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Preparation and characterization of the electrodeposited Cr–Al_2O_3/SiC composite coating

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ABSTRACT

To increase the SiC content in Cr-based coatings, Cr–Al_2O_3/SiC composite coatings were plated in Cr(VI) baths which contained Al_2O_3-coated SiC powders. The Al_2O_3-coated SiC composite particles were synthesized by calcining the precursor prepared by heterogeneous deposition method. The transmission electron microscopy analysis of the particles showed that the nano-SiC particle was packaged by alumina. The zeta potential of the particles collected from the bath was up to +23 mV, a favorable condition for the co-deposition of the particles and chromium. Pulse current was used during the electrodeposition. Scanning Electron Microscopy (SEM) indicated that the coating was compact and combined well with the substrate. Energy dispersive X-ray analysis of Cr–Al_2O_3/SiC coatings demonstrated that the concentration of SiC in the coating reached about 2.5 wt.%. The corrosion behavior of the composite coating was studied by potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The data obtained suggested that the Al_2O_3/SiC particles significantly enhanced the corrosion resistance of the composite coating in 0.05 M HCl solution.

1. Introduction

Composite coatings produced by electrodeposition of particles such as carbides or oxides have been used to improve the corrosion resistance and hardness of the coatings. According to the prior studies [1,2], the presence of ceramic particles in the electrolyte leads to extensive modifications of the structure and microstructure of the metal matrix even if they are not incorporated into the deposit. Addition of ZrO_2, Al_2O_3, WC, TiC and other ceramic particles can significantly improve the wear resistance and corrosion resistance of Ni coating [3–6]. Micron sized SiC particles (5 and 0.3 μm) have been used to enhance the corrosion resistance of a Ni coating as a result of the change in grain morphology and texture of the coating [7,8]. Also, SiC, WC, TiO_2, MoO_2 and other ceramics have been incorporated into Cr-plating coating to improve the properties of the composite coatings [9,10]. Previous studies shows that MoO_2 and TiO_2 can reduce the inner stress of the Cr-composite coating, and adding WC particles can ameliorate the coating morphology thus enhance the corrosion resistance [11,12].

The electrodeposition efficiency of SiC particles is significantly influenced by the electrostatic attraction that exists between the particles and the cathode surface [13]. In accordance with literature data [14], 0.3–0.4 wt.% of SiC is sufficient to remarkably enhance the wear resistance of a Cr coating (about 1.5–2 times). But the SiC content in chromium coating cannot be increased to a satisfactory degree due to the poor electrostatic attraction between SiC particle and the cathode in Cr(VI) plating bath. The agglomeration of fine SiC powders also reduces the efficiency of the codeposition. Among the parameters that affect the co-electrodeposition, the zeta potential of the ceramic particles may be the key factor to influence the amount of the second phase in the coatings [15].

Also, the deposition current has an important effect on the co-electrodepositon of metal–ceramic composite coatings [16,17]. Beside the commonly used direct current deposition method, pulse current may be used to prepare more homogeneous composition and to improve the deposition efficiency of the ceramic particles during the co-electrodeposition of metal–ceramic composite coating [18–20].

In the present work, α-Al_2O_3-coated SiC powders were prepared by sol-gel method and used as the dispersed particles in Cr(VI) plating bath. A Cr–Al_2O_3/SiC composite coating was fabricated through pulse electrodeposition. The aim of this paper was to develop a method to increase the content of SiC in the Cr coating during the co-electrodeposition and to investigate the effects of modification of nano ceramics on the properties of the coating by co-electrodeposition.

2. Experimental

The samples were plated on martensitic steels with dimensions of 45 mm × 30 mm × 2 mm and the chemical composition

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Table 1
Chemical composition of the steel employed in this experiment in wt%.

C	Mn	P	S	Ni	Cr	V	Mo	Si	Fe
0.12	0.53	0.018	0.005	0.06	9.11	0.08	0.01	0.12	Balance

of this steel was shown in Table 1. The electrolyte contained 130 g dm^{-3} of chromic anhydride (CrO_3), 4 g dm^{-3} of surfactant Fs-10 and a certain amount of fluoride. In addition, 12 g dm^{-3} of α-Al_2O_3/SiC powder was dispersed in the bath.

The Al_2O_3/SiC particles with the size of about 300 nm were ball-milled from the calcined $Al(OH)_3$/SiC precursor which was prepared by heterogeneous precipitation. 40 mol% of nanosized SiC particles were dispersed in ethanol via certain surfactant. The suspension was then added into 0.4 mol/L aluminum nitrate aqueous solution. The pH was adjusted to 8.5 by adding diluted NH_4OH into the solution when the mixture was being stirred for 30 min. Finally, the precursor of $Al(OH)_3$ coated SiC was leached, dried at 80 °C and calcined at 1150 °C for 2 h to obtain the α-Al_2O_3/SiC powders.

Prior to electrolysis, the solution was ultrasonic dispersed with a power density of 2800 W dm^{-3} for 30 min and mechanically stirred for over 3 h. The steel substrates were mechanically polished, degreased with acetone, rinsed thoroughly, activated in diluted HCl (1:1) solution and then rinsed with distilled water. The steel cathode with a vertical anode parallel to it was set in the plating bath with a volume of 300 cm^3. The samples were pulse-plated at a current density of 40 A dm^{-2} and a constant temperature of 55 °C with the stirring rate of 200 rpm.

The cross-section and the surface morphology of the composite coatings were examined using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) after the specimen was cleaned by ultrasonic in ethanol. The phase analysis of the composite coating was performed by X-ray diffraction (XRD) using an X-pert PRO diffractometer (Panalytical BV, Almelo, Holland) with Cu Kα radiation (λ = 0.154 nm).

The transmission electron microscopy (TEM) images of the Al_2O_3/SiC particles were obtained using a Tecnai G2 20 TEM (FEI Corp., Holland). To investigate the effect of modification (coated with Al_2O_3) on the dispersibility and the isoelectric point of the composite particles, the zeta potential of the composite particles was measured using a zeta potential analyzer (ZetaProbe^{TM}, Colloidal Dynamics Corp., USA). Before measurement, the particles suspension was diluted in deionized water. For each pH value, the zeta (ζ) potential was measured for five times and the average was recorded.

Polarization curve and electrochemical impedance spectroscopy (EIS) were used to evaluate the electrochemical properties of the samples. The coating samples were embedded in epoxy resin leaving an area of 1 cm^2 exposed as working electrodes. The electrochemical properties of the composite coating were studied in a conventional three-electrode electrolyte cell system with Pt as an auxiliary electrode and a saturated calomel electrode (SCE) as reference. All the experiments were conducted in 0.05 M HCl at 25 °C. The polarization curves were scanned from −500 mV to 500 mV vs the open circuit potential (OCP) at a scan rate of 1 mV s^{-1} after a steady-state of the working electrode in the solution had been established. The impedance measurements were performed at open-circuit potentials with 10 mV sinusoidal perturbations in frequency range from 100 kHz to 10 mHz. The spectra were recorded. The electrochemical impedance spectra were analyzed using commercial software ZSimpWin.

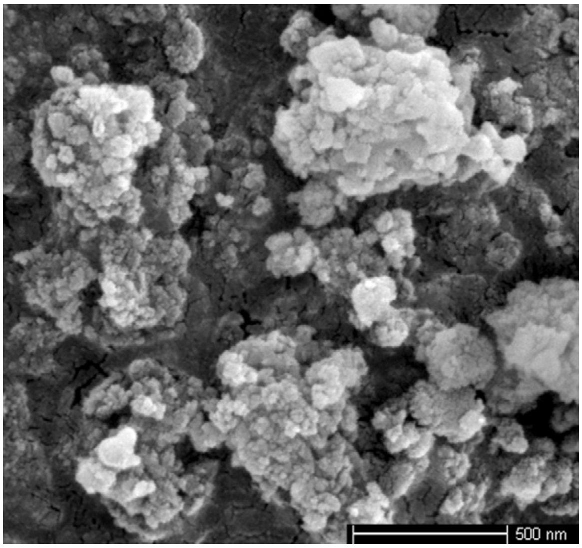

Fig. 1. FSEM image of the Al_2O_3 coated SiC particles after ball-milled.

3. Results and discussion

3.1. Particle characterization

Fig. 1 presented the field emission scanning electron microscopy (FSEM) image of composite $A1_2O_3$/SiC particles after being ball milled. It could be observed that the size of the composite particles (aggregated from nanocrystals of about 60 nm) was in the range of 100–400 nm. The microscopic structure of the nano composite particles was determined by TEM (Fig. 2). The individual nanoparticles were irregular with a diameter between 30 and 60 nm. The particles mainly appeared in aggregates with dimension of about 200 nm in which the nano-SiC particles were coated by thin Al_2O_3 layer. Researches showed that the aggregate size of particles in the plating bath mainly depended on the composition and the pH of the electrolyte [21]. At the working pH of the Cr plating bath in this study, the size of Al_2O_3/SiC agglomerate was measured to be 300 nm.

As the ζ potential of the Al_2O_3/SiC nanoparticles in hexavalent chromium electrolytes was higher than that of SiC particles, the composite particles exhibited higher deposition efficiency. Fig. 3

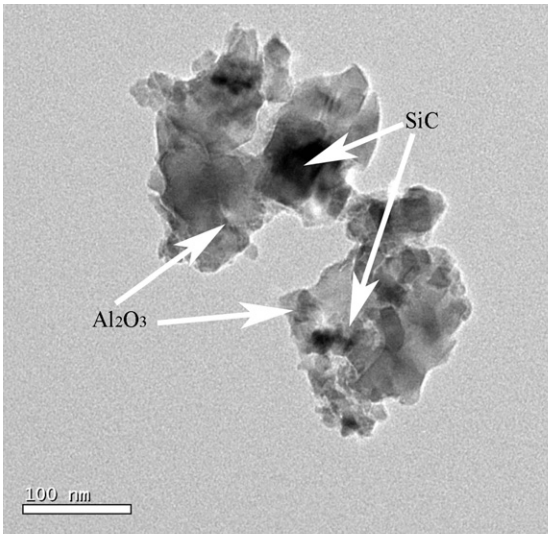

Fig. 2. TEM image of the Al_2O_3 coated SiC particles.