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



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ABSTRACT

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

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1. Introduction

Development and study of new materials and films for hightemperature 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 SiO₂ substrates [18,19]. It was shown that addition of Ni²⁺ ions to the plating bath is required to start the induced co-deposition of Re. Moreover, Ni²⁺ 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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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 ₂ O	3.45 34 5	iron-group metal source
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	170	complexing agent
DMAB	100	reducing agent
[Re]/[Me]	10	
pН	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 (KReO₄) and sulfate heptahydrates of irongroup metals (MeSO₄·7H₂O) were employed as the sources of the divalent metals. Citric acid (Na₃C₆H₅O₇·2H₂O) and dimethylamineborane (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: $\text{ReO}_{4}^{-}/\text{Me} = 10$, 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/SiO₂ substrates. The copper foil was treated in an acidic solution of H_3PO_4 :HNO₃:CH₃COOH (11:4:5) for 1 min to remove the oxide before plating, while the sputtered copper was dipped in CH₃COOH:H₂O (1:50) for 1 min. Afterwards, all substrates were rinsed in deionized water. The predeposition 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, HNO₃:HCI:H₂O (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-nitrogencooled 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 $(3.3 \times 10^{-10} \text{ mbar})$ 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: $4 \text{ mm} \times 4 \text{ mm}$, sputtering rate SiO₂/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. **1a**. CCD images of coatings are presented in Fig. **1b**. The substrate was introduced into the solution before the addition of DMAB. Thus, the horizontal lines on the left side of Fig. **1a** 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 irongroup salts were not added to the solution. In this case the source of metal ions was only perrhenate ReO₄⁻. After adding Co²⁺ or Ni²⁺ ions to the electrolyte, the measured potential was almost the same (about -0.23 V), whereas addition of Fe²⁺ 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.

has been immersed. A drift of the potential in the cathodic direction is evident in Fig. 1a. Introduction of any of the iron-group metal ions to the electrolyte containing ReO_{4}^{-} shifted the mixedpotential of the reaction in the anodic direction, thus enhancing the reduction of ReO₄⁻ and allowing the formation of Re-Me alloys. Two regions can be observed after addition of DMAB: (1) a linear increase of the potential due to initial alloy formation on copper, and (2) stabilization of the value of the mixed-potential, leading to autocatalytic alloy deposition. A quick shift of potential in the anodic direction, at a rate of 15.7 mV s^{-1} and 2.56 mV s^{-1} for Re-Co and Re-Ni alloy deposition, respectively, were observed (see inset in Fig. 1a). It should be noted that Re-Co deposit is formed on the copper substrate almost immediately (i.e. after only 8 s), while Re-Ni films appear on the substrate after 30 s. This can be explained by the difference between the binding energies of Cu-Co (167 kJ mol^{-1}) and Cu-Ni (202 kJ mol^{-1}) [22].

Steady-state mixed-potentials of -0.87 V (after 70 s) and -0.83 V (after 40 s) were measured for deposition of Re-Ni and Re-Co, respectively. Re-Co and Re-Ni coatings with good surface coverage were deposited, as illustrated in Fig. 1b. At the same time, only a very thin coating of Re-Fe was formed. This indicates that the deposition rate of the Re-Fe alloy is much lower than that of Re-Co and Re-Ni alloys. It can also be seen in Fig. 1b that metallic coating was not formed in the attempt to deposit pure Re. However, a darker surface was obtained compared to the bare surface of the Cu-substrate. This is probably the outcome of deposition of some Re-oxides (*e.g.* ReO₂ and ReO₃).

It was shown in our previous study that some deposits of Re can also be formed on SiO_2 substrate. However, the layer did not continue to grow significantly in the absence of Ni²⁺ ions [19]. Here, the potential continued to shift over time in the anodic direction in the cases of both Re-Fe and pure Re deposition, and the steady-state potential could not be reached, as seen in Fig. 1**a**.

OCP measurements were also performed for both Ni and Co, in the absence of perrhenate ions in the electrolyte (c.f. Table 1). For Ni, Co and Fe, steady-state was reached at a mixed-potential of about -1.13 V, -1.09 V and -0.99 V, respectively. The mixedpotential observed is more negative than that shown in Fig. 1a, and very close to that of hydrogen evolution. This is most likely the potential generated by the cathodic evolution of hydrogen and the anodic dissolution of the iron-group metal used. It is important to note that the concentration of the iron-group ions in the electrolyte was very low (3.4 mmol dm⁻³) compared to that of the citrate (170 mmol dm⁻³). Hence, all the divalent metal ions in solution must be heavily complexed.

3.2. Electrochemical polarization study

Chemical catalytic reduction of metal ions is based on the oxidation of the reducing agent, with transfer of electrons to the electrode surface, which shifts its potential to values sufficient for reduction of the divalent metal to occur. It should be noted that both reactions occur simultaneously. At steady-state, a mixed-potential is formed when the rates of the two reactions are equal. Therefore, according to the mixed-potential theory [23,24] the polarization study was performed in the absence of either Re, Me or the reducing agent (DMAB). The intersection of the polarization current density, at which steady-state deposition takes place [25].

Electroless plating is usually associated with an auto-catalytic reaction on the surface of the growing film. Thus, in order to obtain the theoretical deposition rate using the mixed-potential theory it is important to perform the measurements on pre-deposited alloys. In this case, before the polarization measurements, predeposition of Re-Me alloys was conducted on a copper substrate, applying the mixed-potential obtained from the OCP measurements (Fig. 1a) for 30 min in 10 mL solution. Taking into account that the substrate material is highly important for all partial reactions, a polarization study on copper electrode was also conducted. This allowed us to distinguish between the initial stages of deposition (namely, until full coverage is obtained on the copper substrate) and the subsequent growth stage of Re-Me film (in which the copper substrate should not affect deposition any more). The measurements were performed in the electrolytes listed in Table 1 under the same deposition conditions (T=85 °C, pH=9.5).

Different sweep rates were tested in order to select the best sweep rate for our measurements. Fig. 2 shows the potential vs. current density curves recorded at different scan rates for Re-Co alloy deposition on copper electrode. The values of E_p are shifted in the negative direction with increasing sweep rates and the value of j_p is also increased. The same behavior is also observed for Re-Ni and Re-Fe formation. The value of j_p shows a linear dependence on log v (slop of ~0.4), which confirms that metal reduction on copper electrodes is mass transport controlled [26].

It should be borne in mind that electroless plating is investigated, thus in order to perform polarization measurements on the copper electrode the deposition of the Re-based alloys should be eliminated during measurement. That is the reason for choosing the highest scan rate of 25 mV s^{-1} .

The current-potential dependences for cathodic reduction of Re-Me alloys and anodic oxidation of the DMAB on Cu are presented in Fig. 3. In order to study the influence of iron-group metals on the induced co-deposition process, measurements in solutions containing only ReO_4^- (*i.e.* in the absence of other metals) were also performed, see Fig. 3. Moreover, the polarization of only citrate without the addition of metal ions to the electrolyte was also measured (Fig. 3) to study the reduction process of ReO_4^- on copper substrate.

The points of intersection of the polarization curves in Fig. 3 represent the mixed-potential (E_{mix}) and deposition current density (j_{dep}) values for Re and Re-Me electroless plating [25]. The data obtained are summarized in Table 2. According to Fig. 3, a positive shift of the mixed-potential was observed, from -943 mV for both pure Re and Re-Fe to -854 mV for Re-Co alloy deposition. The corresponding deposition current density at this point was the highest, 1.4 mA cm⁻². For the Re-Ni alloy, the positive shift of the mixed-potential was +49 mV compared to that of pure Re, and j_{dep} increased from a value of 0.92 mA cm⁻² to 1.29 mA cm⁻².

Fig. 2. Potential vs. current density curves for the reduction of Re-Co alloy on copper electrode at different scan rates (v): 1, 5 and 25 mV s⁻¹. The composition of the electrolyte is shown in Table 1.





Fig. 3. Potential *versus* current density curves for the reduction of metal ions (Re and/or Ni, Co and Fe) and the oxidation of the DMAB on copper electrode, pH = 9.5, $T = 85 \degree$ C.

Table 2

 E_{mix} and j_{dep} values for Re-Me deposition on copper and pre-deposited alloys, extracted from the Tafel plots in Figs. 3 and 4. Potential values are reported *versus* Ag/AgCl/KCl(sat).

System	OCP [V]	Mixed-potential [V]		Current density, <i>j</i> _{dep} [mA cm ⁻²]	
		Cu	Re-Me	Cu	Re-Me
Re-Ni	-0.87	-0.894	-0.876	1.29	2.9
Re-Co	-0.83	-0.854	-0.824	1.40	0.9
Re-Fe	-	-0.947	-0.884	0.90	1.7
Re	-	-0.943	-	0.92	-

The behavior of Re-Fe is different. Addition of Fe²⁺ to the plating bath containing ReO₄⁻ affects neither the mixed-potential nor the value of j_{dep} . It can be concluded, based on Fig. 3, that both Co and Ni catalyze the reduction of ReO₄⁻ to metallic Re, with Co²⁺ being more active than Ni²⁺ on a copper substrate. This result is in good agreement with the data obtained from the OCP measurements (cf. Fig. 1a), where it was shown that steady-state was reached much faster for Re-Co than for Re-Ni on Cu substrate.

The current-potential dependences for cathodic reduction of Re-Me alloys and anodic oxidation of the DMAB on pre-deposited alloys are presented in Fig. 4. The points of intersection of



Fig. 4. Potential vs. current density for reduction of metal ions (curves 1-3) and oxidation of DMAB (curves 1'-3') on pre-deposited substrates. Point A: Re-Co, Point B: Re-Ni, Point C: Re-Fe.

polarization curves A (curve 1 and curve 1'), B (curve 2 and curve 2') and C (curve 3 and curve 3') represent the mixed-potential and deposition current density values for the Re-Co, Re-Ni and Re-Fe systems, respectively. The data are summarized in Table 2.

As seen in Figs. 3 and 4, oxidation of DMAB is accelerated on pre-deposited alloys, which improves the anodic process, resulting in higher j_{dep} values than on copper. At the same time, no significant changes in E_{mix} of all systems were observed compared to copper substrates (Table 2). It should be noted that under steady-state condition, electroless plating takes place on the growing film and is affected by its composition. Therefore, the influence of the substrate on the deposition process is most important for the initial stages of the film formation. This is confirmed by similar values of E_{mix} determined for alloy deposition on different substrates (Table 2), showing larger influence of the electrode material on DMAB anodic oxidation than on cathodic metal reduction.

Moreover, there is a difference between the curves for the cathodic reduction of the Re-Co alloy on copper and on the predeposited alloy. A peak within the range of -0.76 and -0.93 V appears in Fig. 3 where measurements were conducted on copper electrode, while only some change in the slope is observed after the point of the mixed-potential obtained for pre-deposited alloys, as illustrated in Fig. 4. According to Refs. [26,27], it is possible to estimate that the aforementioned peak is related to the reduction of ReO₄⁻ ions to metallic rhenium and rhenium oxides. For both the Re-Fe system and the pure Re system, a shoulder is also observed within the range of -0.81 and -0.90 V (c.f. Fig. 3). In the case of Re-Ni alloy on copper, a change in the slope between -0.78 V and -1 V is noted. Note that no changes of the peak current or the slope were observed in this region when only citrate (i.e. in the absence of ReO₄⁻ and Me ions) was measured. In our previous study it was concluded that the reduction of ReO_4^- ions to metallic Re at the initial stages of deposition involves rhenium oxides (ReO₂ and ReO₃) prior to deposition of metallic Re [19]. Thus, it may be assumed that the reduction of ReO_{4}^{-} to rhenium oxides on copper is more enhanced when Co⁺² is added to the plating bath than when Ni²⁺ is added.

The type of overpotential in electroless plating can indicate the rate-determining step. Basically, there are three types of potential: charge transfer (activation), mass transport (diffusion), and solution resistance [28]. Fig. 4 describes an actual Re-Me electroless plating process. It is evident that the estimated current densities for Re-Ni and Re-Fe deposition are significantly higher than those on copper electrode, while for Re-Co deposition a decrease in j_{dep} is observed (Fig. 4, Table 2). It should be noted that for all studied Re-Me systems, the electroless deposition rate on pre-deposited substrates is most likely controlled by a mixedcontrol reaction rather than by mass transport of ions. In contrast, on bare copper substrate the Re-Co and Re-Ni electroless deposition seems to be controlled by mass transport of the reducing agent (c.f. Fig. 3). In Ref. [29], the measured polarization curves for the anodic oxidation of DMAB on copper electrode at pH = 7 showed dissolution of the Cu electrode without exhibiting an oxidation of DMAB. On the other hand, the highest current values were obtained for oxidation of DMAB on nickel and cobalt electrodes. It

Table	3
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The concentration of Re in the deposited alloy and the deposition rate for Re-Me alloys deposited on pre-deposited substrates, as obtained from the Tafel plots shown in Fig. 4.

System	at.% of Re	Deposition rate, mg/(h cm ²)	Deposition rate, nm \min^{-1}
Re-Ni	78	2.94	27.0
Re-Co	65	0.93	9.2
Re-Fe	60	1.72	17.4



Fig. 5. The thickness evolution of Re-Ni, Co-Re and Fe-Re layers with time. Solution chemistry shown in Table 1.

was noted that Cu electrode is less active for hydrogen adsorption than Co and Ni. This may explain the lower value of limiting current for oxidation of DMAB on Cu substrate compared to that obtained on pre-deposited alloys.

The deposition rates are calculated here on the basis of the value of the deposition current density j_{dep} obtained for each system using Faraday's law (Eq. (1)) and the values presented in Table 3. The relationship between the mass of a deposited metal on the electrode during electrolysis and the quantity of electricity transferred at that electrode is given by Faraday's equation:

$$W = \left(\frac{Q}{F}\right) \left(\frac{M}{z}\right) \tag{1}$$

where Q is the total electric charge passed through the electrode, *F* is the Faraday constant (96,485C mol⁻¹), and (*M*/*z*) is the equivalent weight of the deposited metal, z_i the number of electrons transferred per atom of each metal (z_i = 2 and 7 for Me and Re, respectively). The equivalent weight of the relevant alloys (27.2, 27.6 and 27.13 gequiv⁻¹ for Re-Ni, Re-Co and Re-Fe, respectively).

Assuming that j_{dep} is constant during electroless plating, the deposition rate, Wt, was calculated based on the deposition current density extracted from the *E*-*j* curves (Fig. 4) and the measured concentration of Re and Me in the deposited alloy, using Faraday's law:

Wt. _{*Re-Ni*}
$$[mg/(h cm^2)] = j_{dep} [mA cm^{-2}] \times 1.015$$
 (2.1)

Wt. _{*Re-Co*} [mg/(h cm²)] =
$$j_{dep}$$
 [mA cm⁻²] × 1.030 (2.2)

Wt. _{*Re-Fe*}
$$[mg/(h cm^2)] = j_{dep} [mA cm^{-2}] \times 1.012$$
 (2.3)

In contrast to deposition on Cu, a significantly higher j_{dep} was observed for Re-Ni than for Re-Co deposition on pre-deposited alloys (Table 2). The values of the deposition rates are summarized in Table 3. It is noted that in the case of pre-deposited alloys the highest deposition rate is for Re-Ni (in contrast to deposition on Cu substrates where the highest deposition rate was of Re-Co). According to Ref. [27], the formation of rhenium and rhenium oxides from ReO_{4}^{-} ions is influenced by the adsorption of hydrogen atoms on the electrode surface. The oxidation of DMAB is accompanied by hydrogen evolution and, hence, its adsorption on the electrode accelerates the reduction of ReO_{4}^{-} ions. Therefore, taking into account the enhanced rate of hydrogen adsorption on Re-Ni surface, high Re-content and highest deposition rate are observed in this alloy (Table 3). This result is in good agreement with Ref. [30], where the higher deposition rate of Ni-B compared to Co-B alloys was related to the high catalytic activity of the Ni-B electrode for DMAB oxidation.

3.3. Deposition rate and chemical composition

The values of the deposition rates calculated from Tafel plots were compared with those obtained by film thickness measurements. The evolution of the thickness of Re-Me layers over time is illustrated in Fig. 5. Rates of 28 nm min^{-1} , 8 nm min^{-1} , and 0.6 nm min^{-1} are thus determined for Re-Ni, Re-Co and Re-Fe alloys, respectively. Good agreement is observed between the values in Table 3 those in Fig. 5 for Re-Co and Re-Ni alloys.

Surprisingly, the deposition rate for Re-Fe is found to be about 47 times smaller than that of Re-Ni (c.f. Fig. 5 and Table 3). It explains the formation of very thin and transparent Re-Fe film, as shown in Fig. 1b and Fig. 7. At the same time, relatively thick (\sim 46 nm) Fe films and good surface coverage were prepared on copper from ReO₄⁻ free solution (Fig. 6) using the same deposition time of 15 min. This shows clearly that ReO₄⁻ significantly reduces the film deposition rate. This phenomenon can be explained by the high rate of iron corrosion in ReO₄⁻ solution, as demonstrated in Ref. [31].

The composition of Re–Me films on Cu substrates was determined using XPS. All coatings were plated for 15 min,



Fig. 6. (a) The thickness of Fe films vs. deposition time from a solution containing 3.45 mmol dm⁻³ iron ions, 170 mmol dm⁻³ sodium citrate and 100 mmol dm⁻³ DMAB, in the absence of ReO₄⁻ ions. (b) CCD camera image of the deposits on a Cu-foil substrate.



Fig. 7. XPS depth profiles of: (a) Re-Ni, (b) Re-Co, and (c) Re-Fe alloy coatings.

therefore films of different thicknesses were analyzed; Re-Ni having the thickest layer (c.f. Fig. 7a). XPS depth profiles are shown in Fig. 7. Re-contents of 79 at.%, 65 at.%, and 60 at.% were measured

on the surface for Re-Ni, Re-Co and Re-Fe films, respectively. Moreover, uniform element distribution was observed in Re-Ni and Re-Co films, but not in Re-Fe. A small amount of oxygen (about



Fig. 8. Top raw: ESEM backscattered electron (BSE) images acquired from metallographic cross-section. Bottom raw: ESEM secondary electron (SE) surface view images. (a) Re-Ni, (b) Re-Co, and (c) Re-Fe films formed during 1 h electroless deposition on copper substrates.

3 at.%) was found in Re-Co and Re-Ni alloys, while in Re-Fe it was higher (about 5 at.%). This may be partly attributed to the oxidized Cu substrate due to the thin Re-Fe film (Fig. 7c). In the case of electroless Re-Co alloy there is an increase in the amount of oxygen at the interface with the copper substrate, from 3 at.% to 5 at.%. Note that although DMAB was used as the reducing agent, boron was not detected in the XPS spectra of any of the Re-Me alloys. The XRD pattern for all as-deposited Re-Me films showed the formation of single amorphous Re-Me phase.

3.4. The surface morphology of the deposited films

The surface morphology of the Re–Me films was studied by SEM. The samples were prepared in 30 mL solution for 1 h deposition time. Fig. 8 shows typical images of both the cross-section (top three backscattered electron images) and top view of the surface (bottom three images). Uniform coatings of ~2150 nm Re-Ni (Fig. 8a) and ~550 nm Re-Co (Fig. 8b) were deposited. However, Re-Fe film was not clearly observed in cross-section image (Fig. 8c). It can be explained by preferable dissolution of the iron deposit in the perrhenate-containing solution, compared to its growth on the substrate, as suggested above.

The whirlpool dots in Fig. 8 (bottom images) result from the generation of hydrogen bubbles on the surface during deposition. Several cracks also appear on the surface of the Re-Ni film. Such cracks have not been observed in thinner (~40 nm) coatings reported in our previews studies [18,19]. Since Re-Me alloys have low overvoltage for hydrogen evolution, formation of cracks in thick deposits can most likely be attributed to the hydrogen embrittlement or residual stresses [7,32]. Mismatch in lattice parameters can lead to residual stresses especially in the case of formation of the Re-oxides on the surface as was discussed in our previous study.

4. Conclusions

In this work the electroless deposition of Re-Me alloys (where Me = Ni, Co or Fe) was studied. The influence of the iron-group metals on the process kinetics, film chemical composition and surface morphology was investigated. Uniform films of Re-Ni and Re-Co alloys with Re-contents of 78 at.% and 65 at.%, respectively, were prepared. Open-circuit potential and electrochemical polarization measurements were used to determine the mixed-potential of the alloy and the film deposition rate. The catalytic effect of irongroup metals on ReO₄⁻ reduction was demonstrated. A dependence on the substrate material was also observed. It was shown that Re-Me surface accelerates DMAB oxidation compared to copper, therefore the overall rate of the auto-catalytic reaction on an alloy substrate is significantly higher than that on Cu substrate, except in the case of Re-Co. The accelerated deposition of Re-Co on copper may be attributed to high Cu-Co binding energy. Good agreement between the E_{mix} values determined by OCP and polarization measurements were found. The calculated deposition rate for Re-Ni and Re-Co alloys shows good agreement with that obtained based on film thickness measurements. The deposition rate of Re-Fe was found to be significantly lower, probably due to the ability of the ion to oxidize and dissolve most of the metallic iron. It was also shown that the heterogeneous reaction on the surface of all deposited Re-Me alloys during their electroless deposition is controlled by a mixed-control reaction rather than by mass transport of the reducing agent and metal ions.

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