preparation of Co/ZrO_2 composite layers

The composite materials were obtained by using dispersed micro sized ZrO_2 particles and cobalt plating electrolyte based on cobalt chloride and cobalt sulfate, using as support for coating deposition on stainless steel (304 L). The compositions of the solution and operating parameters for electrodeposition are shown in Table 1. A bath solution without additive was used because they could give reactions with zirconium oxide (ZrO_2) particles and the results could not be interpreted properly. Analytical reagents and double-distilled water were used to prepare the plating solutions. Before deposition, the electrolyte was stirred for 24 h to ensure a good dispersion avoiding the agglomeration of particles suspended in the electrolyte.

A double-electrode cell was employed to carry out electroplating experiments. The cathode, made of 304 L stainless steel foils with an exposed area of 5 cm^2, was positioned in vertical plane with anode. A similar dimension of pure cobalt foil was used as the anode. The distance between cathode and anode was fixed at 4 cm. Schematic illustration of the electrochemical deposition process is shown in Fig. 1. Pure dispersed zirconium oxide (ZrO_2) at concentrations of 20–50 g/L was suspended in the electrolysis bath. The particles have had different shapes with an average particle size of 5 μm (size dispersion between less that 1 μm and 10 μm), Fig. 1. The particles were kept in suspension by magnetic stirring at a rotation speed of 300 r.p.m. The cobalt foil was used as an anode to make sure that the cobalt ions concentration remains constant during the electrodeposition.

Prior to plating, the stainless steel cathode was polished with emery papers, rinsed in distilled water and ethylic alcohol. The electrolyte was stirred by magnetic stirring in order to prevent particles sedimentation. For comparison, cobalt films were also deposited in the same electroplating conditions but without addition of ZrO_2 bio ceramic particles.

The surface morphologies, cross section thickness and the components of the coatings were studied, using SEM (Jeol JSM-T220 A Scanning Microscope Oxford Instrument) with energy dispersive X-ray analysis (EDS) attachment. Thickness of pure cobalt and composite deposits were verified by measuring the weight before and after deposition and also by light microscopy on cross section of electrodeposited coatings. Coating roughness was measured with an optical fiber (light microscopy—Stil). On every electroplated surface

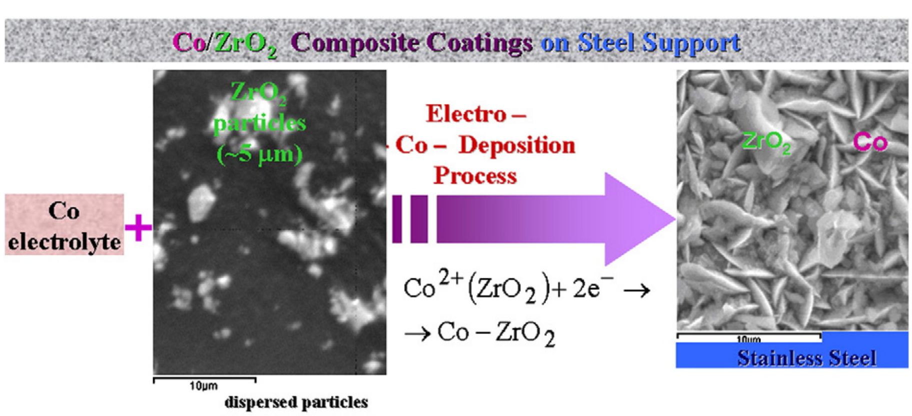

Fig. 1. Schematic illustration of the electrochemical deposition of ZrO_2 bioceramic particles with cobalt to obtain composite coatings.