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The Mechanism of Induced Codeposition of Ni-W Alloys

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The term *induced codeposition* was coined by Brenner in 1963, to describe a situation where "a metal, which cannot be deposited alone from its aqueous solution, is codeposited in the presence of another metal, forming an alloy". An overview of the mechanism suggested in our earlier papers for electrodeposition of Ni-W alloys from solutions containing citrate as the complexing agent, and the experimental observations that support it, are presented in this paper. It is postulated that induced codeposition results from the formation of a mixed-metal complex, such as $\left[(\mathrm{Ni})(\mathrm{WO}_4)(\mathrm{H})(\mathrm{Cit})\right]^{2-}$, which is the precursor for deposition of the alloy. Tungsten can only be deposited from this complex, while there are parallel paths for deposition of Ni. The concentration of this complex was calculated on the basis of an observed mass-transport limitation on the partial current for deposition of W.

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Introduction

It is appropriate to start any discussion of metal deposition, be it a single metal or an alloy, by noting that electrode reactions in general are divided into two classes: outer-sphere charge transfer, and metal deposition or dissolution. A typical example of the former is the reduction of a ferric ion in solution, forming a ferrous ion, given by the equation

$$\left[\mathrm{Fe}\left(\mathrm{H_2O}\right)_n\right]^{3+}_{\mathrm{soln}} + \mathrm{e}^-_{\mathrm{crys}} \rightarrow \left[\mathrm{Fe}\left(\mathrm{H_2O}\right)_n\right]^{2+}_{\mathrm{soln}}. \qquad [1]$$

The closest environment of the ion (*i.e.* its solvation shell) is approximately maintained following electron transfer, although it is reorganized, and the solvent-reorganization energy plays a central role in theories developed to describe such processes (1-8). The solvated ion does not have to cross the interface, although its distance from the surface of the metal could change slightly. Charge is carried across the interface by electrons, over a distance that is typically of the order of 0.5-0.6 nm. Moreover, in the case shown above, the standard electrode potential is $E^0 = +0.790$ V *vs.* SHE. It is relatively easy to ensure, following standard methods of purification and of removal of oxygen, that the process shown in Eq. 1 is the only charge transfer reaction taking place, so that the current-potential relationship observed experimentally represents the true dependence of the rate of this electrode reaction on applied potential. In Eq. 1 and similar equations below we ignore, for the sake of convenience, the fact that the number of water molecules in the solvation shell might change following charge transfer, since these numbers are not always known, and they are not relevant to the point being discussed.

Metal deposition is very different, and much more complex, than outer-sphere charge transfer, for a number of reasons. Consider the simple case of silver deposition, written as

$$\left[\mathrm{Ag}\left(\mathrm{H_2O}\right)_n\right]^{+}_{\mathrm{soln}} + \mathrm{e}^-_{\mathrm{crys}} \rightarrow \mathrm{Ag}^{\mathrm{o}}_{\mathrm{crys}} + \mathrm{n}\cdot\left(\mathrm{H_2O}\right). \qquad [2]$$

It is evident that in this case both mass and charge have to cross the interface. These two processes occur on widely different time scales. Electron transfer occurs on a time scale of femto seconds. In contrast, the characteristic time for diffusion of an atom or ion across the double layer is $\tau_{\mathrm{dl}} = 10^5\text{-}10^6$ fs. Since mass transfer and electron transfer occur on such widely different time scales (9), the process shown in Eq. 2 cannot be assumed to occur simultaneously, and cannot be regarded as a single elementary step in the reaction sequence.

The obvious question then presents itself: is charge carried across the interface by electrons, leaving behind a neutral metal atom that will diffuse relatively slowly until it reaches the metal and is incorporated in it, or is it the ion that carries both mass and charge across the interface? Interestingly, several noted electrochemists (10-13) have stated explicitly that in metal deposition charge is carried across the interface by the metal ions, not by the electrons. With this in mind, one may expect that the mechanism of metal deposition and dissolution should be treated in quite a different manner than electrode reactions, in which mass is not carried across the interface. For example, there is no basis to assume that in metal deposition the symmetry factor β would be even close to the value of 0.5, commonly assumed in the analysis of the kinetics of multi-step electrode reactions. Nevertheless, this difference has not been taken into account in the analysis of the mechanism of metal deposition and dissolution.

The question of charge transfer in metal deposition and dissolution has been treated by one of the present authors recently (14-17). It was concluded that whenever the transfer of mass is involved, electron transfer could not be implicated as the vehicle of transferring charge across the interface, since it would create highly unstable intermediates in solution, in violation of the first law of thermodynamics. Stabilization of such intermediates by adsorption on the surface or by incorporation in the electrode material itself occurs on a time scale that is 5-6 orders of magnitude longer than electron transfer, hence it cannot supply the additional energy needed to create the intermediate in solution by thermal fluctuations.

Induced Codeposition of Ni-W Alloys

General Comments

It was observed a long time ago that tungsten cannot be deposited from any aqueous solution, but alloys of this metal with the iron-group transition metals (Ni, Co and Fe) can readily be electroplated. The work published in this area until 1963 was reviewed in detail by Brenner (18) and updated in several recent publications (19-23). Many attempts have been made to explain the mechanism of this process, specifically how the transition metal ion helps to bring about the deposition of tungsten from the tungstate ion $\mathrm{WO_4^{2-}}$, but none were confirmed experimentally (18). In the present paper, a mechanism is proposed to explain this phenomenon, by assuming the formation of a mixed-metal complex, containing both metals and citrate as a complexing agent. Although the complex, assumed to be the precursor for deposition of the alloy, was not observed directly, ample evidence for its existence is provided, as will be shown below. The discussion will be applicable strictly to alloys of Ni-W, but it probably applies to Co-W and Fe-W alloys, as well as to similar alloys of molybdenum (24,25).

The Importance of Knowing the Solution Chemistry

A detailed understanding of the species formed in solution and their relative concentrations (which can be pH dependent) is essential for the understanding of the factors controlling the performance of the plating bath. For example, $\mathrm{NH_3}$ is a well-known ligand, forming complexes of the type $\left[\mathrm{M(NH_3)_n}\right]^{2+}$, where M could be Ni, Co, Fe and many other metals, and *n* could assume values between 2 and 6. All such complexes are good precursors for the deposition of the metal. This simple fact is often ignored when $\mathrm{NH_4OH}$ is added to plating baths "to adjust the pH", not taking into account its influence on the distribution of species in solution. Citrate is an excellent ligand that can stabilize the same metal ions in alkaline solutions, forming a complex such as $\left[\mathrm{MCit}\right]^{-}$ at or around pH 8. On the other hand, an excess of citrate will form a different complex, $\left[\mathrm{MCit_2}\right]^{4-}$, which, for example, binds $\mathrm{Ni^{2+}}$ so strongly that it can hardly be deposited. These and other aspects of the solution chemistry relevant to induced codeposition of tungsten and nickel will be discussed below.

The Assumed Precursor for the Deposition of the Alloy

The main ingredients for deposition of Ni-W alloys in this work were: $NiSO_4$, Na_2WO_4 and Na_3Cit or H_3Cit. The pH was set to 8 (except where the effect of pH was studied) by adding either H_2SO_4 or NaOH, as required. In some of the experiments NH_4OH was also added. Since the main purpose of this work was to understand the mechanism of induced electrodeposition, not to produce the best practical coatings, no additives were added, to avoid further complications in the analysis of the results. Plating was conducted on rotating cylinder electrodes. Details of the experimental techniques were described elsewhere (20-23). The precursor of alloy deposition is assumed to be the complex $[(\mathrm{Ni})(\mathrm{WO}_4)(\mathrm{H})(\mathrm{Cit})]^{2-}$, which is formed by the reaction

$$[(\mathrm{Ni})(\mathrm{Cit})]^{-} + [(\mathrm{WO}_4)(\mathrm{Cit})(\mathrm{H})]^{4-} \rightarrow [(\mathrm{Ni})(\mathrm{WO}_4)(\mathrm{H})(\mathrm{Cit})]^{2-} + (\mathrm{Cit})^{3-}. \qquad [3]$$

It is noted that this species is formed in a reaction between two negatively charged ions, one having a charge of (-4), hence it is reasonable to assume that its rate of formation is low, even if it is relatively stable thermodynamically. A very similar complex containing two protons, and hence a negative charge of (-1), can also act as a precursor at lower pH.

Fig. 1a shows the stepwise deprotonation of citric acid with increasing pH, while Fig. 1b shows similar data for the $[(\mathrm{WO}_4)(\mathrm{Cit})(\mathrm{H})_n]^{-(5-n)}$ complexes. In Fig. 1c the speciation of ammonia is shown as a function of pH. Considering Fig. 1, the following conclusions can be drawn:

(i) In the pH range of 7-9 the predominant citrate species is Cit^{3-}. Thus, choosing a value of pH = 8 can ensure stable operation.

(ii) It so happens that the most stable complex of tungstate and citrate at pH = 8 is $[(\mathrm{WO}_4)(\mathrm{Cit})(\mathrm{H})]^{4-}$, which is written as $[1,1,1]^{4-}$ for brevity. However, in the range of pH = 6-8, the species containing two protons $[1,1,2]^{3-}$ comes into play and can form the complex $[(\mathrm{Ni})(\mathrm{WO}_4)(\mathrm{H})_2(\mathrm{Cit})]^{1-}$, which could also act as a precursor for alloy deposition. Indeed, when the concentrations of the two species are comparable, around pH = 7, the species having a lower charge of (-3) may react faster to form the precursor for alloy deposition. A comparison between the concentration of the different species and the atom per cent (a/o) of W found in the alloy is shown in Fig. 2a-2d, plotted as a function of pH. The best correlation is found when the variation of the sum of the concentrations of $[1,1,1]^{4-}$ and $[1,1,2]^{3-}$ is shown, together with the dependence of the a/o of W on pH.

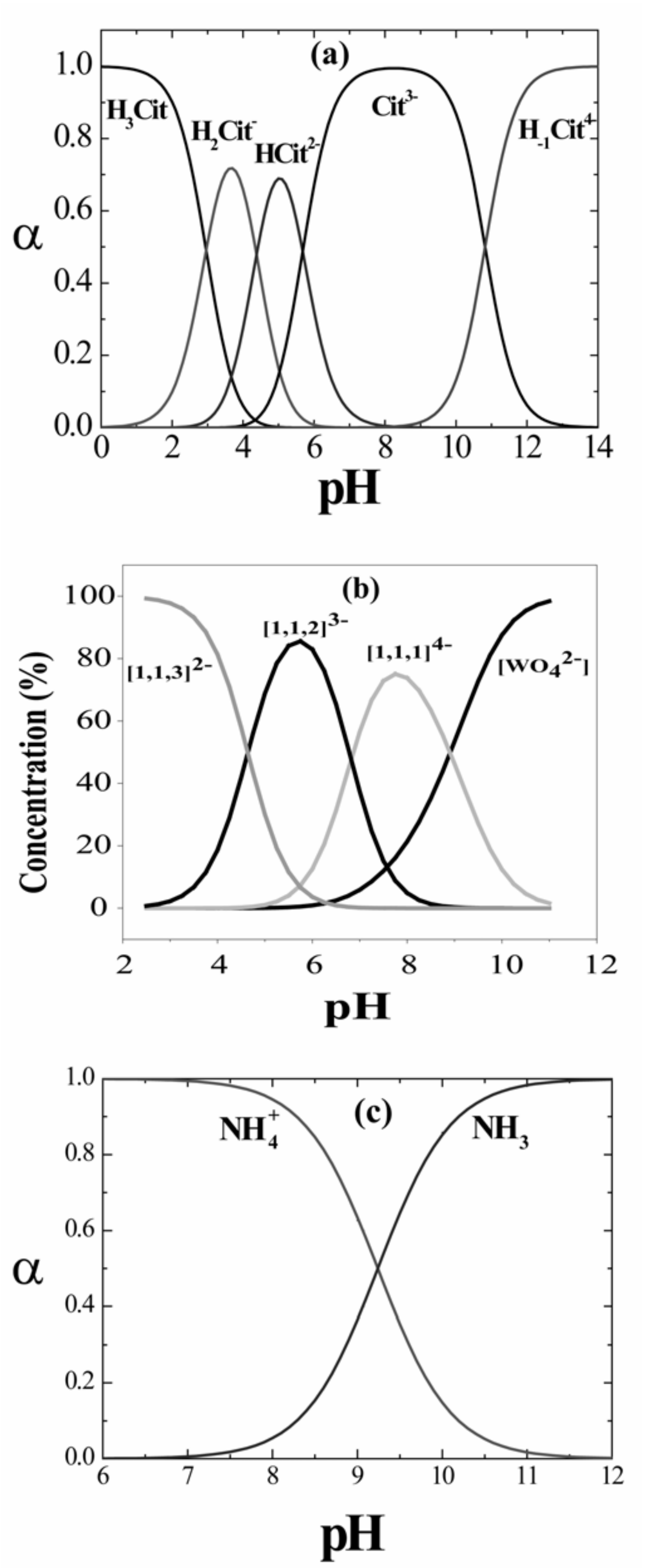

Figure 1. The pH dependence of: (a) Deprotonation of citric acid. (b) Distribution of tungstate-cirtate complexes ($[\mathrm{Cit}^{3-}]$ = 0.5 M, $[\mathrm{WO}_4^{2-}]$ = 0.1 M). $[1,1,n]^{-(5\text{-}n)}$ is written instead of $\left[(\mathrm{WO}_4)(\mathrm{Cit})(\mathrm{H})_n\right]^{-(5-n)}$; (c) Ionization of ammonium hydroxide (p*K*a = 9.24).

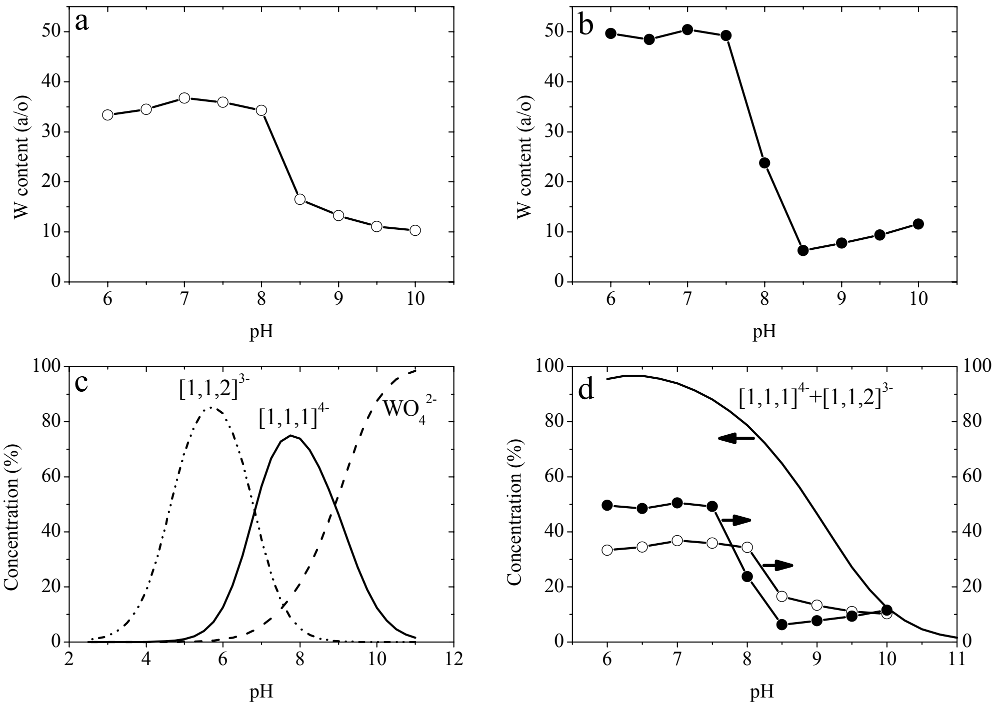

Figure 2. Comparison of the change of a/o W in the alloy and of the concentration of tungstate-citrate complexes as a function of pH. (a) and (b) The a/o W variation in two sets of experiments; (c) Relative abundance of tungstate-citrate complexes; (d) Superimposition of the data in figures (a)-(c).

(iii) It is also shown in Fig. 1b that at pH > 8 the concentration of the $[1,1,1]^{4-}$ complex declines, and WO_4^{2-} gradually becomes the predominant species. This apparently does not form a complex with Cit^{3-} (since it would be destabilized by the high negative charge). Hence, at higher pH values, the concentration of the precursors for alloy deposition declines, as evident by the sharp lowering of the a/o of tungsten found in the alloy (see Fig. 3).

(iv) NH_3 forms several complexes with nickel. Thus, it competes with Cit^{3-} for the Ni^{2+} in solution, reducing the concentration of $[(Ni)(Cit)]^-$ and, hence, the concentration of the precursor for alloy deposition, shown in Eq. 3. The value of the ion dissociation constant of ammonium hydroxide is p*K*a = 9.24. Hence, at pH = 7 virtually all of it is in the form of NH_4^+, as shown if Fig. 1c As the pH is increased, the concentration of NH_3 increases, capturing some of the Ni^{2+} ions in solution, thus leading to a decrease in the a/o of tungsten in the alloy, as demonstrated in Fig. 4.

The Effect of Mass-Transport Limitation

The limiting current density for a rotating cylinder electrode is given by

$$j_L = 0.079 n \mathrm{F} r^{0.4} D^{0.64} \nu^{-0.34} c_\infty \omega^{0.7}, \qquad [4]$$

where n is the number of electrons transferred in the reaction, F is Faraday's constant, r is the radius of the rotating cylinder, D is the diffusion coefficient, ν is the kinematic viscosity, c_∞ is the bulk concentration of the electroactive species, and ω is the angular velocity.

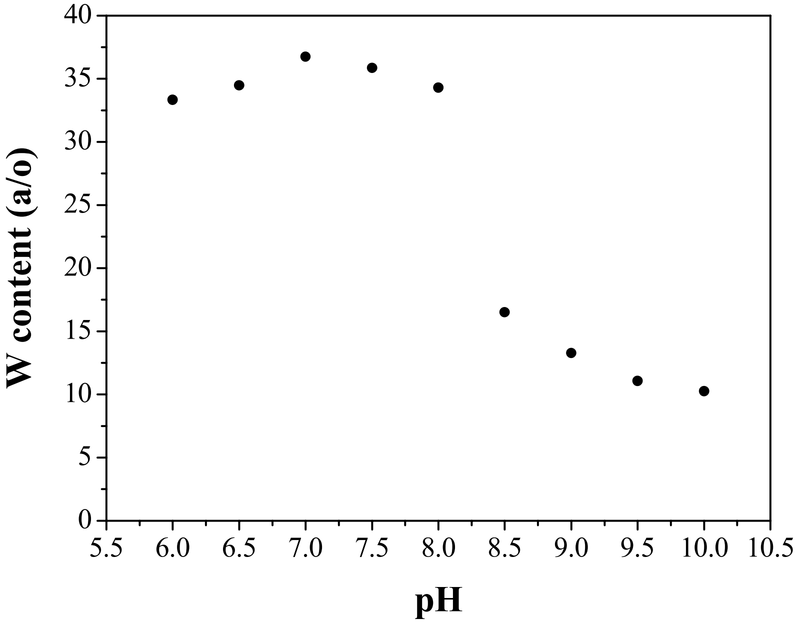

Figure 3. Dependence of the a/o of W in the alloy on pH (in the presence of NH_3).

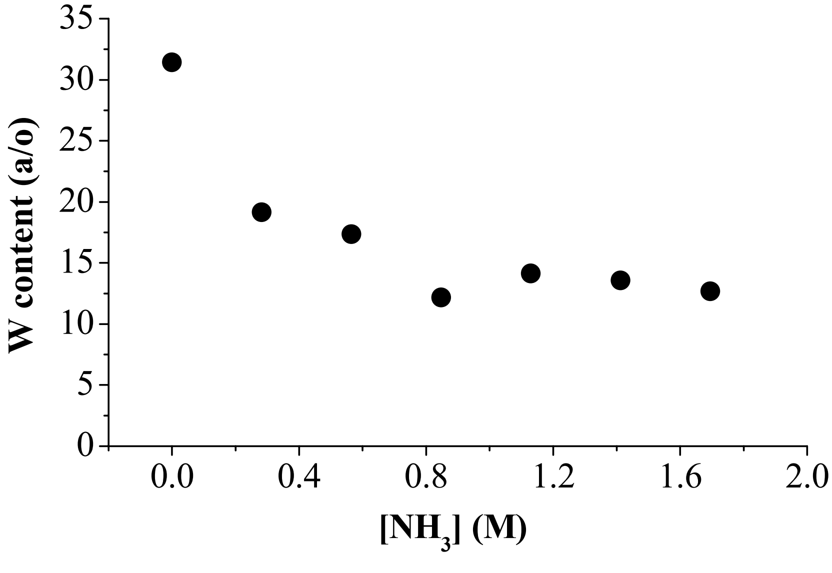

Figure 4. The effect of addition of ammonia on the concentration of W in the alloy.

The effect of mass transport was tested in two solutions: one containing 0.04 M Na_2WO_4 and 0.4 M $NiSO_4$, and another in which the ratio of concentrations of the two salts was inversed. The partial current densities for deposition of tungsten at 2,000 and 5,000 rpm were <u>calculated</u> to be $j_{L,W}$ = 72 and 132 mA/cm^2, respectively. In comparison, the <u>observed</u> limiting current densities for the same process were $j_{L,W}$ = 2.2 and 3.0 mA/cm^2, respectively, for the same rotation rates. Hence, one would not expect to observe an effect of rotation rate on the rate of deposition of tungsten, but a clear effect is observed, as shown in Fig. 5. These data were analyzed using a Levich-type plot of

$$1/j_W = 1/j_{ac} + 1/B\omega^{0.7} , \qquad [5]$$

where

$$B \equiv 0.079n\mathrm{F}r^{0.4}D^{0.64}\nu^{-0.34}c_\infty . \qquad [6]$$

The value of the parameter *B* was calculated from the slope of the line based on Eq. 5, and from it – the concentrations of the assumed precursor were obtained as 2.3 and 4.1 mM in solutions containing 0.04 and 0.4 M Na_2WO_4, respectively. Evidently, tungsten is not deposited from the tungstate ion in solution, but from some other species formed from it, which we assume to be the mixed-metal complex shown by Eq. 3. The fact that this complex is not at fast equilibrium with its constituents can readily be explained by the kinetic hindrance associated with reactions between ions of the same sign, particularly since one of these ions carries a high charge.

The Synergistic Effects of Nickel and Tungsten

One of the best indications to the existence of a precursor that contains both Ni and W for deposition of tungsten is the mutual enhancement of the rate of deposition of one metal by the addition of the other to the solution. This has been suggested in earlier studies, but here it has been quantified. When the partial current density j_W for deposition of W is plotted as a function of the concentration of Ni^{2+} in solution, a distinct synergistic effect is observed, as shown in Fig. 6b. It should be noted that the a/o of W in the alloy decreases, because the rate of deposition of Ni increases faster than that of W, as shown in Fig. 6a. Nevertheless, the fact remains that addition of nickel ions to the solution increases the rate of deposition of tungsten. Moreover, Fig. 7 shows that the addition of WO_4^{2-} to the solution increases the rate of Ni deposition, in addition to increasing the partial current density for deposition of W, of course. This is entirely consistent with Eq. 3 above, in which it is assumed that the precursor for the deposition of Ni-W alloys is the mixed-metal complex, formed from a reaction between $[(\mathrm{Ni})(\mathrm{Cit})]^{1-}$ and $[(\mathrm{WO}_4)(\mathrm{Cit})(\mathrm{H})]^{4-}$.

The above argument leaves one apparent issue to be resolved. If the precursor for deposition of the alloy contains one atom of Ni and one atom of W (cf. Eq. 3), one may expect that the alloy would have the simple composition of NiW, namely it should have a 50 a/o of W. This is contrary to our own observations, as well as to those of everybody else in the field. Indeed, we have been able to deposit alloys with any composition from

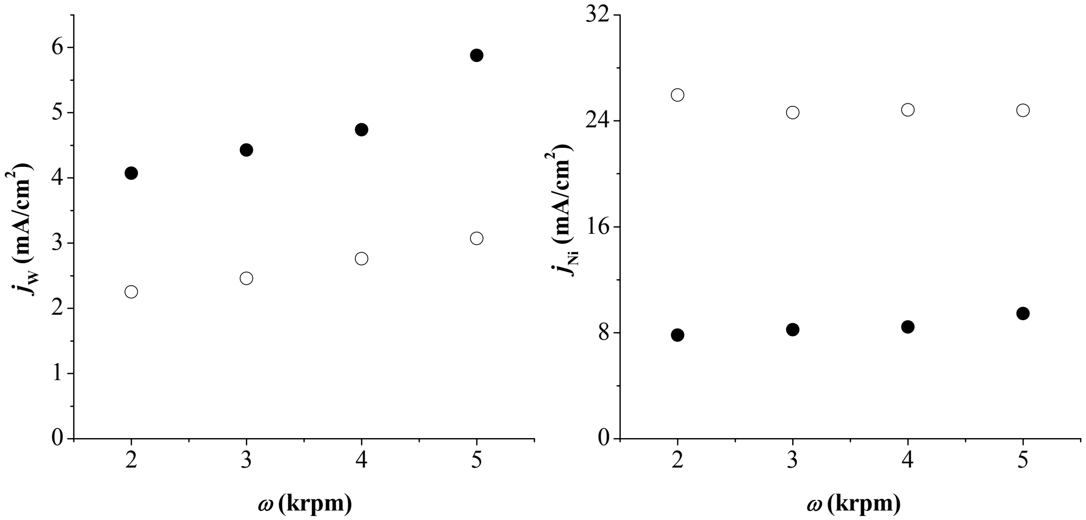

Figure 5. Mass-transport limitation of the partial current densities for deposition of W and Ni. Hollow circles (ooo): 0.04 M Na_2WO_4, 0.4 M $NiSO_4$;
filled circles (●●●): 0.4 M Na_2WO_4, 0.04 M $NiSO_4$.

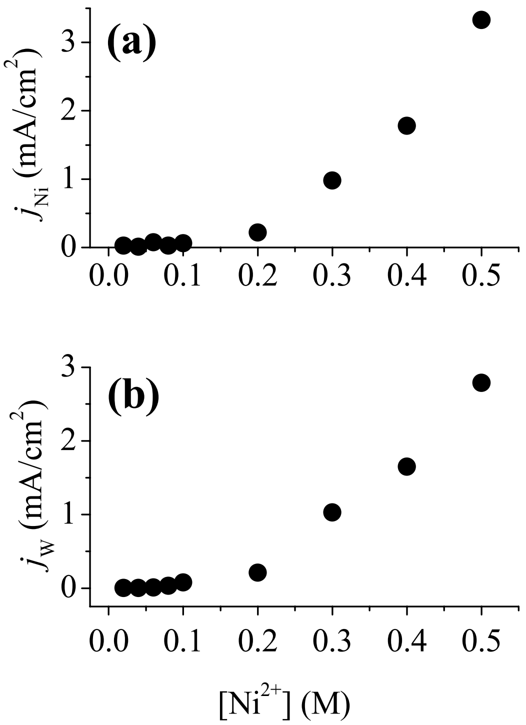

Figure 6. The effect of Ni^{2+} ion concentration on the partial current densities of nickel (a) and tungsten (b). All baths contained 0.1 M WO_4^{2-} and 0.6 M Cit^{3-}.

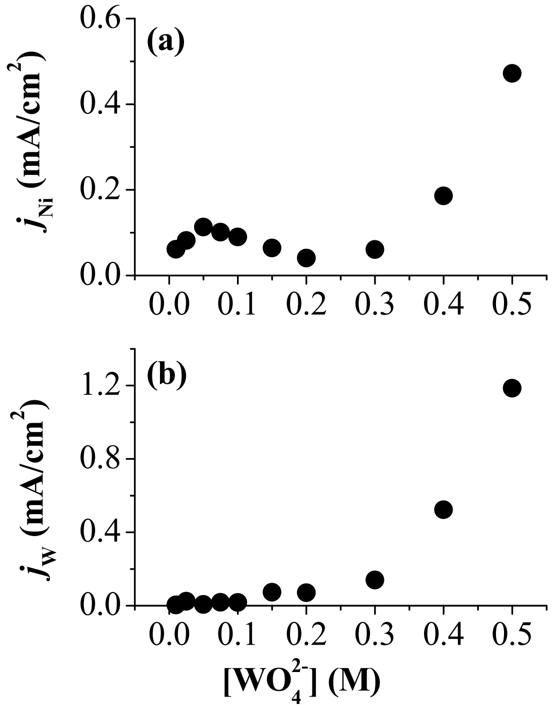

Figure 7. The effect of WO_4^{2-} ion concentration on the partial current densities of nickel (a) and tungsten (b). All baths contained 0.1 M Ni^{2+} and 0.6 M Cit^{3-}.

a few a/o W up to the expected 50 a/o W, including the well-know Ni_4W phase, which has not been prepared before by electroplating (26-28). This is easy to understand when one remembers that tungsten can only be deposited from its mixed-metal complex, shown in Eq. 3, while Ni can also be deposited from its complexes with citrate and with NH_3. Thus, there can be several parallel reactions leading to deposition of Ni, while only one or two pathways in which Ni and W are deposited in a 1:1 ratio.

The Linear Dependence of j_W on the Rate of Formation of the Mixed-Metal Complex

The rate of formation of the mixed-metal complex, according to Eq. 3, can be written as

$$v = k[(Ni)(Cit)]^{-} \times [(WO_4)(Cit)(H)]^{4-}, \qquad [7]$$

where k is a rate constant. The concentration of the mixed-metal complex was shown above to be approximately 2.3 mM, while the concentrations of $NiSO_4$, Na_2WO_4 and Na_3Cit were 0.4, 0.04 and 0.6 M, respectively. In view of the partial mass-transport limitation observed for deposition of tungsten, it can be concluded that this complex is not at equilibrium with its constituents in solution. Hence, the partial current density for deposition of tungsten must be proportional to the rate of its formation:

$$j_{\mathrm{W}} = n\mathrm{F}\mathrm{v} = n\mathrm{F}k\left[(\mathrm{Ni})(\mathrm{Cit})\right]^{-} \times \left[(\mathrm{WO}_4)(\mathrm{Cit})(\mathrm{H})\right]^{4-}. \qquad [8]$$

Figure 8a shows plots of the concentrations of the two complexes in Eq. 8 as a function of the concentration of WO_4^{2-} in solution. In Fig. 8b, the partial current density for deposition of tungsten is drawn *vs.* the product of the two concentrations included in Eqs. 7 and 8. A well established linear dependence is observed, supporting the validity of Eq. 8. The same procedure was repeated in several solutions, and in each case a linear relationship was observed, lending further strong support for the existence of the mixed-metal complex shown in Eq. 3. This can explain the role of Ni in assisting the deposition of W (as a Ni-W alloy) from aqueous solutions. The induced codeposition of W with Co and Fe, as well as that of Mo with the same transition metals, can probably be associated with the same mechanism.

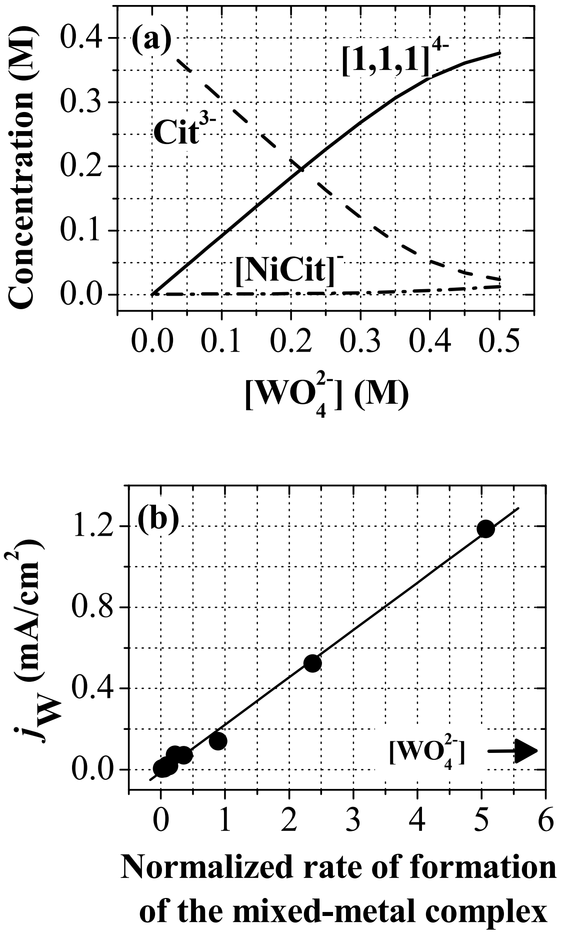

Figure 8. (a) The concentrations of the nickel citrate, tungsten citrate and free citrate ions as a function of the concentration of WO_4^{2-}. (b) Linear dependence of the partial current density of deposition of tungsten on the rate of formation of the mixed-metal complex. The concentrations of Cit^{3-} and Ni^{2+} were 0.6 and 0.1 M, respectively.

Conclusions

A clear distinction is made between outer-sphere charge transfer processes, in which both reactant and product reside on the solution side of the interface, and metal deposition/dissolution reactions, where both mass and charge must cross the interface. Theories have been developed for the former class, where it is obvious that the charge is carried across the interface by electrons, but not for the latter, where the charge is carried across the interface by the ions. The common practice of treating metal deposition/dissolution following the formalism developed for electron transfer is criticized.

The mechanism of induced codeposition of tungsten with nickel is elusive. Acceptable explanations were not given until recently (21,22), although many tentative suggestions have been proposed since this process was discovered, about seventy years ago (18).

The mechanism proposed here postulates the existence of a mixed-metal complex, containing the ions of both metals, with citrate as the complexing agent – holding the two metals together. One or two protons are also included in the complex (depending on pH), helping to reduce the total charge and, thereby, increase the stability of the complex. Unfortunately, the existence of the mixed-metal complex has not yet been confirmed directly, but there is ample indirect evidence to support its existence and the interpretation of the mechanism of induced codeposition proposed here.

The chemistry of the solution was considered. It was observed that, at or around pH = 8, the predominant species in solution are $[(\mathrm{Ni})(\mathrm{Cit})]^-$, $[(\mathrm{HWO_4})(\mathrm{Cit})]^{4-}$ and Cit^{3-}. The former two can interact, giving rise to a mixed-metal complex, $[(\mathrm{Ni})(\mathrm{WO_4})(\mathrm{H})(\mathrm{Cit})]^{2-}$, according to Eq. 3. Tungsten can only be deposited from this complex (or a very similar one containing two protons, at lower pH), as evident by the fact that it cannot be deposited in the absence of Ni^{2+} ions in solution. On the other hand, nickel can be deposited from its complex with citrate (or with NH_3), providing several alternative routes for deposition of this metal. Thus, alloys with a wide range of compositions, from a few a/o up to 50 a/o W, have been routinely obtained by proper selection of the composition of the solution. Under extreme conditions, where tungstate was in very large excess ($\mathrm{WO_4^{2-}}/\mathrm{Ni}^{2+} \geq 20$), an alloy with a composition corresponding to NiW_2 was found (22). This was assumed to result from a reaction such as

$$[(\mathrm{Ni})(\mathrm{WO_4})(\mathrm{H})(\mathrm{Cit})]^{2-} + [(\mathrm{WO_4})(\mathrm{H})(\mathrm{Cit})]^{4-} \rightarrow [(\mathrm{Ni})(\mathrm{WO_4})_2(\mathrm{H})_2(\mathrm{Cit})]^{3-} + \mathrm{Cit}^{3-}. \quad [9]$$

The evidence for the existence of the mixed-metal complex is supported by: (a) The mutual synergistic influence of each metal on the deposition rate of the other; (b) The observed dependence of the partial current density for deposition of tungsten on the rate of mass transport, which can only be explained if it is assumed that the concentration of the precursor is relatively low. This concentration was calculated to be 2.3 and 4.1 mM in solutions containing 40 and 400 mM of the W-Cit complex, respectively; (c) The effect of pH on the composition of the alloy also supports the existence of the mixed-metal complex as the precursor, based on the known distribution of the Ni-Cit and the W-Cit complexes and the dependence of each of them on pH; (d) Finally, the linear dependence of the partial current density for deposition of tungsten or the rate of formation of the mixed-metal complex supports very strongly the assumption that it is indeed this mixed-metal complex that serves as the precursor for deposition of the Ni-W alloy.

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