

Electrochemical Corrosion Behavior of Carbon Nanotube-Doped Hard Chromium Coatings Electrodeposited from Cr(III) Baths

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Homogeneous chromium-multiwalled carbon nanotube (Cr-MWNT) composite coatings were electrodeposited from trivalent chromium [Cr(III)] electrolyte containing MWNTs under ultrasonic agitation. The microstructure, mechanical properties, and electrochemical corrosion behavior of Cr-MWNT composite coatings were investigated with a field-emission scanning electron microscope, an X-ray photoelectron spectrometer, a Vickers hardness indenter, and an electrochemical workstation. The introduction of MWNTs obviously improves the hardness and toughness of Cr coatings due to the "fiber reinforcement." Also, the electrochemical tests show that in H_2SO_4 solution MWNTs can provide a lot of active sites to accelerate the formation of Cr_2O_3 passive film, and in KOH solution they can adsorb $Cr_n(OH)_x$ polymer film to decrease the corrosion rate of Cr composite coatings. © 2009 The Electrochemical Society. [DOI: 10.1149/1.3073550] All rights reserved.

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Carbon nanotubes (CNTs) exhibit excellent properties such as high mechanical properties, unique electrical and thermal conductivity, ¹⁻⁵ as well as adsorbability.⁶ Therefore, CNTs could be used as a dopant in various matrices to improve electrical, mechanical, or thermal properties.⁷⁻⁹ Indeed, CNT composites such as polymer-,¹⁰⁻¹² ceramic-,^{13,14} and metal-CNT^{15,16} composite materials have been extensively studied for their mechanical, thermal, electrical, and optical properties.^{17,18} Nevertheless, CNTs may also play an important role in the electrochemical corrosion process of anticorrosion composite coatings, due to their adsorbability, nanoscale effect, and electrical conductivity. Unfortunately, the research on the electrochemical corrosion behavior of metal-CNT composite coatings has been overlooked. Electrodeposited Cr coatings are widely used for antiwear, decoration, and anticorrosion. Hence, in this work, the hard chromium-multiwalled CNT (Cr-MWNT) composite coatings are electrodeposited from the "environmentally acceptable" Cr(III) electrolyte containing MWNTs. The comparison of the electrochemical corrosion behavior of Cr-MWNT composite coatings to that of pure Cr coatings is conducted in order to reveal the role of MWNTs in the electrochemical corrosion process.

Experimental

Electrodeposition of Cr-MWNT composite coatings.— Cr-MWNT composite coatings (20 μ m thick) were deposited from Cr(III) baths composed of CrCl₃·6H₂O (200 g L⁻¹), HCOOH (32 mL L⁻¹), CH₃COOH (10 mL L⁻¹), NH₄Br (30 g L⁻¹), KCl (60 g L⁻¹), H₃BO₃ (30 g L⁻¹), and MWNTs (1 g L⁻¹) under ultrasonic agitation with a direct current density of 30 A dm⁻² and pH value of 2 at 35°C. MWNTs (98% purity, commercially obtained from Shenzhen Nanotechnologies Co., Ltd., China) are about 30–60 nm in outer diameter and 1–2 μ m in length. Copper plates with an area of 5 cm² were used as substrates. Dimensionally stable titanium anodes (commercially obtained from Xinxiang Future Hydrochemistry Co., China) with an area of 12 cm² were used in order to reduce the anodic oxidation of Cr(III). Before plating, the substrates were polished and "activated" in HCl solution with a concentration of 1.5 mol L⁻¹.

Characterizations.— A JSM-6701F field-emission scanning electron microscope (FE-SEM) (JEOL, Japan) was used to investigate the morphology of the Cr-MWNT composite coating surface and fracture section. Mechanical properties were measured by a Vickers hardness indenter. A Perkin-Elmer PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS) (Physical Electronics, USA) was used to determine the composition of products during the electrochemical process, using Al K α radiation (photon energy 1486.6 eV) as the excitation source. The XPS spectra were collected in constant analyzer energy mode at a chamber pressure of 10⁻⁸ Pa, pass energy of 29.4 eV, and resolution of ±0.2 eV. The corrections for the background, smoothing, and Gaussian deconvolution of XPS spectra were accomplished using appropriate software. Using a CHI760B potentiostat/galvanostat system, the potentiodynamic polarization was performed in KOH (50 g L⁻¹) and H₂SO₄ (mol L⁻¹) solutions, respectively, with an applied potential from -0.8 to 1.2 V_{SCE} and sweep rate of 0.01 V s⁻¹. All electrochemical measurements were carried out in a three-electrode cell, wherein a coated copper plate was used as working electrode and a platinum plate and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

Results and Discussion

Microstructure and mechanical properties of Cr-MWNT composite coatings.— The content of MWNT in the composite coatings is about 1 mass % determined by the energy-dispersive X-ray spectroscopy analysis tool attached to the FE-SEM. Figures 1a and b show the FE-SEM photos of the top and bottom surfaces of Cr-MWNT composite coating, respectively. MWNTs are nearly monodispersed in Cr matrix. Figure 1c shows the fracture section microstructure of Cr-MWNT composite coating, where MWNTs are also distributed uniformly in the body of the composite coatings.

Figure 2 demonstrates the indentations on specimens after being indented by the diamond indenter under different loads for 5 s. The hardness is about 8 GPa for pure Cr coatings and 10.5 GPa for Cr-MWNT composite coatings. On the pure Cr coating surface, some indention-induced cracks and collapses appear around the indentations. In contrast, on the Cr-MWNT composite coating surface, the areas of indentations are relatively small and no obvious cracks and collapses are found. Obviously, the introduction of MWNTs significantly increases the hardness and toughness of Cr coatings, which may be attributed to the "fiber reinforcement" of MWNTs.

The role of MWNTs in the electrochemical corrosion process of Cr coatings.— Figures 3 and 4 express the potentiodynamic polarization curves of the coatings measured in H_2SO_4 (1 mol L⁻¹) and KOH (50 g L⁻¹) solutions, respectively. As shown in Fig. 3, cathodic segments in the H_2SO_4 solution correspond to hydrogen evolution, ¹⁵ which can be expressed by two reactions as follows

$$\mathbf{H}^{+} + \mathbf{e} \to \mathbf{H}$$
 [1]

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Figure 1. FE-SEM photo of the (a) top surface, (b) bottom surface, and (c) fracture section of Cr-MWNT composite coatings.

$$H + H \rightarrow H_2$$
 [2]

The cathodic segment of curve 2 for Cr-MWNT composite coatings shifts to the positive potential direction compared to that of curve 1 for pure Cr coatings, indicating that the introduction of MWNTs into Cr coatings can accelerate hydrogen evolution.

The anodic segment of the potentiodynamic polarization curves, following an active-passive-transpassive form, corresponds to active dissolution and passivation processes of Cr coatings. The segments in areas A, B, C, and D marked in Fig. 3 are attributed to active dissolution of Cr metal, the formation of passive film, the stable passivation state, and the transpassivation stage, respectively. With respect to the anodic segment of pure Cr coatings, two waves in area A indicate the dissolution of Cr metal via two steps. Wave 1 is attributed to the electrochemical oxidation reaction (Eq. 3) of Cr and the precipitation reaction (Eq. 4) of Cr^{2+} and OH^- on the Cr surface as the result of electromigration

$$Cr - 2e \rightarrow Cr^{2+}$$
 [3]

$$Cr^{2+} + 2OH^- \rightarrow Cr(OH)_2$$
 [4]

 Cr_2O_3 is the primary component of the passive film on the Cr surface generated during the anodic electrochemical polarization.^{19,20}



Figure 2. Indentations on the (a) single Cr and (b) Cr-MWNT composite coatings after being indented by the diamond indenter under different loads for 5 s.



Figure 3. Potentiodynamic polarization curves of single Cr films and Cr-MWNT composite films measured in H_2SO_4 (1 mol L⁻¹) solution.



Figure 4. Potentiodynamic polarization curves of single Cr films and Cr-MWNT composite films measured in KOH (50 g L^{-1}) solution.

Thus, wave 2 is ascribed to the reaction as follows

$$2Cr(OH)_2 - 2e + 2OH^- \rightarrow Cr_2O_3 + 3H_2O$$
[5]

With a further potential shift to the positive direction, as shown in areas B and C, Cr_2O_3 completely covers the coating surface, as confirmed by current density decreasing first and then keeping constant in spite of further increase in potential. The critical passive current density is about 2.95×10^{-3} A cm⁻². When the potential is higher than 1.0 V, the electrochemical behavior enters the transpassivation stage.

Similarly, the anodic polarization of Cr-MWNT composite coatings also undergoes active-passive-transpassive process. But, the process of passive film formation is different from that of pure Cr coatings. The critical passive current density for Cr-MWNT composite coatings is 1.1×10^{-3} A cm⁻², about two times less than that of pure Cr coatings, and no current density drop occurs before the current density remains constant. This indicates that the active dissolution of Cr and the formation of passive film occur simultaneously in the case of Cr-MWNT composite coatings, which can be expressed by the following electrochemical reaction

$$2Cr - 6e + 3H_2O \rightarrow Cr_2O_3 + 6H^+$$
 [6]

Obviously, the passive film can be generated more easily on Cr-MWNT composite coatings than on pure Cr coatings. The reason is that MWNTs, with nanoscale diameter and good electrical conductivity, can provide a large number of active sites to accelerate the formation of passive film.

Figure 4 shows the potentiodynamic polarization curves in KOH (50 g L^{-1}) solution. The cathodic segment in KOH solution corresponds to the reduction of oxygen, which can be expressed by the reaction as follows

$$O_2 + 4e + 2H_2O \rightarrow 4OH^-$$
[7]

The cathodic segment of curve 4 for Cr-MWNT composite coatings shifts to the positive potential direction compared to that of curve 3 for pure Cr coatings. This indicates that oxygen is reduced more easily on Cr-MWNT composite coatings than on pure Cr coatings. MWNTs can adsorb oxygen in solutions,²¹ which is beneficial to the reduction of oxygen on the coating surface. In addition, the positive shift of the corrosion potential indicates that Cr-MWNT composite coatings exhibit better antiself-corrosion ability than pure Cr coatings.

In regard to the anodic polarization process, no obvious passivation occurs. Figure 5 shows the XPS analysis of the products after anodic polarization. In the XPS spectra of the Cr $2p_{3/2}$ band, the decomposed peaks located at about 577.0 and 574.5 eV are attributed to Cr in the form of chromium hydroxide and Cr in metal Cr, respectively.²²⁻²⁴ In the presence of OH⁻, the olation reaction²⁵⁻²⁷ tends to occur between chromium ion and OH⁻. Thus, the wave at about $-0.4 V_{SCF}$ is attributed to Reactions 8 and 9

$$Cr - 2e \rightarrow Cr^{2+}$$
 [8]

$$n\operatorname{Cr}^{2+} + x\operatorname{OH}^{-} \to \operatorname{Cr}_{n}(\operatorname{OH})_{x}^{2n-x}$$
 [9]

And, the wave near $-0.17 V_{\text{SCE}}$ is attributed to the following reaction

$$\operatorname{Cr}_{n}(\operatorname{OH})_{x}^{2n-x} - \operatorname{ye} \to \operatorname{Cr}_{n}(\operatorname{OH})_{x}^{2n+y-x}$$
 [10]

The $Cr_n(OH)_x$ polymer film with flocculent structure cannot cover the coating surface compactly and completely as Cr_2O_3 does. Accordingly, when $Cr_n(OH)_x$ polymer film is formed, the current density drops to a low value, but no obvious typical passivation occurs during the anodic polarization process. At the same potential, the current density in the anodic polarization process of Cr-MWNT composite coatings is about 10 times less than that of pure Cr coatings, which indicates that the dissolution rate of Cr-MWNT composite coatings is about 10 times less than that of pure Cr coatings in KOH (50 g L⁻¹) solution. The relatively low dissolution rate of Cr-MWNT composite coatings is attributed to the ability of MWNTs to



Figure 5. XPS analysis of the products on (a) Cr and (b) Cr-MWNTs after electrochemical tests.

adsorb $Cr_n(OH)_x$ polymer film, which can strengthen the adhesion of $Cr_n(OH)_x$ polymer film to the composite coatings to some extent.

Conclusions

The Cr-MWNT composite coatings were electrodeposited from trivalent Cr electrolytes containing MWNTs under ultrasonic agitation. The effect of MWNTs on the electrochemical corrosion processes of Cr coatings in H_2SO_4 (1 mol L⁻¹) and KOH (50 g L⁻¹) solutions were investigated.

In H₂SO₄ solution, MWNTs can provide a large number of active sites to accelerate the formation of passive film, due to their nanoscale diameter and electrical conductivity. Thus, Cr-MWNT composite coatings exhibit lower critical passive current density than that of pure Cr coatings. While in KOH solution, MWNTs can adsorb $Cr_n(OH)_x$ polymer film to alleviate the dissolution of Cr coatings. Accordingly, Cr-MWNT composite coatings exhibit a lower dissolution rate during the anodic polarization process than pure Cr coatings.

In addition, the introduction of MWNTs can significantly improve the mechanical properties of Cr coatings, which is attributed to the "fiber reinforcement" of MWNTs.

Therefore, MWNT is an excellent dopant to Cr coating to enhance its mechanical and anticorrosion properties significantly.

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