Electrochemical deposition and phase structure of electrodeposited Ni–W alloys

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The induced deposition of W in the presence or iron-group metals has been known for a long time without a proper understanding of the mechanism of the codepostion. Hints were made by several authors, concerning primarily a similar case of codeposition of Mo, which were not sufficiently substantiated by proper kinetic investigations, as the research was oriented mainly toward practical aims. In the present investigation the induced deposition of W with Ni was studied primarily from the viewpoint of the composition and phase structure of the resulting Ni–W alloy. The method of anodic linear sweep voltammetry was used to analyze the deposits obtained at a rotating disc electrode, as this has proved to be a good tool for the analysis of thin-layer deposits. The polarization diagram was found to exhibit a sharp current maximum and a subsequent decay at potentials at which Ni deposition starts. As some W oxide was found to deposit at less negative potential, the sharp rise of current and the maximum are acribed to the catalytic effect of the oxide on hydrogen evolution, larger than that of the depositing Ni–W alloy. The deposit was found to exhibit two peaks upon anodic dissolution, both at significantly more positive potentials than that of Ni dissolution. The first peak is of a limited quantity of electricity, independent on the amount of the deposit which is reflected in the second peak only. An aging effect was found, rendering an alloy requiring much more positive potentials for dissolution than those for dissolution of freshly deposited alloys.

Key words: nickel–wolfram, induced codeposition, phase structure.

The electrochemical codeposition of elements which cannot be directly reduced to the metallic state from aqueous solutions, such as W and Mo, with iron-group metals (Fe, Ni, Co) has attracted significant attention for a long period of time for two basic reasons:

(a) such alloy deposits exhibit properties (*e.g.,* significant corrosion resistance in various media, wear resistance, catalytic activity for H_2, *etc.*) useful in practical applications and

(b) they represent cases of the so-called "induced deposition" whereby the iron-group metal enables the reduction of oxides of those elements to the metallic

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state, thus exhibiting a "catalytic" action whose mechanism is of fundamental interest from the viewpoint of electrochemical kinetics.

The fact that W and Mo cannot be obtained in the metallic state by electrodeposition from aqueous solutions has been known for more than 100 years.* However, as early as in the 1930s, several authors reproted obtaining W and Mo alloys with ferrous group metals. Thus, Fink and Jones[1] obtained an Fe–W alloy, virtually by chance, as their electrolyte contained Fe as an impurity. Of the early work, one should note that of Gol'tz and Kharlamov[2] who developed ammoniacal baths suitable for the deposition of Ni–W alloys usable in practice (0.2 mm thick film with 30% current efficiency).

A brakthrough in terms of practical alloy deposition was made in the 1940s with the use of ammoniacal baths containing salts of organic oxy-acids tartrate and citrate.[3-7]

Most of the authors were dedicated to establishing the effect of the electrolysis conditions (bath composition, pH, current density, temperature) on the content of W (or Mo) in the alloy and to the current efficiency of deposition. However, some also made attempts to elucidate the mechanism of the process.

Thus, Holt[8] suggested several possible schemes. Following an observation of a non-metallic layer at the cathode, he visualized the formation of a colloidal diaphragm, consisting of lower-valency oxides of W, which prevents the approach of large ions, like WO_4^{2-} and stop further reduction. The ions of the iron-group metals were supposed to penetrate into the diaphragm destroying its structure. Furthermore, these ions exhibit a "catalytic effect", enabling W-species to be reduced to the metallic state. He was also the first to suggest that reduction occurs via the formation of complex species of the type $[Ni_x(WO_4)_y]^{(x-y)+}$ whereby $x>y$.[9]

Glasunov and Yolkin[10] observed the formation of a metallic film in the early phase of deposition which vanishes during further electrolysis. Hence, they suggested that the WO_4^{2-} ions are first reduced to lower-valency oxides which are subsequently reduced to W by atomic hydrogen which is evolving simultaneously. However, the metallic film is then sissolved again by a proportionation reaction with accumulating excess WO_4^{2-}.

$$W + W^{4+} \rightarrow 2W^{2+}$$
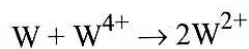
Recording the potentials at which deposition of W-alloys occurs, some authors[2,5,11] observed that it exhibits depolarization with respect to deposition poentials of both Ni (or Fe) and W. As the standard poential of W, calculated on the basis of thermodynamic data, should be –1.1 V *vs.* SCE,[12] the depolarisation amounted to at least 0.3 to 0.7 V. This was ascribed to the strong interaction between W and iron-group metals. Solovyeva and Vagramyan[11] assumed the formation of an intermetallic compound Fe_2W.

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* This was contested by Viacheslavov Grilihcs and Burkof in *Galvanic Coatings of Noble and Rare Metals*, (in Russian), Mashinostroicnic, Leningrad (1970), p. 284

The above mentioned authors, however, did not substantiate their claims with some detailed experimental confirmation, as their work was oriented towards results usable in practice.

Frantsevich-Zabludovskaya and Zayats[13] devoted their work to a more detailed investigation of the polarisation behavior of the systems Ni–W and Ni–Mo, but they did not comment on the causes of the significant depolarisation they recorded.

As can be seen, in the earlier work little attention was given to conventional electrode kinetics aspects, which could render some insight into the mechanism of induced deposition. Also, few attempts were made to determine the phase structure of the deposits. Some X-ray diffraction data indicated homogeneity, ascribable to a solid solution of W in Ni, in spite of the fact that some layered structure was observed in the deposit.[13]

It was the recent work of Podlaha and Landolt,[14] on induced deposition of Mo, which resulted in a number of interesting observation from the viewpoint of electrode kinetics. The most significant observation was that, up to a certain rate of rotation of the electrode, the rate of Mo deposition is diffusion controlled, while above it, the ratio of the partial currents of Ni and Mo remain constant. As it is unlikely that the reduction kinetics of such widely different species, as are the citrate complex of Ni and the MoO_4^{2-} ion, have a similar dependence on the electrode potential, the observed fact is an indication that MoO_4^{2-} reduction to Mo is directly dependent on the reduction of the Ni-species. This speaks against the earlier proposed mechanism involving hydrogen in "status nascendi". Hence, they proposed a mechanism whereby, in order to obtain metallic Mo, it is necessary to obtain an intermediate species of the formula $[NiCitMoO_2]_{ads}$.

They also observed that of the three iron-group metals, iron exhibits an anomalous behavior in that the Mo partial current (and hence the Mo content in the alloy) is significantly smaller than in the case of codeposition with Ni or Co. They ascribed this to a partial reduction of the Fe-species to Fe(OH) which forms an adsorbed layer on the electrode inhibiting the reduction of molybdate. Indeed, this is in accordance with the finding of Beltowska-Lehman[15] that in acid citrate there is significantly more Mo in the alloy with Fe than in that with Ni, as at such a pH the existence of an adsorbed film of Fe(OH) is unlikely.

No report of corresponding work on Ni–W alloys could be found in the literature. In the present work, and before engaging in a detailed kinetic investigation of the induced deposition of Ni–W alloys, an attempt was made to establish the effect of plating variables in the process of codeposition, following a known recipe[16] on the quality of the deposit in terms of composition and phase structure. The deposits were analyzed for both, using anodic linear sweep voltammetry (ALSV), which has been shown to be a good tool for the analysis of thin layer deposits.[17] Further research is in progress.

EXPERIMENTAL

Samples of Ni–W alloys were electrodeposited on a rotating disc (RDE) assembly (Tacussel, Controvit) on Au and glassy-carbon discs, (of 0.159 cm^2 surface area) from a bath composed of NiSO$_4$ (0.075 M), Na$_2$WO$_4$ (0.2 M), citric acid (0.3 M), whose pH of 8.6 was adjusted by addition of NH$_4$OH. All chemicals were of reagent grade quality and were dissolved in triply distilled (18 MΩ) water. Deposition was carried out at two different constant temperatures of 23 °C and 40 °C. A conventional glass electrolytic cell was used with SCE reference electrode, a Pt-counter electrode in a separate compartment and provisions for thermostating and purging of the electrolyte free of oxygen with purified nitrogen.

In order to establish the potential and current density (cd) range in which good metallic deposits can be obtained, potential sweep experiments were first carried out using a universal programmer (PAR 1-3) connected to the cell *via* a potentiostat (PAR 273).

For the ALSV analysis, the electrodes with deposits were transferred into another solution consisting of 1 M NaCl and 0.01 M HCl to overcome Ni passivation. The ALSV experiment were carried out at room temperature. The scan rate was 0.5 mV s^{-1}, unless otherwise stated.

The composition of the alloys was determined by analyzing spectrophotometrically the quantity of Ni in the solution in which the samples were dissolved .The content of W was found by integrating the recorded ALSV, subtracting the quantity of electricity due to Ni (assuming a 2-electron exchange) and calculating the amount of W (assuming a 6-electron exchange) from the difference.

Some samples were submitted to Energy Dispersive Spectroscopy (EDS) for a direct determination of both the W and Ni content.

RESULTS

a) Polarisation behavior of the system

Potential sweep recording on the Au RDE at a very low sweep-rate (1 mV s^{-1}) renders quasi-steady-state polarisation behavior (Fig. 1). Recordings were made separately in the basic electrolyte free of both Ni and W, in the same electrolyte but containing the Ni-salt and finally in the electrolyte containing both the Ni-salt and tungstate, all present in the concentraitons cited above (*cf.* alloy deposition bath in the Experimental section). It is seen that the polarisation curve obtained in the presence of Ni follows that obtained in the basic electrolyte down to a potential of −1.31 V. Upon further polarisation it separates from the former in the direction of higher cds. A curent step is observed at a cd of 25 mA cm^{-2}. In the presence of tungstate, significant currents are recorded already at −1.0 V. A curent peak appears at the potential at which the current in the presence of Ni starts deviating from the base line. A current minimum is recorded at the potential of the beginning of the current step in the latter case, *i.e.*, at −1.35 V. Further on, the polarisaiton curve in the presence of both tungstate and Ni runs virtually parallel to that in the presence of Ni alone, but with cds higher by about 36 mA cm^{-2}.

When the polarisation curve was recorded in the former electrolyte but at an electrode already covered by a layer of the Ni-W alloy, obtained in the cd region of 200 mA cm^{-2}, (returning the potential in the positive direction) it did not exhibit the previously recorded maximum.

In a visual observation of the electrode during polarisation in the electrolyte containing both W and Ni, it was noted that, up to the cd maximum, the electrode
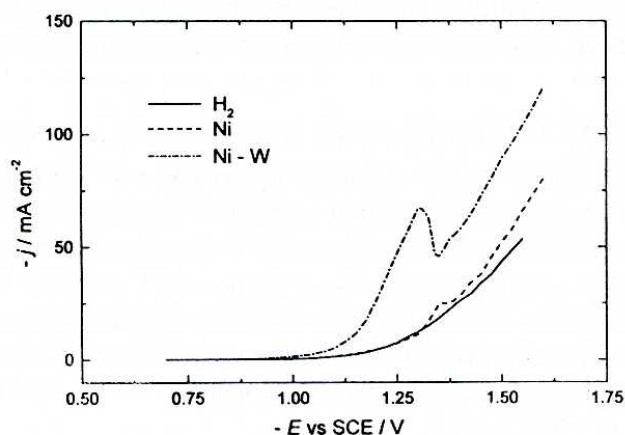
Fig. 1. Polarisation diagram for the processes occurring at a RD Au electrode in the base electrolyte a), in the presence of Ni-species only b), as well as in the presence of both Ni and W containing species. Temperature 23 °C; rotation rate 1000 rpm; sweep rate 1 mV s^{-1}.

was covered with some dull black deposit. At more negative potentials, a transition was observed to a smooth and shiny metallic deposit.

As shown in Fig. 2, the same trends were observed at the elevated temperature of 40 °C, the peak and minimum cds being significantly more pronounced and the corresponding potentials being somewhat shifted in the negative direction.

Virtually linear Tafel plots, shown in Fig. 3, were obtained, but they exhibit somewhat different slopes in the low and the high cd region. One should note that
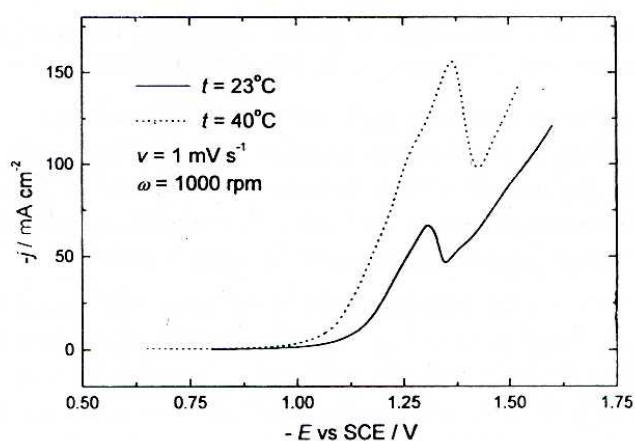

Fig. 2. Polarisation diagrams for the codeposition of Ni and W on a RD Au electrode at two different temperatutes: a) 23 °C; b) 40 °C. Rotation rate 1000 rpm; sweep rate 1 mV s^{-1}.

the transition leading to higher slopes occurs close to the cd at which the deposition of Ni was observed. The passivation-like loop reflects the maxima and minima in Figs. 1 and 2.

b) Dissolution of Ni–W alloys by anodic linear sweep of potential

The anodic linear sweep voltammogram (ALSV) obtained when Ni was deposited in the absence of tungstate in solution is shown in Fig. 4. It is seen that in the electrolyte used for anodic dissolution (*cf.* Experimental), it renders a relatively sharp single peak at a peak potential, E_p, at about -0.1 V *vs.* SCE. There is, however, a rather slow rise in the dissolution current before the peak is reached. The current efficiency of Ni deposition, obtained by integration of the peak and comparison with the amount of electricity spent during the deposition, was found to be about 0.2 at a deposition cd of 40 mA cm^{-2}.

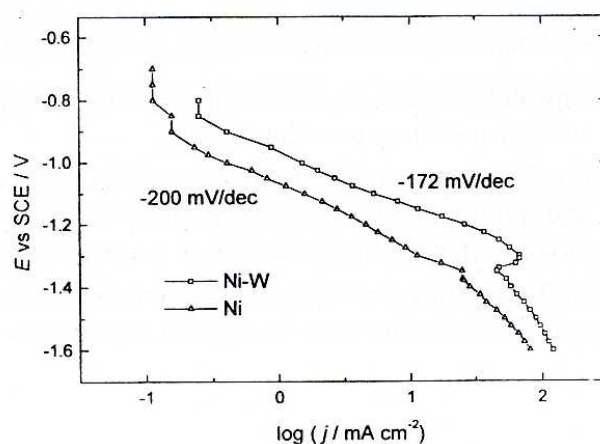Fig. 3. Tafel plots for the codeposition of H$_2$ and Ni (a) as well as for H$_2$ and the Ni–W alloys. Temperature 23 °C; rotation rate 1000 rpm; sweep rate 1 mV s^{-1}.

On lowering the cd, however, it is becoming significantly lower. Also, the rotation rate of the RDE during deposition was found to have an effect on the extension of the peak. Thus, in the absence of rotation, the current rise in the ALSV is relatively slow and, for one and the same sweep rate (0.5 mV s^{-1}), a significantly lower peak is reached at a potential shifted in the positive direction by some 55 mV.

Typical ALSV for the dissolution of Ni–W alloys deposited in layers equivalent to 1 to 5 C cm^{-2} are given in Fig. 5. Characteristic of all the ALSV, except that of 1 C cm^{-2}, are two peaks, one at a potential of about 0 V *vs.* SCE and the other between 0.1 nd 0.2 V. It is noteworthy that the first peak does not grow with increasing amount of the deposit. Hence, all of the alloy deposited in excess of 1 C cm^{-2} is of the kind rendering the second peak.
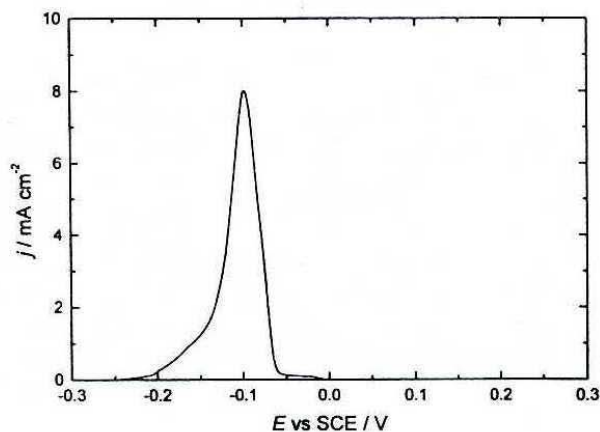
Fig. 4. ALSV of a deposit obtained from a solution containing only Ni-species at 1000 rpm with 40 mA cm^{-2}; temperature 23 °C; sweep rate 0.5 mV s^{-1}.

It was found that a very low sweep rate (below 1 mV s^{-1}) was required for the two peaks in the voltammogram to be relatively well separated.

Integration of the ALSV and comparison with the amount of electricity spent during deposition allowed the current efficiency of deposition to be determined. This was found to increase on increasing the amount of the deposit from 0.22 to 0.35. No Ni was found in the deposit obtained in the amount equivalent to 1 C cm^{-2}.
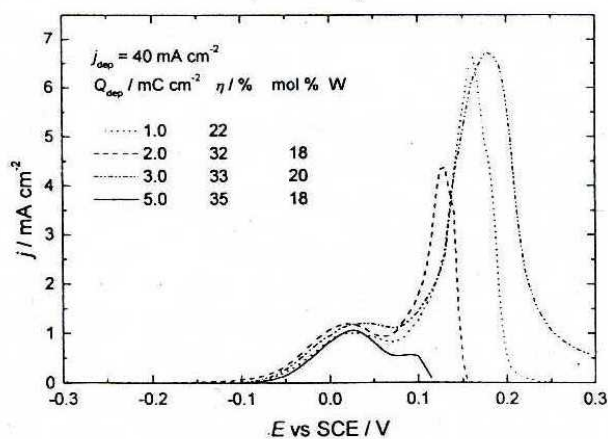

Fig. 5. ALSV of deposits obtained from the alloy deposition bath at 1000 rpm with 40 mA cm^{-2} by passing different quantities of electricity. Temperature 23 °C; sweep rate 0.5 mV s^{-1}.

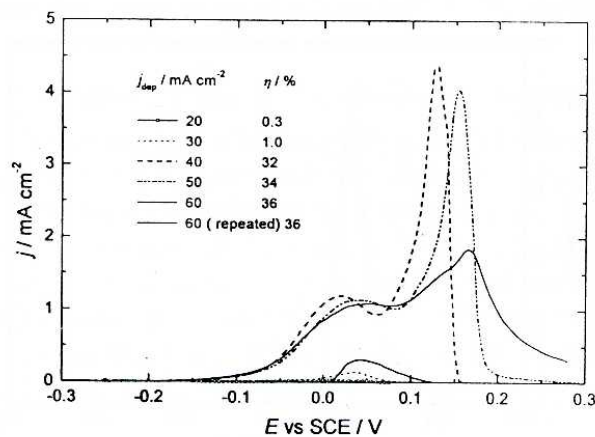Fig. 6. Dependence of the ALSV on the current density of deposition, *i.e.*, after passing one and the same quantity of electricity of 2 C cm^{-2}; calculated current efficiency of deposition, η_d, noted in the figure; temperature 23 °C; sweep rate 0.5 mV s^{-1}.

In thicker deposits Ni prevailed. The W content of the alloy, however, remained virtually independent of the amount of the deposit, amounting to 18–20%.

The *cd* of deposition proved to be a very important parameter exhibitng a critical value. As seen in Fig. 6, insignificant quantities of the deposit were obtained below 40 mA cm^{-2}, the current efficiency being of the ordeer of 1% or lower. Above 40 mA cm^{-2} a major increase in the current efficiency occurred. For one and the

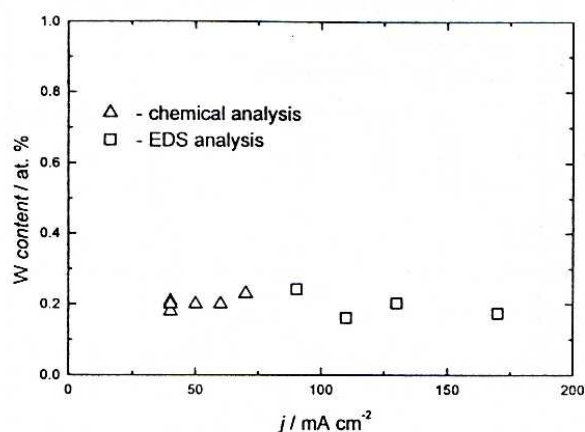Fig. 7. The W content of the alloys as a function of the cd of deposition, $\triangle$ – obtained by chemical analysis; $\square$ – obtained by EDS.
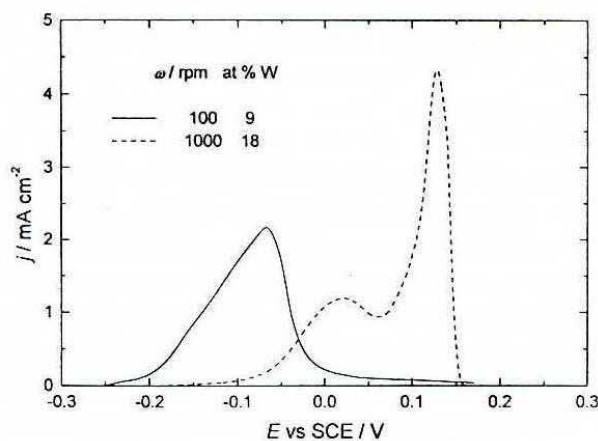
Fig. 8. Effect of the rotation rate of the RDE during alloy desposition with 40 mA cm^{-2} after passing 2 C cm^{-2} of electricity; temperature 23 °C; sweep rate 0.5 mV s^{-1}.

same amount of deposit, increasing the cd had virtually no effect on the structure of the deposit, except that dissolution was slower, so that, for a given sweep rate, it could not be completed within a single sweep. The current efficiency exhibited some small rise (0.32 to 0.36 with a rise of the cd from 40 to 60 mA cm^{-2}). The critical cd was found to increase with increasing deposition temperature. Thus, at 40 °C it was found to be 70 mA cm^{-2}. It should be noted, that the analysis of the W content in the alloy, as seen in Fig. 7, exhibited no clear dependence on the cd of deposition.

It is found that the structure of the ALSV strongly depends on the rotation rate of the electrode during the deposition. Thus, Fig. 8 shows that, at the relatively low rotation rate of 100 rpm, a single peak is obtained with a E_p similar to that obtained for pure Ni dissolution. Both the current efficiency of deposition and the W content of the alloy were found to be significantly smaller than when the electrode was rotated at 1000 rpm (0.24 vs. 0.32 and 9% vs. 18%, resp.). A separation of the peaks was obtained when the deposition was carried out between 250 and 500 rpm. In these cases, a sweep rate of 0.5 mV s^{-1} was found to be insufficient for complete dissolution of the alloy within the first sweep. Hence, sweeping had to be repeated.

The increase in the Ni concentration in solution above that used in all the experiments reported so far, resulted in a single peak at the ALSV with a E_p between those of the two peaks of the previous voltammograms.

The phenomenon of aging of the alloy, resulting in a significant stabilization with time, was observed, as shown in Fig. 9. Thus, the peaks were found to become much broader and the peak potentials shifted by several hundred mV.

DISCUSSION

Polarisation recordings indicate that Ni is not deposited till the cathodic potential of −1.31V is reached. The recorded current in the Ni containing electrolyte is due to hydrogen evolution only. Ni starts to deposit after −1.31 V and soon attains some limiting current plateau. Calculations using the Levich equation indicate that for the concentration of Ni in solution (0.075 M) and the rotation speed (1000 rpm) used in there experiment, the diffusion limiting current at the RDE should have a value of the order of 90 mA cm^{-2}. After subtracting the hydrogen evolution current from the current step, it appears that the recorded limiting current is lower by an order of magnitude than the calculated value. Hence, it can be concluded that the beginning of deposition involves some minority Ni species (either Ni^{2+} ions or some lower complex) and that only after overcoming the current plateau Ni deposits from the prevailing ammonium complex. In the presence of tungstate, down to the potential of Ni deposition, the significant increase in the cd must be due to the reduction of the tungstate to lower valency state oxides, which deposit at the electrode in the form of a dull black coating. It appears, however, that it also reflects an increase in the partial current of hydrogen evolution due to the significant catalytic activity of the oxide for this reaction.
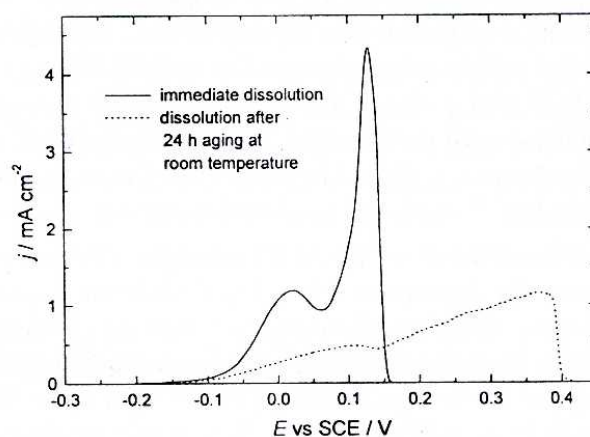

Fig. 9. The effect of aging of the alloy deposit obtained with 40 mA cm^{-2} after passing 2 C cm^{-2} of electricity; temperature 23 °C; rotation rate 1000 rpm; sweep rate 0.5 mV s^{-1}. Curves (a): immediately after deposition; (b) after 20 h.

As Ni starts depositing and covering the oxide (or causing its reduction to W), the catalytic activity for hydrogen evolution subsides. After the minimum in the cd is reached, the further increase in the cd with the negative potential going should be due to the codeposition of W and Ni, but also to an increase in the hydrogen evolution rate similar to that on pure Ni. The parallelism of the increase of the two currents – that of deposition of pure Ni and of deposition of the Ni–W alloy – indicates that the deposition of W is closely related to the reduction of Ni, much along the lines of the mechanism suggested by Podlaha and Landolt[14] for the deposition of molybdenum.

It is interesting to note that the relatively large cd of hydrogen evolution in the absence of both W and Ni-species in the electrolyte (Fig. 1), and the relatively small increase in cd in the presence of Ni alone would suggest a relatively low current efficiency for Ni deposition. If this was also so in the presence of tungstate and the codeposition of the alloy, the relatively large increase in the cd at a given potential would suggest a large W content in the alloy. As the analyses show that this is not so, it appears that deposition of W has a catalytic effect on the Ni deposition as well.

The ALSV analysis of the alloy deposit compared to that of the pure Ni indicates the more noble character (more positive dissolution potentials) of the former. If it is assumed that this is due to stronger bonding of the atoms in the alloy lattice than in that of Ni, the difference of 0.3 V between the Ni peak and the dominant peak of the alloy is tantamount to about 79 kJ mol^{-1} of an alloy containing 18 at% W, requiring 2.72 Faradays per mole for dissolution. This represents a substantial difference in bond energy. The fact that no dissolution peak of Ni is observed indicates that all Ni is bound in the alloy lattice.

The appearance of two peaks in the ALSV is open to speculation. Usually it is ascribed to the presence of two different phases. In this case, however, the fact is that the first peak does not grow with increasing amount of electricity used for the deposition. This could be an indication of the existence of a layer of tungsten oxide deposited first at the electrode before the tungstate reduction attained such a concentration polarisation that Ni starts depositing. Tungstate reduciton, however, requires some codeposition of Ni as it does not appear at cd of deposition at which Ni does not deposit. The dominant peak should reflect dissolution of the solid solution of W in Ni as indicated by the phase diagram.

Alternatively, there could be a layer deposited on top of the alloy deposit, which is a precursor of the alloy formation. The fact that some aging effect is observed (Fig. 9), points to the relative instability of the deposit immediately after deposition, which is the situation of all the ALSV presented above.

The fact that very low sweep rates are needed for the separation of the two peaks, speaks in favor of the second case, implying difficulties in penetration of the solution into the porous alloy layer and the elution of the reaction products through it.

The observation that an increease in the deposition cd results in some shift of E_p in the positive direction, as well as in difficulties of dissolving the entire alloy layer within a single sweep, points to an increasing compactness (stability) of the deposit or of the overlayer.

The effect that reducing the rotation rate of the RDE results in a reduction of the current efficiency because of an increase in concentration polarisation of the Ni-species could be expected. However, the dramatic change in the W content of the alloy is contrary to expectation. As the rate of rotation is reduced by ten times the former is seen to be reduced by 50%.

Also, the formed alloy is found to dissolve in a single peak, with E_p close to that of dissolution of pure Ni. This phenomenon is at present difficult to explain and, among other aspects, is the subject of further investigation.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ТАЛОЖЕЊЕ И ФАЗНА СТРУКТУРА ЛЕГУРА Ni–W

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Таложење волфрама у присуству метала групе гвожђа, индуковано таложење, је феномен који је одавно познат. Међутим, механизам кодепозиције није разјашњен. Досадашња истраживања индукованог таложења (и то најчешће молибдена) првенствено су била усмерена ка примени у пракси, а недовољно праћена одговарајућим кинетичким испитивањима. У овом раду испитивано је индуковано таложење W са Ni првенствено са становишта састава и фазне структуре добијених Ni–W легура. Метода анодне линеарне промене потенцијала (ALSV) употребљена је за анализу превлака добијених на ротирајућој диск електроди. На катодним поларизационим дијаграмима таложења нађен је оштар струјни максимум на потенцијалу који одговара почетку таложења Ni. Пад струје се може приписати споријем издвајању водоника на легури Ni–W, него на оксиду волфрама који се добија при мање негативним потенцијалима. На анодним волтамограмима растварања јављају се два карактеристична струјна врха, оба на потенцијалима знатно позитивнијим од оних који оговарају растварању чистог Ni. Количина наелектрисања која одговара првом струјном врху је ограничена односно, повећање количине наелектрисања при таложењу одражава се у одговарајућем порасту наелектриања другог анодног струјног врха. Нађено је да се легуре, које су стајале на собној температури у току неколико часова после таложења, растварају на знатно позитивнијим потенцијалим од оних које су испитиване непосредно после таложења, што указује на стабилизацију процесом у чврстој фази.

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