

An investigation of ruthenium coating from LiCl–KCl eutectic melt

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ARTICLE INFO

Article history:

Received 16 June 2014

Received in revised form 1 August 2014

Accepted 20 August 2014

Available online 27 August 2014

Keywords:

Electrodeposition

LiCl–KCl eutectic

Ruthenium coating

Molten salt

ABSTRACT

In this study, electrodeposition of ruthenium (Ru) from LiCl–KCl eutectic melt was investigated in a systematic manner and the effects of process parameters namely current density, time and agitation of electrolyte on the thickness and morphology of Ru layer were explored. The presence of Ru on graphite substrates was confirmed by thin film X-ray diffraction method. The Ru coatings formed at all electrodeposition conditions appeared as a white/gray deposit. The typical “faceted structure” was observed on the surface of Ru deposited at 3 and 7 mA/cm². Fracture cross-section examinations revealed the columnar morphology of Ru which was twinned with boundaries. The smooth appearance of Ru coating became uneven and rough with coarse nodules at 12 mA/cm². The thickness of Ru increased with increasing both current density and time at stationary electrodeposition conditions. A dense and 7.5 μm thick Ru coating was possible to grow on graphite without any agitation at 3 mA/cm² for 2 h. The highest cathodic current efficiency (η), 99.68%, was achieved at 3 mA/cm² after 2 h of electrodeposition time with the rotating cathode speed of 50 rpm. The cross sectional micro-indentation studies indicated that the Ru layer has hardness as high as 450 ± 10 HV.

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1. Introduction

Ruthenium (Ru) is a suitable candidate as a coating material for insert contacts, slip rings and reed switches, electrodes, etc. due to its high hardness, catalytic nature and perfect inertness against chemical attacks (i.e. hot mineral acids or aqua regia) [1–8]. Early reports revealed that Ru coated electrical contacts are perfectly substituted for Rh, Au coatings without losing their functional quality with considerably lower prizes [1,4]. Moreover, Ru coated electrodes can be served as cathode and anode materials for hydrogen or oxygen evolutions, respectively along with better electro-catalytic activity and longer service life [5–8].

Electroplating of Ru from aqueous electrolytes is extremely challenging because of its eight different valence states and consequently the occurrence of its complex compounds. Therefore, electrochemical cells with special diaphragms have been designed to separate the anolyte and catholyte compartments in order to maintain Ru stability and prevent RuO₄ formation. However, thin, stressful and cracked Ru coatings with low cathodic current efficiencies are still the major problems. Ru deposition thicker than 2.5 μm exhibits serious amount of cracks, but the thinner

coatings (e.g. ≤1.5 μm) are mostly crack-free. For these reasons, electrodeposition of Ru from aqueous solutions can be considered as inefficient [1–4,9,10]. So far, many coordinated ligands have been developed to improve the stability of simple Ru salts. The current efficiency values for the commercially available electrolytes namely (NH₄)₃[Ru₂^{IV}NCI₈(H₂O₂)₂] and Ru^{III}(NO)(NH₂SO₃)₃ are up to 58% and 8%, respectively at constant conditions, 65 °C, 5 A/dm², 1.5 pH. On the other hand, higher current efficiency (as high as 90%) was also reported for 2 μm thick Ru coating at 90 °C in the bath containing complex binuclear nitrogen bridged Ru(IV)Cl₄ species. In all cases, gold flash coating is recommended to be applied previously for such aqueous electrolytes in order to have better adhesion and reduce crack formation tendency [1–4].

Alternatively, molten salt electrolysis is the only way to produce a uniformly thick and stress-free PGMs coating with a high current efficiency. Up to now, limited number of studies has been carried out on the electrodeposition of PGMs and their alloys from molten salt electrolysis. The appeared publications regarding Ru electrodeposition preferred to employ NaCl–KCl–CsCl melts as the solvent and stated LiCl–KCl eutectic as an unsuitable media [9,11,12]. On the other hand, molten LiCl eutectic has been extensively utilized as an electrolyte for electrochemical researches, probably owing to its low melting temperature (361 °C) [13–17].

The aim of the present study is to investigate the electrodeposition of Ru from LiCl–KCl melt in a systematic manner for the first

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Table 1
Experimental parameters in molten salt electrolysis.

Group	Parameter	Constant parameters	Variables
I	Current density, i	LiCl–KCl (45–55 wt%) + Ru (0.5 wt%), HCl gas atmosphere, 500 °C, 1 h	3 mA/cm ² , 7 mA/cm ² , 12 mA/cm ²
II	Time, t	LiCl–KCl (45–55 wt%) + Ru (0.5–wt%), HCl gas atmosphere, 500 °C	60 min at 3 and 7 mA/cm ² 90 min at 3 and 7 mA/cm ² 120 min at 3 and 7 mA/cm ²
III	Agitation speed	LiCl–KCl (45–55–wt%) + Ru (0.5–wt%), HCl gas atmosphere, 500 °C, 3 mA/cm ²	0 rpm for 1 and 2 h 50 rpm for 1 and 2 h 100 rpm for 2 h

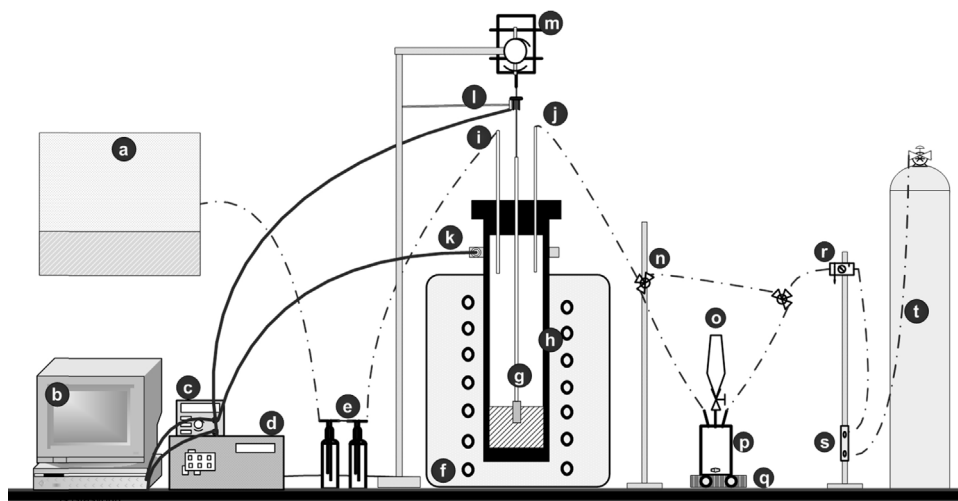


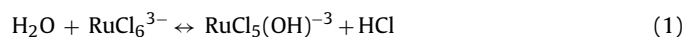
Fig. 1. Schematic drawing of the experimental setup (a – fume hood, b – data acquisition system with a computer connection, c – direct current source (± 0.001 mA), d – furnace controller, e – gas washing bottle, f – furnace, g – cathode, h – graphite crucible, i – gas outlet, j – gas inlet, k – anode polarization cable, l – cathode polarization cable, m – stirrer, n – valve, o – HCl glass container with a teflon needle valve, p – H₂SO₄ container with a 3-way adapter, q – magnetic stirrer, r – s – flow meters, t – N₂ tube (gas streams in the system was shown by the dashed lines, whereas electrical connections were displayed with the straight lines).

time and to determine the effect of process parameters, namely current density, electrolysis duration and agitation of electrolyte on the morphology and thickness of Ru coating. The results received from this study may offer a different point of view for the electrolytic coating of PGMs via molten salt, particularly from LiCl–KCl eutectic salt.

2. Materials and methods

2.1. Electrodeposition of ruthenium

Electrolysis experiments were conducted under different conditions (Table 1) for the purpose of determining the optimum parameters for the electrodeposition of Ru from LiCl–KCl eutectic melt. The key point of the LiCl–KCl system is the complete removal of moisture; otherwise, OH[–] ions form and consequently precipitate solute metal ions. Many researcher showed that a moisture-free LiCl–KCl melt could be obtainable by implementing vacuum, HCl and N₂ purging, as well as treating the melt with chloride [10,14–17]. Bettelheim et al. [10] suggested the hydrolysis reaction for Ru(III) ions in molten LiCl–KCl melt as shown in Eq. (1). Based on the equation, they claimed that the hydrolytic decomposition of molten LiCl–KCl was promoted by the presence of water and suppressed by gaseous HCl [10].



Schematic drawing of the experimental setup was given in Fig. 1. The eutectic mixture of LiCl–KCl molten salt (45–55 wt%) was used

as the solvent and RuCl₃ was added as the source of Ru with 0.5 wt%. LiCl–KCl and RuCl₃ salts were first oven-dried at 105 °C for 48 h before placing in the graphite crucible. The electrochemical cell was hermetically sealed with graphite cap and gradually heated up to 500 °C. As illustrated in Fig. 2, the heating was conducted under inert N₂ gas atmosphere until the temperature reached to 300 °C then HCl gas was passed through the cell with the help of N₂ flow. The generation of HCl gas was carried out at the integrated system in which muriatic acid, a mixture of water and HCl, was slowly dripped into a stirred flask containing sulfuric acid. Because of the strong affinity for water, sulfuric acid dehydrates dropping muriatic acid by absorbing water and liberating HCl (g) according to Eq. (2).

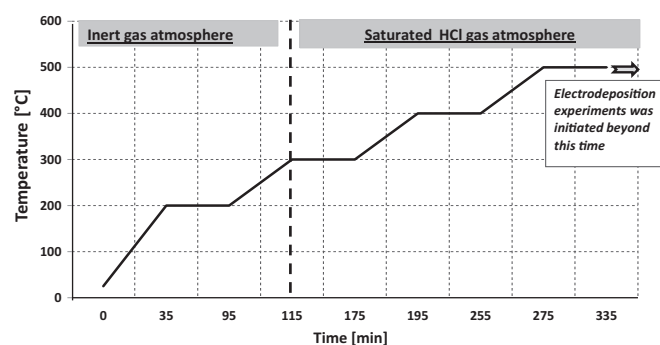


Fig. 2. Heating regime of the electrochemical cell with its controlled atmosphere periods.

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