Surface & Coatings Technology xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Electrodeposited Co-W alloys and their prospects as effective anode for methanol oxidation in acidic media

E. Vernickaite [a], N. Tsyntsaru [a,b], H. Cesiulis [a,*]

[a] *Vilnius University, Dept. Phys. Chem., Naugarduko str. 24, Vilnius, Lithuania*
[b] *Institute of Applied Physics of ASM, Academiei str. 5, Chisinau, Republic of Moldova*

ARTICLE INFO

Article history:
Received 31 March 2016
Revised 15 July 2016
Accepted in revised form 16 July 2016
Available online xxxx

Keywords:
Electrodeposition
Cobalt-tungsten alloys
Anode
Methanol electrooxidation
Annealing

ABSTRACT

Electrodeposited Co-W alloys having different composition and structure were tested as anodes for methanol electrooxidation. The structure of electrodeposited Co-W alloys having various tungsten content is either nanocrystalline (3 and 18 at.% of W) or "amorphous-like" (30 at.% of W). The electrodeposition was performed on the stainless steel substrate from citrate-borate bath at 60 °C and a cathodic current density 10 mA·cm^{-2}. Alloys having different compositions were obtained by varying pH from 5 to 8. A well-defined crystalline structure was indicated for Co-W having 3 at.% and 18 at.% of W: these deposits have a hexagonal close packed (hpc) structure typical for electrodeposited pure Co. The high content of W in the alloy (~30 at.%) leads to the formation of nanocrystalline structure ("amorphous-like"). The electrocatalytic activity of prepared Co-W alloys was examined by means of cyclic voltammetry in the mixture of 1 M CH_3OH and 0.1 M H_2SO_4. The electrooxidation of methanol depends on the content of W in the alloy. It was found that the crystalline Co-3 W and Co-18 W alloys are inactive for methanol oxidation, and the electrochemical alloys dissolution occurs in the tested media. Whereas, the high content of W (~30 at.%) in the Co-W coating prevents the continuous Co-W alloy dissolution and it might be used as anode for the methanol oxidation in the acidic media. The annealing of Co-W deposits was performed at 600 °C for 1 h in the air and formation of Co_3O_4 and $CoWO_4$ compounds with simultaneous decrease of tungsten content in the alloys were detected. The annealed Co-W coatings show lower activity toward methanol electroxidation compared to as-deposited Co-30 at.% W.

1. Introduction

Fuel cells based on methanol oxidation reaction (MOR) could replace combustion engines for a variety of applications due to their easy transportation, handling, storage, low operating temperatures and higher energy density compared to the hydrogen [1–3]. Methanol oxidation has been extensively investigated since the early 1970's and a multistep oxidation mechanism was determined involving O—H bond scission in methanol followed by sequential dehydrogenation to CH_2O, then to CO or CO_2 [4]. The resulted products of oxidation (CO_2, HCHO, HCOOH and $HCOOCH_3$) depend on methanol concentration, temperature, electrode roughness and time of electrolysis. Platinum is the most common catalyst for methanol oxidation, but it is very sensitive to the reaction intermediates such as CO as it poisoning losses catalyst activity [5]. It was found that in the acidic media platinum exhibits the higher catalytic activity for the oxidation of methanol and it is more resistant toward poisoning by CO, so usually perchloric and sulfuric acids are commonly used as the supporting electrolytes for studies of methanol electrooxidation [6]. The interest in investigation of methanol oxidation on platinum electrodes in alkaline media is lower due to its progressive carbonation by CO_2 [7]. Accordingly, the acidic electrolytes are generally preferred for practical application. Nevertheless, the price of pure platinum is relatively high and the search of more active and less expensive catalysts with great stability for the methanol oxidation reaction has resulted in the development of new binary and ternary catalysts based on modifications of Pt with some other metal [4,8]. Therefore, a number of other materials have been investigated for their suitability as methanol oxidation catalysts, including TiO_2 [9] and Cu(111) [10]. Meanwhile, as the small price of electrodes for methanol fuel cells has been still a key factor, only a few studies have been made to investigate electrodeposited alloys as anode materials for possible application in methanol oxidation reaction. Relatively cheap electrodeposition technique offers the possibility to prepare alloy coatings with easy control of their composition, thickness and homogeneity of the surface. In [11] the electro-catalytic activity of electrodeposited Pt-Ni alloy layers on an inert substrate (Au) electrode for methanol oxidation

---

* Corresponding author.
E-mail address: henrikas.cesiulis@chf.vu.lt (H. Cesiulis).

http://dx.doi.org/10.1016/j.surfcoat.2016.07.049
0257-8972/

reaction was investigated. It was shown that the onset of electrooxidation shifted to less anodic potential values (approximately by 160 mV vs Hg/Hg_2SO_4 electrode), while also the current density values obtained for Pt-Ni alloy surfaces were higher for 15 times than those of pure Pt. In [12] it was demonstrated that the anodic current peak, a measure of oxidation reaction rate of methanol, is considerably higher using the electrochemically prepared Fe–W alloy in comparison with pure Fe. In addition, the electrodeposited Co-W alloy was presented as a promising anodic catalyst for direct methanol fuel cells [13]. Partially amorphous structure Co-W alloys with W content < 10 wt.% in the composition exhibited good corrosion resistance and catalytic activity in highly corrosive media such as H_2SO_4 and KOH. It is well known that W alloys with iron group metals, especially Co-W, have drawn much more attention because of their unusual mechanical, tribological, magnetic and anti-corrosion properties toward acidic and alkaline media and ability to improve catalytic properties of alkaline water electrolysis [14,15]. Heat treatment of the electrodeposited Co-W alloys enhances their corrosion resistance and it is attributed to the formation of stoichiometric compounds, surface oxides and the precipitation of stable phases in the microcracks [16]. Moreover, they are considered as environmentally safe alloys and can be easily prepared by simple and effective electrodeposition technique.

Considering the great performance of W alloys for methanol oxidation, the aim of this study was the electrochemical preparation and characterization of optimal composition of Co-W alloys electrodeposited from ammonia-free bath and possibilities to apply these alloys for methanol electrooxidation reaction in the acidic solution.

2. Materials and methods

Co-W deposits were electrodeposited onto stainless steel (type 304) substrates from citrate-borate electrolyte at different pH under galvanostatic mode at 10 $mA\cdot cm^{-2}$. The plating bath consisted of ($mol\cdot L^{-1}$): $CoSO_4\cdot 7H_2O$–0.2, $Na_2WO_4\cdot 2H_2O$–0.2, $C_6H_8O_7$–0.04, H_3BO_3–0.65, $Na_3C_6H_5O_7$–0.25. The pH of solutions was adjusted to 5.0, 6.7 and 8 ± 0.1 by concentrated H_2SO_4 and NaOH solutions. The electrolyte temperature was maintained at 60 ± 2 °C by means of a water bath. The thickness of the deposits was calculated from gravimetric and elemental analysis data and in all cases was ~10 μm.

Electrodeposition was performed in a standard three-electrode cell. A platinum mesh was used as a counter electrode, and saturated Ag/AgCl acted as a reference electrode. All electrode potentials in this paper are presented with respect to the saturated Ag/AgCl electrode. Before the electrodeposition, the stainless steel substrates were washed with detergent and rinsed in the ultrasonic bath with water and then with acetone to remove any contaminants from the surface. In order to improve the adhesion of alloys to the substrates, a nickel seed layer was electrodeposited from an electrolyte containing 1 M $NiCl_2$ and 2.2 M HCl, at a cathodic current density of 10 $mA\cdot cm^{-2}$ for 1 min. Co-W alloy coatings were annealed in air atmosphere in a tube furnace at 600 °C under for 1 h.

The morphology and chemical composition of the coatings was examined by scanning electron microscope (SEM) using Hitachi TM3000 equipment complemented with an energy dispersive X-ray spectroscopy (EDS) analyzer for elemental analysis. The structure of the alloys was studied by X-ray diffraction method using Rigaku MiniFlex II diffractometer with Cu Kα radiation in the 2Θ range from 30 to 100°.

Cyclic voltammetry measurements were performed using programmable potentiostat/galvanostat (Autolab N302). Experiments were performed in the potential range from −0.2 to 2.0 V in 0.1 M H_2SO_4 + 1 M CH_3OH solution at room temperature at the scan rate 10 $mV\,s^{-1}$. A platinum rode was used as a counter electrode and Ag/AgCl was used as a reference electrode. All potentials were measured and presented also against saturated Ag/AgCl electrode.

3. Results and discussions

3.1. Composition, surface morphology and structure of electrodeposited Co-W alloys

In this study the Co-W alloys coatings were electrodeposited from citrate electrolyte. The composition of Co-W alloys from this electrolyte could be varied in a wide range by changing the pH only, because the electrochemical reactions in the given complex system are dependent on a number of Co(II) and W(VI) complexes with citrates and their distribution strongly depends on pH [14,17–20]. Thus, tungsten content is low (< 8 at.%) in Co-W alloys electrodeposited at pH 5, increases from 13 to up to 30 at.% with increasing current density at pH 6.7; whereas at pH 8, the amount of tungsten in the Co-W coatings varies only from 30 to 36 at.%. Thereby, in order to reveal the influence of Co-W alloys composition on their effective use as anode in methanol electrooxidation reaction, there were three marginal cases investigated having different tungsten content (see Table 1), namely Co-3 at.% W (case 1, pH 5), Co-18 at.% W (case 2, pH 6.7), and Co-30 at.% W (case 3, pH 8). The coatings were obtained at the same current density of 10 $mA\cdot cm^{-2}$ and 60 °C.

Anodic oxidation of methanol is heterogeneous reaction; therefore it is very important to investigate the microstructure and morphology of the surface of anode material. SEM images of as-deposited Co-W coatings are shown in Fig. 1. Obviously, even a small amount of W in the coating considerably changes the surface morphology. A needle-like structure with extended acicular crystallites that is typical for electrodeposited pure cobalt coating (Fig. 1a) is eliminated after an introduction of tungsten into the alloy. Co-W deposit having ~3 at.% of tungsten consists of densely packed polyhedral crystallites with pronounced grain boundaries (Fig. 1b). An increase in W percentage up to 18 at.% does not considerably affect the shape of the crystallites, but results in an increase in their size (Fig. 1c). When tungsten content reaches ~30 at.%, the morphology of the Co-W alloy changes considerably, the structure becomes more compact and a spherical cluster surface consists from large number of smaller size nodular-shape grains (Fig. 1d).

The changes of alloy composition and morphology are directly reflected in the structural changes. XRD patterns of investigated alloys are presented in Fig. 2. Noticeably, that even the small tungsten amount ("case 1") incorporated into Co lattice significantly changes the texture of hcp Co lattice: the hexagonal close-packed {100}-textured film, which is characteristic for electrodeposited Co, transforms into {110} textured film while texture {100} weakens sufficiently. This small amount of tungsten causes a strong disorientation of blocs, and maximum angle in the electrodeposited films can reach tens of degrees, that facilitates the growth of defects and multi-domain more readily, therefore, decreasing the texture [21].

The "case 2" is preferentially {101} textured film, whereas the texture of {100} characteristic for electrodeposited cobalt was disappeared. The XRD patterns of this Co-W coating demonstrates a strong peak at 2Θ = 46.5° which is attributed to Co_3W. A small shift of 2Θ position in comparison with indicated in PDF card no 65–3520 occurs probably due to formation of Co solid solution in the Co_3W phase [17]. Nanocrystalline ("amorphous-like") structure of Co-W alloy was observed, when the tungsten content in the coatings deposited at 60 °C is > 25–27 at.%. In this "case 3" only one broad peak in the proximity of 2Θ = 43.5° is seen. It is difficult to determine to which phase this peak is attributed because

Table 1
Influence of the electrolyte pH on Co-W alloy composition and cathodic current efficiency.

pH of the plating bath	W content, at.%	Current efficiency, %
5.0	3.0	75.5
6.7	18.0	70.1
8.0	30.0	25.5

Please cite this article as: E. Vernickaite, et al., Surf. Coat. Technol. (2016), http://dx.doi.org/10.1016/j.surfcoat.2016.07.049