Electrochimica Acta 174 (2015) 660–666

Contents lists available at ScienceDirect

Electrochimica Acta

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

Electroless plating of rhenium-based alloys with nickel, cobalt and iron

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ARTICLE INFO

Article history:
Received 29 March 2015
Received in revised form 7 June 2015
Accepted 8 June 2015
Available online 11 June 2015

Keywords:
Re-Ni alloys
Re-Co alloys
Re-Fe alloys
Electroless plating

ABSTRACT

This paper focuses on electroless deposition of different Re-Me alloys, where Me is Co, Fe or Ni. The possibility to form high-quality Re-Ni films by this process has been demonstrated recently. In the current research we study and compare the influence of the iron-group metals on process kinetics, alloy composition and surface morphology. Alloys of Re-Ni (78 at.%), Re-Co (65 at.%) and Re-Fe (55 at.%) were prepared. Open-circuit potential measurements, as well as a polarization studies, were performed to investigate the induced co-deposition of Re with Ni, Co and Fe. It was shown that for Re-Co and Re-Ni alloys this process is controlled by a mixed-control reaction rather than by mass transport. Good agreement between the calculated and experimentally determined film deposition rates was obtained. Of the three iron-group metals, Ni was found to have the highest catalytic activity for reduction of ReO_4^- and formation of the Re-Me alloys.

1. Introduction

Development and study of new materials and films for high-temperature and extreme environments are essential in many industries such as aviation, aerospace, nuclear and electrical. Rhenium (Re) is a promising refractory metal that has attracted significant attention for such applications. Due to its special properties, it has been widely used as: (a) an alloying element in tungsten- and molybdenum-based heat resistance alloys. Re enhances the high-temperature strength and creep resistance as well as the low-temperature ductility of these metals [1,2]. (b) Platinum-rhenium catalysts, used to produce high octane gasoline [3]; and (c) high-temperature nickel- or cobalt-based superalloys, used in turbine blades and jet engines. Addition of Re to superalloys improves the creep resistance and thermo-mechanical fatigue strength [4,5].

Formation of Re-alloy coatings has been reported mostly for chemical vapor deposition (CVD) and electroplating [6–17]. The electroless deposition process may be attractive for many applications due to the uniform formation of thin layers on both conductive and non-conductive surfaces, simplicity and low processing temperature. The induced co-deposition of Re with Ni by electroless plating has been recently investigated in our group. In our previous study, films with high Re-content (>80 at.%) were deposited on Cu and SiO_2 substrates [18,19]. It was shown that addition of Ni^{2+} ions to the plating bath is required to start the induced co-deposition of Re. Moreover, Ni^{2+} acts as a catalyst for Re reduction. Therefore, it was of interest to know if other iron-group metals (namely, Co and Fe) induce Re electroless plating too.

The goal of this work is to study and to compare the influence of nickel, cobalt and iron on the deposition of Re while forming Re-Me alloys. Formation of Co-Re and Ni-Re films by electroless plating has been reported before [20,21]. However, these alloys had relatively low Re-content (<50 at.%). It should be noted that, to the best of our knowledge, electroless deposition of Re-Fe alloys has not been reported yet. In this work we propose to apply the recently reported procedure for Re-Ni electroless deposition [19] to prepare high Re-content films with Co, Ni and Fe.

The electroless process and the associated oxidation-reduction reactions are studied both on copper substrates and pre-deposited alloys. The mixed-potential is determined based on polarization tests and open-circuit potential measurements. The applicability of the mixed-potential theory to Re-Me systems is estimated by comparison of the experimental values of the film deposition rate with the ones obtained from the polarization measurements. Moreover, the composition, deposition rate and surface morphology are evaluated and compared for all Re-Me alloys. Finally, the influence of iron-group metals on their co-deposition with Re is discussed.

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http://dx.doi.org/10.1016/j.electacta.2015.06.033
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Table 1
Component concentrations and operating conditions for electroless deposition of Re-Me alloys (Me = Ni, Co or Fe).

Chemicals	Concentration [mmol·dm^{-3}]	Comments
$MeSO_4·7H_2O$	3.45	iron-group metal source
$KReO_4$	34.5	rhenium source
$Na_3C_6H_5O_7·2H_2O$	170	complexing agent
DMAB	100	reducing agent
[Re]/[Me]	10	
pH	9.0-9.5	
Temperature (°C)	80-85	

2. Experimental

Compositions of electrolytes used for electroless deposition of Re-Me films (where Me = Ni, Co, or Fe) are summarized in Table 1. All chemicals (ACS grade) were purchased from Sigma-Aldrich. Potassium perrhenate ($KReO_4$) and sulfate heptahydrates of iron-group metals ($MeSO_4·7H_2O$) were employed as the sources of the divalent metals. Citric acid ($Na_3C_6H_5O_7·2H_2O$) and dimethylamine-borane (DMAB) were used both as the reducing and the complexing agents. The pH was adjusted by adding either ammonia (25% in water) or sulfuric acid (5% in water). The following concentration ratios were maintained: $ReO_4^-/Me = 10$,$Cit/Me = 47$. Thus, the ions of the iron-group metals are in an aqueous solution in the form of complexes with citrate.

Re-Me films were deposited on either pure copper foils or sputtered copper (75 nm) on TaN/SiO_2 substrates. The copper foil was treated in an acidic solution of H_3PO_4:HNO_3:CH_3COOH (11:4:5) for 1 min to remove the oxide before plating, while the sputtered copper was dipped in CH_3COOH:H_2O (1:50) for 1 min. Afterwards, all substrates were rinsed in deionized water. The pre-deposition of Re-Me alloys was conducted on a copper substrate, applying the mixed-potential obtained from the OCP measurements (−0.87 V, −0.83 V and −0.99 V vs. Ag/AgCl/KCl(sat) for deposition of Re-Ni, Re-Co and Re-Fe, respectively).

The electrochemical experiments were performed in a conventional three-electrode cell, using Pt counter electrodes of 2 cm^2 area and a Ag/AgCl/KCl(sat) reference electrode. Current-potential curves were obtained from linear sweep voltammetry measurements using EG&G Princeton Applied Research model 273A potentiostat/galvanostat. A potential scan rate of 25 mV s^{-1} was used in all potentiodynamic experiments. All measurements were performed in 10 mL solution. Assuming that metal reduction and DMAB oxidation are two independent processes that depend only on the catalytic properties of the electrode material, the electrolytes in the absence of either the reducing agent or the metal ions were investigated, in order to monitor the partial cathodic and anodic reactions separately.

The film thickness was measured by Tencor Alpha-step 500 profilometer using selective etch steps. For such etching, HNO_3:HCI:H_2O (1:1:3) solution was used. The surface morphology was studied by Environmental Scanning Electron Microscope (ESEM, Quanta 200 FEG from FEI). High vacuum (typically 10^{-5} mbar) mode was chosen for imaging. The attached liquid-nitrogen-cooled Oxford Si EDS detector was used to determine the atomic composition of the alloy. The composition of the alloys near the surface was analyzed by X-ray photoelectron spectroscopy (XPS) using a Physical Electronics PHI model 590A instrument. XPS measurements were performed in UHV (3.3×10^{-10} mbar) using 5600 Multi-Technique System (PHI, USA). The samples were analyzed at the surface and during Ar$^+$ ion sputtering with 2 kV ion gun (raster: 4 mm × 4 mm, sputtering rate SiO_2/Si = 16 Å min^{-1}). Depth profile analysis was used to determine the elements distribution in the material.

3. Results and Discussion

The open-circuit potential and the electrochemical polarization measurements were performed to investigate and compare the influence of iron-group metals on the induced co-deposition of Re.

3.1. Open circuit potential (OCP) measurements

The potential-time dependence for electroless deposition of Re-Me alloys vs. pure Re on copper substrates is shown in Fig. 1**a**. CCD images of coatings are presented in Fig. 1**b**. The substrate was introduced into the solution before the addition of DMAB. Thus, the horizontal lines on the left side of Fig. 1**a** refer to the potential of the copper substrate in baths free of reducing agent. A value of about −0.21 V was observed for the copper substrate when iron-group salts were not added to the solution. In this case the source of metal ions was only perrhenate ReO_4^-. After adding Co^{2+} or Ni^{2+} ions to the electrolyte, the measured potential was almost the same (about −0.23 V), whereas addition of Fe^{2+} ions resulted in a more profound drop of potential (to −0.26 V).

The mixed-potential was determined after adding DMAB to the solutions and once steady-state has been reached. The reducing agent was introduced into the electrolyte 110 s after the substrate

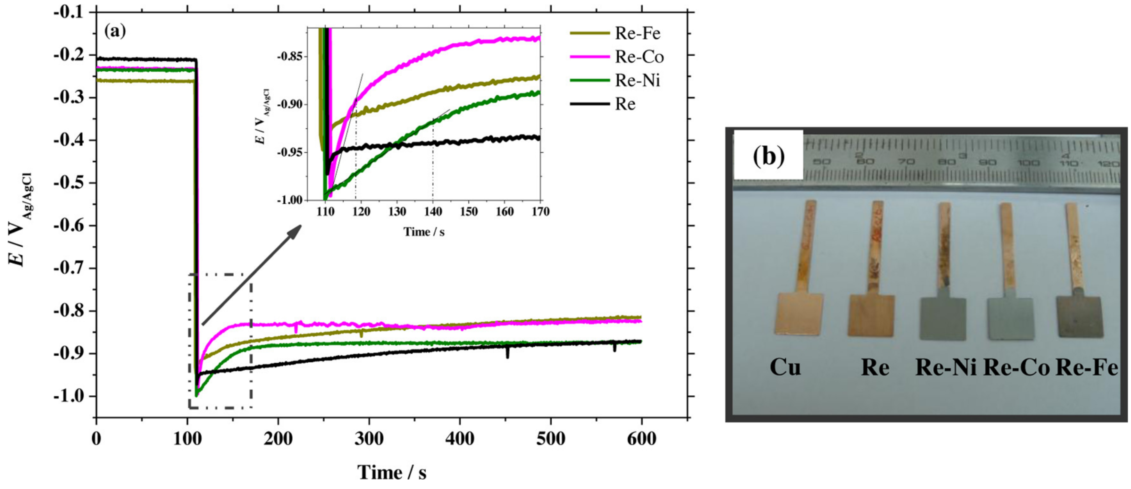

Fig. 1. (a) Open-circuit potential vs. time in the electrolytes used to deposit Re-Me alloys (c.f. Table 1), pH = 9.5, 85 °C. (b) CCD images of the deposits on a Cu-foil substrate after OCP measurements.