



Electrodeposition of Alloys of Rhenium with Iron-Group Metals from Aqueous Solutions

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Rhenium (Re)–Me alloys (where Me = Ni, Fe, or Co) were deposited galvanostatically. The plating bath consisted of ammonium perrhenate, nickel or cobalt sulfamate, or iron sulfate, citric acid, and magnesium sulfamate. The effects of bath chemistry and deposition time on faradaic efficiency (FE), Re content, and partial deposition currents were determined. Rhenium contents as high as 93 atom % or FE values as high as 96% were attained in different solutions. The results are discussed, with emphasis on routes to increase the FE and Re content in the coating. The possible role of the second metal in the electrodeposition of Re is presented. A plausible mechanism by which addition of Ni, Fe, or Co to the solution enhances the rate of the deposition of Re is through a unique type of electroless deposition, in which the reducing agent is Me⁰ formed in situ.
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Rhenium is a refractory metal that has gained significant recognition as a high performance engineering material. It has the second highest melting point of all metals (after W), the third highest Young's modulus of elasticity (after Ir and Os), and the fourth highest density (after Os, Ir, and Pt). Its low coefficient of friction and high hardness lead to excellent wear resistance. Rhenium is the only refractory metal that does not form carbides. Yet, the solubility of carbon in Re is fairly high and the wettability is also high. As a result, excellent bond strength can be achieved between these two elements. Indeed, Re is used in contact with graphite and carbon composites. Rhenium is highly resistant to corrosion in hydrochloric and sulfuric acids as well as in seawater. It also has low permeability to hydrogen and resists attack in hydrogen and inert atmospheres at elevated temperatures.^{1–5}

The unique combination of properties of Re is useful in a variety of applications, such as aircraft, aerospace, nuclear, electrical, catalysis, and biomedical.⁶ The major consumption of Re is in the production of heat-resistant alloys.⁷ Its second highest consumption is as a petroleum reforming catalyst.⁸ Rhenium liners made by powder metallurgy (P/M) and chemical vapor deposition (CVD) coatings were suggested for gun barrels.⁹ Rhenium diboride (ReB₂) is superhard and was thus suggested for cutting tool applications.^{10,11} Presently, the two principal manufacturing processes for Re-based items are P/M and CVD. Electroplating at near-room temperature using nontoxic bath chemistries may become a successful alternative.

Electrodeposition of Re and its alloys was reviewed recently by Eliaz and Giladi.³ Our own preliminary results show that electroplating of pure Re is associated with low faradaic efficiency (FE) ($\leq 7\%$) and gives rise to poor coating quality. However, it has been reported that forming alloys with iron-group metals may lead to better coatings.^{12–33} The mechanism of Re alloy electrodeposition is still open to debate. Jones¹³ suggested that adsorbed perrhenate ions on the cathode enhanced Ni deposition electrocatalytically. Berezina et al.²³ proposed that a stable intermetallic compound Ni₃Re₄ was present at the electrode surface and assumed that a surface complex of Ni–Re acetate was formed. Chavar and Suvorova³² suggested that Re had a great catalytic effect on Ni deposition. It was also suggested that the effect of Ni in enhancing the deposition of a Ni–Re alloy was due to an increase in the hydrogen overvoltage. Fukushima et al.¹⁹ suggested that the mechanism of Re–Ni alloy deposi-

tion was based on the formation of a stable intermetallic compound, corresponding to the composition ReNi, or on the complexation of ions at a ratio of 1:1 in solution.

In our previous work, electrodeposited Re–Ni alloys were studied and reasonably thick (up to 25 μm), hard coatings (928 ± 60 VHN) containing Re as high as 93 atom % or FE as high as 96% were obtained depending on the bath chemistry. The mechanism proposed was based on a special type of electroless plating, in which the reducing agent is metallic Ni formed in situ.¹⁴ The present work is an extension of our previous study. Here, we investigate the electrodeposition of Re–Me alloys, where Me stands for Ni, Fe, or Co. The main goals are to widen our understanding of the mechanisms that control the codeposition of Re–Me alloys, particularly the catalytic effect of the iron-group metals on the rate of Re deposition, and to improve the coating process so that high quality coatings can be produced at acceptable FE.

Experimental

Plating bath chemistry.— The plating baths consisted of 0–93 mM NH₄ReO₄ (ammonium perrhenate), 34–343 mM C₆H₈O₇ (citric acid) as the complexing agent, and 34–124 mM Ni(NH₂SO₃)₂ (nickel sulfamate), Co(NH₂SO₃)₂ (cobalt sulfamate), or FeSO₄ (iron sulfate). In iron sulfate, the sulfamate ion was added in the form of Mg(SO₃NH₂)₂. All components were dissolved in deionized water (Direct-Q3, Millipore). All experiments were conducted at pH 5.0 ± 0.1 . The pH was adjusted at room temperature to the desired value by additions of NaOH and, in some cases, small amounts of H₂SO₄. No additives were used. The volume of the electrolyte in the cell was about 12 mL. Each experiment was conducted in a fresh solution.

Addition of sulfamate in plating baths has been reported to produce better results, higher deposition rates, superior throwing power, and reduced porosity and reduced residual stresses in the deposit.³⁴ Citric acid is a commonly used complexing agent. It is a tribasic acid, which deprotonates gradually as the pH is increased. At pH 5, correcting for the activity coefficient and the temperature, the main species in solution are H₂Cit[−] (11.6%), HCit^{2−} (67.7%), and Cit^{3−} (20.7%).¹⁴ Citrate forms stable complexes with Ni, Co, and Re, which affects the deposition of the alloys of these elements.³⁵

Operating conditions.— A small, single-compartment, three-electrode cell was used. A sheet of copper with an exposed area of 1.57 cm² was used as the working electrode. Two platinum sheets were used as the anodes and were placed at about 0.5 cm away on both sides of the cathode. The diameter of the counter electrode was 20% smaller than that of the working electrode. A Princeton Applied Research model 263A potentiostat/galvanostat was used to control

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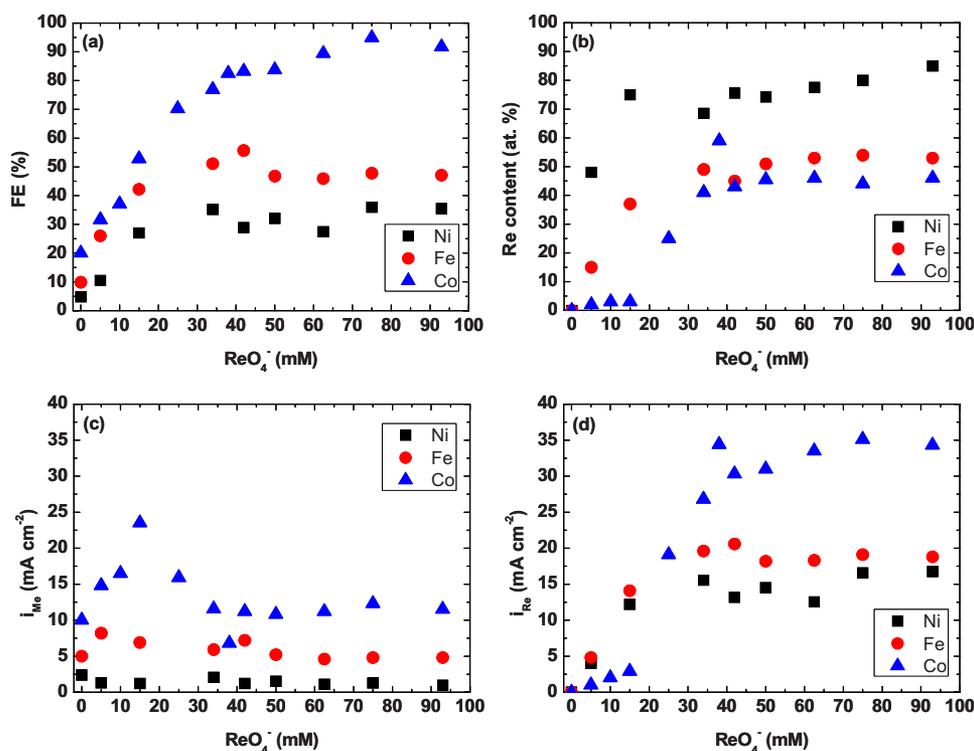


Figure 1. (Color online) The dependence on ReO_4^- concentration of (a) the FE, (b) Re content in the deposit, (c) the partial current density of Me, and (d) the partial current density of Re. The analytical concentrations of Me and citric acid were 93 and 343 mM, respectively. Plating was conducted for 1 h at 70°C , 50 mA cm^{-2} , and $\text{pH } 5.0 \pm 0.1$.

the applied current density at 50 mA cm^{-2} . It was reported that an increase in the current density above this value leads to spongy deposits²⁰ and almost halves the Re content in the deposit.²¹ The FE was calculated from the mass gained, the charge passed, and the chemical composition of the deposit. This was determined by energy-dispersive spectroscopy (EDS) using a liquid-nitrogen-cooled Oxford Si EDS detector attached to an environmental scanning electron microscope (SEM), operated in the high vacuum mode (Quanta 200 FEG from FEI).

The bath was purged with pure nitrogen for about 15 min before turning on the current. Nitrogen was passed above the solution during deposition. In all cases, the plating bath was operated at a temperature of $70 \pm 0.01^\circ\text{C}$. Stirring was applied to maintain the homogeneity of the solution and to reduce pitting that could be caused by accumulation of hydrogen bubbles at the surface of the cathode.³⁴ In most cases, electroplating was conducted for 1 h, but for the determination of the effect of plating time and the rate of deposition of alloys of Re with each of the three iron-group metals, a range of 20–100 min was explored.

Results

In the framework of this study, more than 100 samples were deposited under different bath chemistries and operating conditions and with one of the three iron-group metals, and these were subsequently characterized. The effects of the concentration of perrhenate, each of the alloying elements, and of citrate on the FE, partial current densities, and Re content in the deposited alloy are shown. Also, the effects of deposition time on the FE, partial current densities, Re content, and thickness of the deposit are presented.

The effect of the concentration of ReO_4^- in solution.— In the Experimental section, it was noted that all plating baths consisted of ammonium perrhenate, citric acid, and a salt of one of the iron-group metals. Figure 1a and b shows the effect of the ReO_4^- concentration on the FE and Re content in the deposit, respectively. The dependence of the partial current densities of Me and Re on the concentration of the ReO_4^- ion is shown in Fig. 1c and d, respectively. The concentrations of Me and citric acid in the bath were 93 and 343 mM, respectively.

The effect of increasing the concentration of ReO_4^- above 34 mM on the FE and the Re content in the deposit is rather small, possibly within the experimental error, in Re–Ni and Re–Fe alloys. Considering the partial current densities for deposition, a similar trend is observed for the second metal (Fig. 1c). The partial current density for Re alloyed with Ni or Fe is also nearly independent of the concentration of ReO_4^- in solution, above a concentration of 34 mM. However, in Re–Co alloys, the partial current density for Re deposition increases significantly with the concentration of perrhenate, reaching a nearly constant value at approximately 60 mM ReO_4^- .

When the ReO_4^- concentration in solution was lower than 34 mM, the FE, the Re content in the deposit, and the partial deposition current density of Re increase with the increasing concentration of ReO_4^- in all three systems. As for the partial deposition current density of the second metal, in Ni and Fe it seems to be rather constant, while in Co it exhibits a local maximum at a ReO_4^- concentration of about 15 mM.

When considering the partial current densities, it should be borne in mind that the deposition of one of the iron-group metals requires only two electrons, while that of Re requires seven electrons. Thus, equal partial current densities correspond to an atomic concentration ratio of $\text{Re}:\text{Me} = 1:3.5$ in the deposited alloy.

The effect of deposition time.— The effect of deposition time was studied for $t = 20$ – 100 min under otherwise constant conditions, as shown in Fig. 2. The data for the three iron-group metals follow linear relationships and extrapolate to zero thickness at $t = 0$. This shows that the rate of deposition was uniform, independent of time. For the particular bath composition used in these series of experiments (34 mM ReO_4^- , 93 mM Me^{2+} , and 343 mM Cit), the rate of deposition was quite different for the three alloying elements, namely 10, 14, and $24 \mu\text{m h}^{-1}$ for Re–Ni, Re–Fe, and Re–Co, respectively.

The effect of the concentration of the iron-group metal.— Figure 3 shows the same parameters as Fig. 1, as a function of the concentration of each of the iron-group metals in solution, keeping the concentration of ReO_4^- and citric acid constant. The FE increases with the concentrations of each of the alloying elements (Fig. 3a),

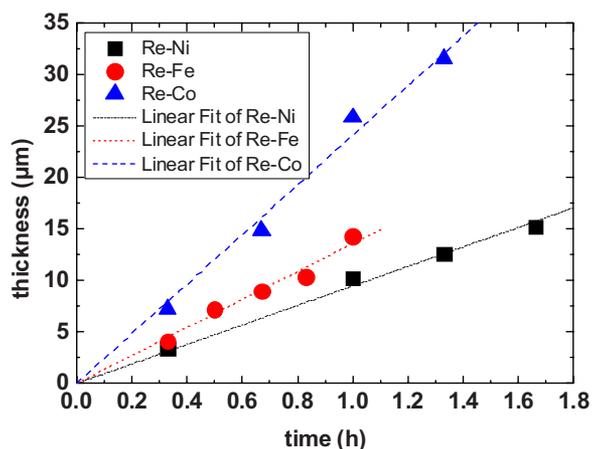


Figure 2. (Color online) Calculated thickness vs time for baths containing 93 mM iron-group metal salt, 34 mM ammonium perrhenate, and 343 mM citric acid. The linear fit, with an origin at (0,0), yields deposition rates of 24, 14, and 10 $\mu\text{m h}^{-1}$ for Re-Co, Re-Fe, and Re-Ni, respectively.

whereas the Re content in the alloy decreases (Fig. 3b). In Fig. 3c and d, it is evident that both the partial current density of Me and that of Re increase as the concentration of the Me ion concentration in the bath is increased.

The effect of citrate concentration.—The effect of the concentration of citrate on the partial current densities of the iron-group metal and for Re is shown in Fig. 4a and b, respectively. The partial current density for the deposition of Fe is independent of the citrate concentration, while that of Ni and Co depends on it in different ways, as shown in these figures.

The surface morphology of the deposits.—Figure 5 shows typical surface morphologies of three different Re-Me alloys in their as-deposited condition. Figure 5a shows the typical surface morphology of Re-Fe alloys. The coating is uniform with no visible

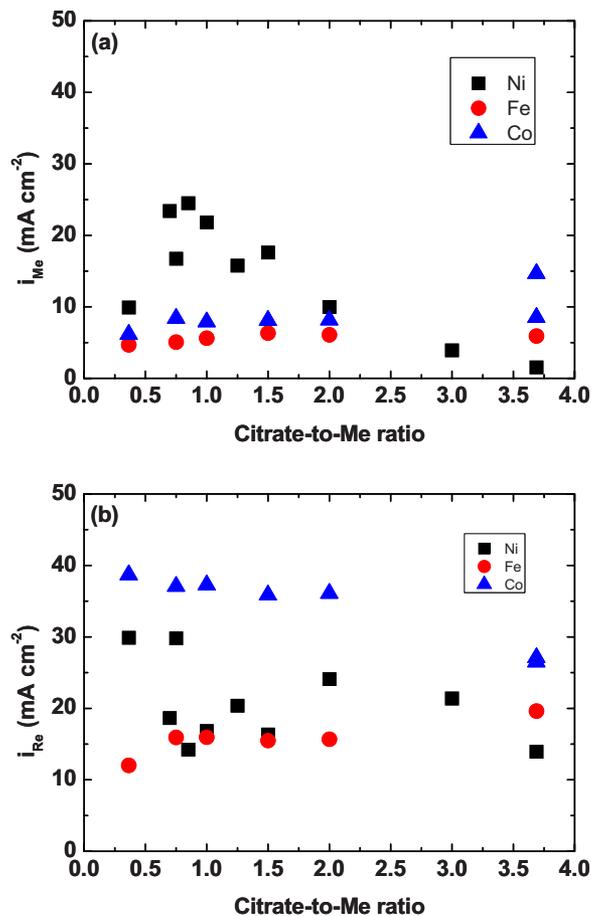


Figure 4. (Color online) The partial deposition current densities (a) of the iron-group metal and (b) of Re as a function of the citrate-to-Me ratio. The ReO_4^- and Me concentrations were 34 and 93 mM, respectively.

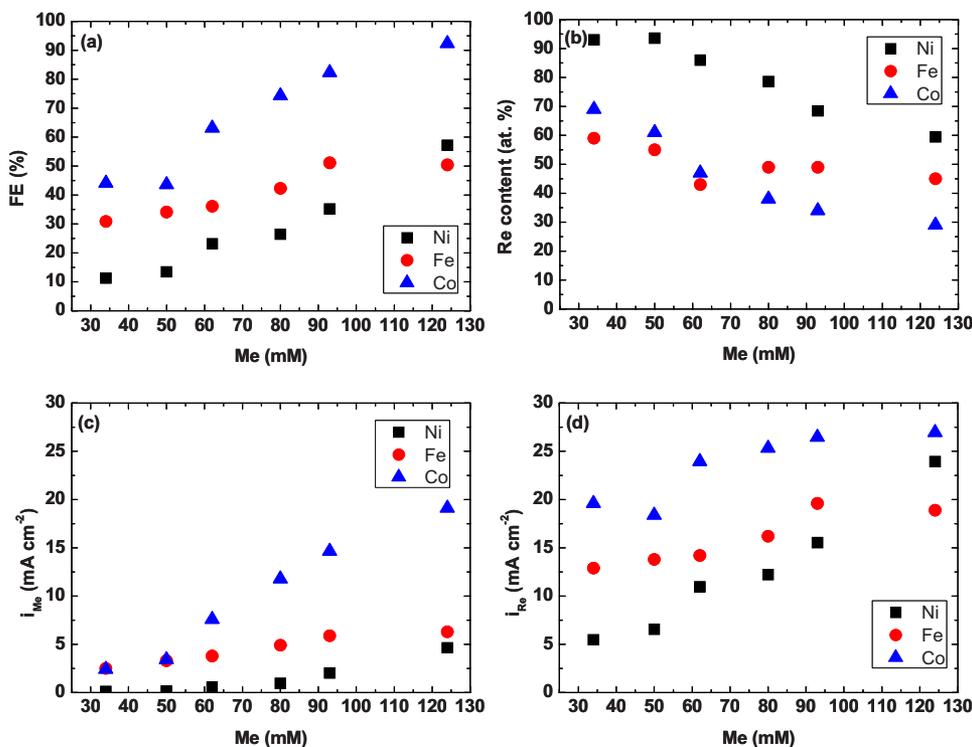


Figure 3. (Color online) The dependence on Me concentration of (a) the FE, (b) Re content in the deposit, (c) the partial current density of Me, and (d) the partial current density of Re. The concentrations of ReO_4^- and citric acid were 34 and 343 mM, respectively. Plating was conducted for 1 h at 70°C, 50 mA cm^{-2} , and pH 5.0 ± 0.1 .

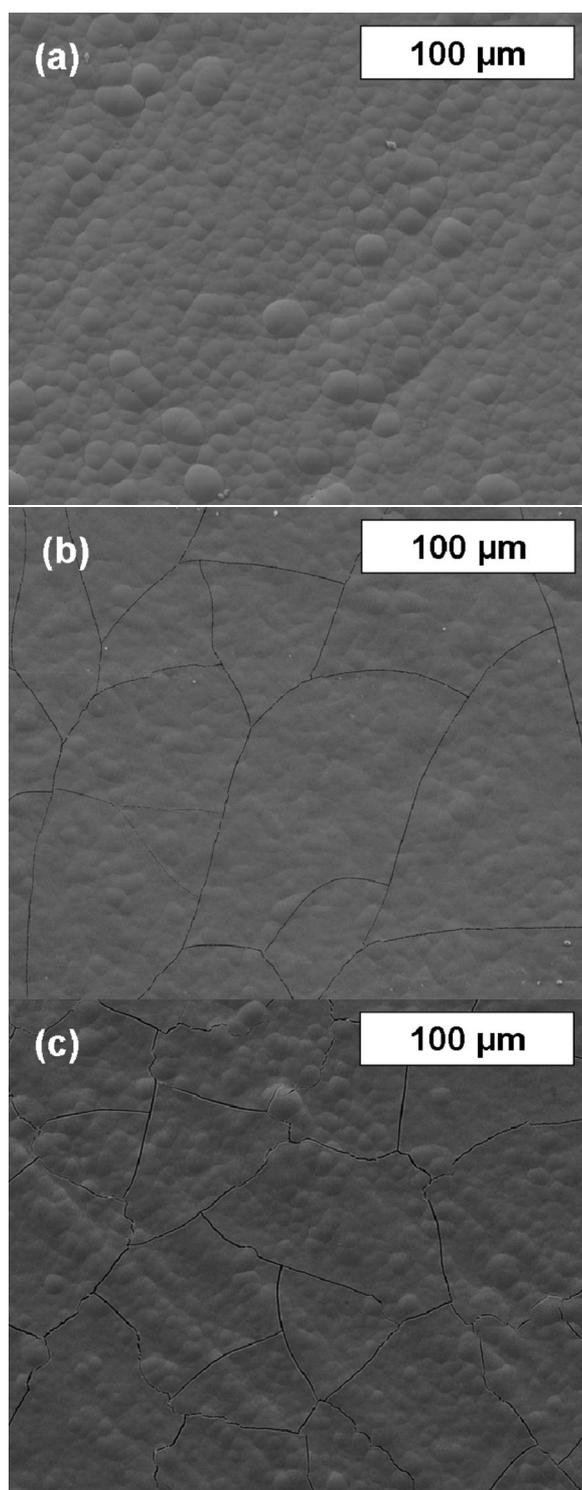


Figure 5. SEM secondary electron images revealing the typical surface morphologies of (a) Re–Fe, (b) Re–Co, and (c) Re–Ni alloys.

cracks. Figure 5b and c presents the typical surface morphologies of Re–Co and Re–Ni alloys, respectively. The coatings are uniform, but each contains a net of microcracks, which may result either from residual stresses or from hydrogen embrittlement. The crack width is typically in the range of a few hundreds of nanometers.

Discussion

Comparison with the Ni–W system.— In previous studies by two of the present authors, the induced codeposition of tungsten with

nickel was analyzed.^{3,34,36–40} The main objective was to suggest a mechanism that could explain the synergistic effect of Ni and W and be consistent with all experimental observations. When a salt of Ni was added to the plating bath, alloys of Ni–W having a wide range of concentrations could be formed. A similar behavior was found when Ni was replaced by Fe or by Co. The conclusion was that this synergism was a result of the unique solution chemistry used, which included WO_4^{2-} , Ni^{2+} , and Cit^{3-} . In that system adjusted to pH 8.0 ± 0.1 , Ni^{2+} forms a complex with Cit^{3-} and, somewhat surprisingly, the WO_4^{2-} ion also forms a complex with Cit^{3-} , according to the reactions

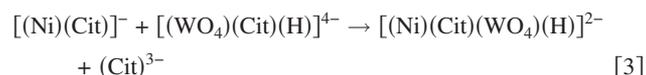


and



While nickel can be electrodeposited from both species shown in Eq. 1, tungsten cannot be deposited from either of the species that contain it in Eq. 2.

The two complexes formed in Eq. 1 and 2 combine to form a complex containing both metals, according to the equation



It was concluded that the precursor for the deposition of the Ni–W alloy is the complex ion containing both metals. This is expected to yield an alloy consisting of equal atomic concentrations of Ni and W. However, Ni can also be deposited from its complex with citrate, while the only precursor for the deposition of W is the ion on the right-hand side of Eq. 3. As a result, the concentration of W in the alloy was usually less than 50 atom %. Indeed, it required a large excess of the WO_4^{2-} ion and fine-tuning of the concentration of the citrate to produce a Ni/W = 1/1 alloy. One of the observations supporting this mechanism was that the synergistic effect between the two metals was mutual. Thus, increasing the concentration of Ni^{2+} in solution increased the partial current density for the deposition of W, and, similarly, increasing the concentration of WO_4^{2-} in solution increased the partial current density for the deposition of Ni^{2+} . This is consistent with Eq. 3 because increasing the concentration of either metal would lead to an increase in the concentration of the complex.

The Ni–Re system.— Rhenium is the 75th element in the periodic table, following tungsten. Indeed, the most stable ion of this metal in solution is ReO_4^- , which is isoelectronic with WO_4^{2-} . Hence, one may expect some similarities in the electrochemical properties of the two metals, although their chemistries are different. In our previous publication on the electrodeposition of Ni–Re alloys¹⁴ we found, indeed, some similarities in the sense that the addition of Ni^{2+} enhanced the rate of deposition of both Re and W, but that is where the similarity ends. Rhenium could be deposited from a solution of NH_4ReO_4 , albeit at a low FE, producing rather poor films. However, the effect of addition of Ni^{2+} ions to the bath was much more dramatic than that in W. Equal molar concentrations of Ni^{2+} and ReO_4^- (34 mM) led to about 93 atom % of Re in the deposited film, but the FE was only 11%. Increasing the concentration of Ni^{2+} to 124 mM led to lowering the concentration of Re to 60 atom %, while the FE rose above 57%, as shown in Fig. 3a and b.

Clearly, the influence of Ni on the deposition of Re must follow a different path than that on W. Thus, forming an alloy that contains 50 atom % W required a ratio of $\text{Ni}^{2+}/\text{WO}_4^{2-} = 1/10$ in solution, while the same concentration of Re in the alloy is reached when the ratio is $\text{Ni}^{2+}/\text{ReO}_4^- = 3.6/1$. In Ni–W, the highest concentration of W in the alloy was 50 atom %, with some indication that an alloy corresponding to the composition of NiW_2 may have been formed at very low FE (which could be explained by assuming that a somewhat similar precursor for the deposition of the alloy, namely $[(\text{Ni})(\text{WO}_4)_2(\text{Cit})]^{3-}$ existed). However, assuming the same

mechanism for Ni–Re deposition, an alloy containing, for example, 90 atom % Re should have a precursor comprising nine ions of ReO_4^- and only one of Ni^{2+} , which is totally improbable.

The strong influence of the addition of Ni^{2+} to the solution, even though it is incorporated in the deposit only as a minor component, points to the role of Ni^{2+} as a catalyst, not as a component of a precursor from which the alloy is deposited. This is the basis for the mechanism that has been discussed tentatively in our previous publication¹⁴ and is developed further here.

The effect of the concentration of ReO_4^- in solution.—An initial survey of different metals to be plated as an alloy with Re showed that Ni, Co, and Fe have the strongest influence on the rate of deposition of the alloy. Among the other metals tested by us (Mn, Zn, Sn, Cu, and Ce), only Sn had a significant effect, but the behavior of the Sn–Re alloy was very different from that of the three iron-group metals, as will be reported elsewhere. Although Ni, Co, and Fe seem to behave in a similar manner, probably following the same mechanism, in some aspects they are different. In Fig. 2, we showed the rate of deposition of the Re alloy with each of the three metals. For each metal, the rate of deposition is independent of time over the range of 20–100 min, but the calculated thickness (assuming bulk density) showed the highest rate of 24 $\mu\text{m h}^{-1}$ for Co, the lowest rate of 10 $\mu\text{m h}^{-1}$ for Ni, and a value of 14 $\mu\text{m h}^{-1}$ in between for Fe.

This implies that a first step, which we believe is the reduction of the divalent metal on the surface, is the rate-determining step in the deposition of the alloy, for example



The metallic Co formed in this step reduces the ReO_4^- ion, as shown in Eq. 5 below.

In Fig. 1b, the most striking result is that the Re content in the alloy is almost independent of the concentration of the ReO_4^- ion in solution at concentrations above 34 mM. The FE was also independent of the ReO_4^- concentration at these concentrations. This is consistent with the notion that reduction of the ReO_4^- ion is not the rate-determining step in the present system, as suggested above, based on the different rates of deposition of the alloy with the three iron-group metals (Fig. 2). The increase in the FE, Re content, and partial deposition current density of Re with increasing ReO_4^- concentration below 34 mM can be attributed to mass-transport limitation of the ReO_4^- ion.

While the FE is a definite measure of the rate of hydrogen evolution (assuming, of course, that it is the only side reaction in this system), the Re content in the alloy is less definitive. For example, its increase could result either from an increase in its rate of deposition or from a decrease in the rate of deposition of the second metal. Thus, more important are the partial current densities shown in Fig. 1c and d for each of the iron-group metals and for Re, respectively. The partial current densities for deposition of the iron-group metal are almost independent of the concentration of ReO_4^- in solution in Ni and Fe. In Fig. 1d, the partial current for the deposition of Re, for perrhenate concentrations higher than 34 mM, depends only little on its concentration in solution. Considering that the rate of deposition of the Co–Re alloy in solution with a relatively high concentration of ReO_4^- is about twice as high as that of the Ni–Re and Fe–Re alloys, it is easy to see that the deposition of the Co–Re alloy is most affected by mass-transport limitation. Moreover, the behavior of the partial deposition current density of Co differs from that of Ni and Fe and exhibits a local maximum at a ReO_4^- concentration of about 15 mM, which cannot be explained at this stage.

The effect of the concentration of the iron-group metal.—The effects of the concentration of the iron-group metal, while keeping the concentration of ReO_4^- constant, are shown in Fig. 3. In this case, the behavior observed is as expected, and the interpretation is rather straightforward. The FE for all three iron-group metals increases

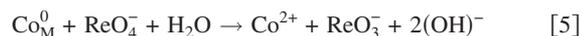
with increasing concentration (Fig. 3a), while the Re content in the alloy decreases (Fig. 3b). This may be because Re is a much better catalyst for hydrogen evolution than any of the three iron-group metals, so that lowering the proportion of Re in the alloy can be expected to lead to a decrease in the rate of hydrogen evolution and, hence, to an increase in the FE. However, it should be borne in mind that the experiments were carried out under galvanostatic conditions, so an increase in the partial current density of Re and of the iron-group metal should result in a decrease in the partial current density for hydrogen evolution.

The partial current density for all the iron-group metals increased with an increase in their concentration in solution, as expected (Fig. 3c). However, the partial current density of Re deposition also increased, although the Re content in the alloy decreased. Thus, in contrast to the Ni–W system, the synergism here is one sided; increasing the concentration of ReO_4^- does not increase the partial current density for the deposition of the iron-group metal, pointing again to a different mechanism governing the deposition of the Re alloys.

The effect of the concentration of citrate.—The effect of increasing the concentration of the Cit^{3-} ion, keeping the concentration of both metals constant, was also investigated. The partial current density for Co deposition increased moderately with increasing concentration of citrate, whereas that of Fe was essentially independent of it. The partial current density for Re deposition increased when Fe was the second metal and decreased when it was Co. The data for Ni were rather complex, showing a maximum in the current density for Ni deposition and a corresponding local minimum for Re deposition, as shown in Fig. 4a and b, respectively. These results probably depend on the different complexes of each of the elements with citrate, but some of the values of the stability constants for the complexes needed for a quantitative analysis are not available. Suffice it to say that the most satisfactory results, from the point of view of the quality of the electrodeposited film, as observed by SEM studies, were obtained at the highest concentration of Cit^{3-} used in this study (343 mM). The role of citrate is probably to sequester the ions of the iron-group metal, slowing down their rate of deposition. This is most likely the reason that the concentration of ReO_4^- has very little effect on the rate of the overall process of alloy formation, while this rate is sensitive to the concentration of the iron-group metals and shows significant differences between Co, Ni, and Fe.

The proposed mechanism.—Based on the experimental data acquired in this work, the following mechanism is proposed to explain the effect of Ni^{2+} , Co^{2+} , and Fe^{2+} ions on the rate of deposition of the respective alloy with Re.

The first step is the electroreduction of the divalent ion, as given by Eq. 4. The next step is the chemical reduction of ReO_4^-



Because the ReO_4^- ion is the most stable ion of Re in solution, it is very difficult to deposit metallic Re from it directly. However, its chemical reduction to the five-valent state may make it easier to reduce it further electrochemically to the metallic state



An alternative path could be the further chemical reduction of ReO_3^- in several steps to form metallic Re, but we consider this a less likely mechanism.⁴¹

Electroless deposition with in situ generation of the reducing agent.—The mechanism proposed above is, in effect, an electroless plating process. Its unique feature in our case is that the reducing agent is formed and regenerated in situ, thus alleviating the problem of the inherent instability of common electroless plating baths, where the reducing agent is one of the components of the bath. The other advantage is that the thickness of the deposited layer is not

limited to 1 μm or less, as in most electroless plating baths. However, it has the disadvantage that it can only be applied to conducting surfaces.

The values of the partial current densities for the deposition of the iron-group metal are somewhat misleading because they are calculated on the basis of the atomic concentration of each of these elements in the resulting alloy. This concentration represents the difference between the current density corresponding to the process shown in Eq. 4 (which is the true rate of deposition of the divalent metal) and that corresponding to the chemical redox reaction shown in Eq. 5, in which it is regenerated. The fact that alloys containing above 90 atom % Re (and, hence, less than 10 atom % Me) are formed supports the claim that the iron-group metals act as true catalysts for the deposition of Re. Indeed, the presence of Ni, Co, or Fe in the alloy may result from occlusion of a fraction of the atoms formed in Eq. 4 in the deposit, rather than from true alloy formation. If this is the case, it should be possible to obtain high quality deposits containing (almost) pure Re in a bath containing Ni^{2+} , for example, by fine-tuning the composition of the bath, the temperature, and the current density. However, without addition of the divalent ion, it is very hard to deposit pure Re.

Recently, we have conducted a series of experiments, including electroless deposition of Re on substrates made of iron-group metals. The results of these experiments support the mechanism proposed herein and will be presented in a successive publication.

Conclusions

Factors affecting the electrodeposition of Re–Me alloys, in particular the FE, Re content, and partial deposition current densities, were studied. Conditions for the formation of Re–Me coatings with Re as high as 93 atom % or FE as high as 96%, depending on the composition of the plating bath, were identified. The following conclusions may be drawn:

1. The perrhenate ion concentration does not seem to have a significant effect on the deposition of Re–Me alloys above a concentration of 34 mM. This shows that the deposition of Re is not the rate-determining step in the formation of Re–Me alloys. At lower concentrations of perrhenate, the FE, Re content in the deposit, and partial deposition current density of Re increase with increasing concentration of perrhenate due to mass-transport limitation.

2. As the concentration of Me^{2+} ion in the bath is increased, the FE and the partial deposition current densities of both Me and Re increase, whereas the Re content in the deposit decreases. The three different binary systems behave similarly, showing a catalytic effect on the deposition of Re but presenting highly different rates of deposition.

3. A mechanism of induced codeposition involving a mixed-metal complex can be ruled out. A plausible mechanism is proposed, according to which addition of Ni^{2+} , Fe^{2+} , or Co^{2+} to the solution enhances the rate of deposition of Re through a unique type of electroless plating, in which the reducing agent Me^0 is formed in situ.

4. The citrate-to-Me ratio has a different effect on the three alloy systems probably due to the different stability of the Me–citrate complexes. In this regard, Re–Fe behaves differently from Re–Ni and Re–Co.

5. The effect of deposition time on the Re–Me alloy deposition was studied. The mass gain shows a linear dependence on time, showing a uniform rate of deposition, regardless of the coating

thickness. The deposition rate of Re–Co is the highest, and that of Re–Ni is the lowest.

6. Although the deposition of pure Re suffers from low FE, the experiments reported here show that plating of alloys of Re with the iron-group metals can be performed and controlled to yield high FE and Re content within wide limits.

7. The possible role of partial mass-transport limitation in the deposition of Re–Me alloys should be investigated.

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