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High surface area coatings for hydrogen evolution cathodes prepared by magnetron sputtering

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ABSTRACT

A novel magnetron sputtering technique is described for the deposition of durable, high surface area metal and alloy deposits (thickness up to several microns) onto nickel and steel substrates. The materials deposited include platinum, nickel, nickel alloys and steels. The structure of the deposits is characterised and it is demonstrated that some high surface area coatings are efficient and effective electrocatalysts for hydrogen evolution in alkaline media and coated mesh electrodes have been tested in a modern water electrolyser configuration.

Introduction

High area electrode surfaces have an important role in modern electrochemical technology [1–3] since they allow performance goals to be achieved with lower energy consumption. This is particularly the case with energy intensive processes such as the chlor-alkali process and water electrolysis. Water electrolysis is one route to hydrogen production and hydrogen is predicted to have an increasing role as a fuel and energy storage medium in green energy economies [4,5]. There are substantial advantages in employing an alkaline electrolyte for water electrolysis and there are great opportunities for the development of non-precious metal electrocatalysts for both hydrogen and oxygen evolution [6]. Such electrodes must be low cost, stable in the cell operating conditions, robust and operate at high current densities with a low overpotential. High area nickel, nickel alloys and steels are candidates for such applications [6–12].

Similar to other Physical Vapour Deposition (PVD) processes, magnetron sputtering is fundamentally an environmentally benign process [13–17]. It requires no hazardous

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Table 1 – Comparison of the compositions of the deposits with those of the magnetron targets. Target compositions are taken from specification. % compositions of the deposits are determined by EDAX.

Element	Ni80Cr20		Monel 400		Hastelloy C276		Hastelloy C22	
	Target	Deposit	Target	Deposit	Target	Deposit	Target	Deposit
Cr	20.0	21.5			16.0	16.5	22.0	21.5
Ni	80.0	78.5	65.0	65.5	55.5	53.5	56.0	52.5
Fe			2.0	5.0	7.0	7.5	3.0	5.0
Cu			33.0	29.5				
Mn								
Mo					18.0	18.5	13.5	16.5
W					3.5	4.0	3.0	3.0
Co							2.5	1.5
Thickness		1.5 μm		1.4 μm		1.5 μm		1.5 μm

liquids or toxic/flammable materials and there are no noxious by-products which could result in air pollution or hazardous waste. This contrasts strongly with other common deposition processes such as Chemical Vapour Deposition (CVD), spraying and electroplating [18–20]. In addition, magnetron sputtering can lead to coatings with controlled and variable composition, good adhesion, crystalline structure, controlled, variable and uniform thickness [13–17] and such coatings can be achieved with a wide range of both substrates (metal, polymer, carbon cloth, glass, rubber, ceramics and wood in various forms including flat surfaces, meshes, powders, fibres and particles) and depositing materials (metals, alloys, oxides, nitrides and carbides as well as multilayered structures or mixtures) [21,22]. It is therefore well-suited to the fabrication of electrode coatings.

In this paper, a novel magnetron sputtering technique is described that allows the deposition of typically micron thick coatings with significantly increased surface areas. The details of deposition method and conditions refer to a recently published patent [23]. Metallic and alloy high surface area coatings (HSACs) have been achieved by changing the arrangement of the deposition system and the deposition parameters, including: magnetron configuration, working gases, deposition pressure, and the sputtering power. The advantage of this approach is illustrated by the preparation of coated nickel and steel meshes with coatings that are appropriate for high performance, hydrogen evolution cathodes in alkaline water electrolysers. A recent paper [24] has described the application of NiAl coatings prepared by PVD and used as cathodes in alkaline water electrolysis.

Experimental

Deposition conditions

Coatings were deposited using a Teer Coatings Ltd magnetron sputter ion-plating UDP 650 system [25]. Four targets (metal, alloy or compound) could be used during deposition processes. Table 1 shows the alloy target materials used in this work. Argon, or argon plus helium (both 99.999% purity and supplied by BOC Edwards), was used as the working gases. The distance between the target and the substrates was about 150 mm. The substrates could either be static or rotated, passing the targets at a controlled rotation speed of 1–10 rpm.

Nickel mesh (DeXmet Corporation, 4 Ni 6-040, 0.00400 nominal thickness, 0.00600 strand width, 0.04000 long diagonal of the diamond) or stainless steel 316L mesh (DeXmet Corporation, 4SS 5-050, 0.00400 nominal thickness, 0.00500 strand width, 0.05000 long diagonal of the diamond) were used as substrates for the cathode and anode electrodes respectively. 316L stainless steel (ASTM A240) and M42 hardened high speed tool steel (ASTM A600, RHC 65 ± 1) flat test pieces were used as witness samples for thickness measurement and adhesion tests. Si wafer pieces were used as substrates for scanning electron microscope (SEM) analyses.

The substrates were cleaned with acetone for 15 min immersed in an ultrasonic bath before drying and mounting into deposition chamber. The chamber pressure before deposition was less than 3.0×10^{-5} Torr (4.0×10^{-3} Pa). The substrates were plasma-ion-cleaned prior to deposition for 15 min, under an argon pressure of 3.0×10^{-3} Torr (0.4 Pa), and an average approximately −400 V substrate bias from a pulsed direct current (DC) power supply of 250 kHz pulse frequency and 500 ns pulse duration.

HSACs were deposited as a single layer or on top of a smooth dense layer, i.e. a dense under-layer was first deposited via a conventional sputtering processes, with argon as the working gas at a pressure of ~0.4 Pa (~3 mTorr) and −35 ~ −55 V substrate bias. HSACs were deposited at a relatively high deposition pressure of 10.0 Pa (75.0 mTorr) achieved by adjusting the throttle valve of the pumping system, with an Ar and He mixture as the working gas (Ar/He flow ratio = 1:2), a type I unbalanced magnetron [15,26] and a negative self-bias from the floating potential of the substrates. Pt, Ni, Mo (all 99.5% purity), 316L stainless steel, Monel alloy 400, and Hastelloy C276, C22 and B3 (all industrial grade) were used as sputtering targets. The metal or alloy target was connected to a DC power supply and a current of 5.5 A was applied during deposition processes. The thickness of the coatings was controlled by changing the duration of the deposition. No additional heating was applied during deposition process and the substrate temperature remained below 473 K.

Thickness measurement

Coating thickness was assessed using a ball crater taper cross-section method (ASTM E1182-93) on coatings deposited on steel substrates. Three measurements were taken for each sample and the average values are reported.