INVESTIGATION OF CATHODIC POLARIZATION OCCURRING DURING SIMULTANEOUS DISCHARGE OF IRON AND TUNGSTEN IONS

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The preparation of alloys of tungsten with various metals is a problem of great practical importance at the present time. Many papers have appeared on this problem during recent years. A review and detailed analysis of these papers up to 1940 has been given in an article by Sklyarenko and Druzhinina [1]. The most practical method appears to be the preparation of tungsten from aqueous solutions, and most of the papers, therefore, have been concerned with work in that direction.

The difficulty of preparing tungsten from aqueous solutions is associated with the preferential separation of hydrogen at the cathode owing to the strongly negative potential required for the separation of tungsten and the low value of the hydrogen overvoltage on tungsten. Among the investigations on the preparation of tungsten and its alloys from aqueous solutions, we must draw particular attention to the work of Golts and Kharlamov [2], who, in an investigation in 1936 on the polarization curves obtained in the deposition of tungsten-nickel, demonstrated the lowering of polarization in the deposition of nickel-tungsten, as compared with nickel alone; they showed also that the extent of this lowering increases with rise in temperature, and that this leads to increase in the tungsten content of the deposit.

Further work, by foreign investigators, on the preparation of tungsten alloys developed along the lines indicated by Golts and Kharlamov, namely, increasing of the depolarizing action of the metal codepositing with tungsten by rise in temperature, and addition of ammonium salts to the solution. The investigations on the preparation of tungsten alloys have been directed mainly to the selection of an electrolyte of suitable composition and a satisfactory electrolysis procedure, so as to obtain an alloy of high quality [3]. Very little study, however, has been devoted to the mechanism of the process of depositing electrolytic tungsten alloys. Recently, two papers by Holt and coworkers [4] on the mechanism of simultaneous discharge of ions of tungsten and metals of the iron group have appeared.

In these papers the theory of the so-called "catalytic reduction" of a metal was advanced. According to this theory, tungsten is reduced from aqueous solutions in presence of Ni, Fe, and Co as a result of the catalytic activity of the latter. Holt and Vaaler supposed that the following two reactions occur at the cathode:

$$M^{++} + 2e \longrightarrow M \qquad (1)$$

$$WO_4^{--} + 8H^{+} + 6e \longrightarrow W + 4H_2O \qquad (2)$$

Reaction 1 proceeds at the cathode until it is completely covered with a thin deposit of one of the iron-group metals, which encourages the occurrence of Reaction 2. When the iron-group metal (catalyst) has been covered by a layer of tungsten, Reaction 2 ceases and Reaction 1 proceeds again with the formation of a layer of catalyst.

In this way the periodic deposition of layers of iron-group metal (catalyst) and tungsten occurs at the cathode. The grounds for this point of view were found in polarographic investigations and in the investigation of the structure of electrolytic alloys carried out by Brenner, Burkhead, and Seegmiller [5]. In this connection, Holt and Vaaler point out that attempts to measure the potential for the electrodeposition of the alloy by the "direct" method do not give reproducible results. In a recent investigation, Clark and Lietzke showed that tungsten is deposited on a number of metals (Pb, Zn, Cd, Fe, Co, Ni, Cr, W, Cu, Ag, Pt), but the product of the electrochemical reaction is not the pure metal, but tungsten oxide. It was then noted that the largest amount of tungsten was separated in the case of metals of the iron group. The papers cited leave the following questions obscure:

1. Does the separation of tungsten occur as a result of "catalytic" reduction by hydrogen, or does depolarization occur as a result of the formation of a chemical compound or solid solutions between tungsten and the codepositing metal, as in the case of the discharge of sodium ions at a mercury cathode?

2. In the preparation of a tungsten alloy, is the discharge of the codepositing metal held back as a result of complex formation and leveling to the separation potential of tungsten?

For the investigation of alloy deposition we have used a direct method for the measurement of potentials that differs from the usual compensational method in the possibility of recording continuous change of potential of the electrode at any desired rate on photographic film.

EXPERIMENTAL

Method of Measurement

The potential of the electrode was measured with the aid of a high-resistance cathode voltmeter, taking a current of up to 10^{-12} amp, and a short-period mirror galvanometer having a sensitivity of 10^{-6} amp/mm and a period of 0.01 second. Such a method permits potential measurements to be made without the passage of appreciable current.

A 50-cc glass vessel was used as electrolytic cell. The cathode was formed by the end section of a copper or iron wire fused through the glass, the cathode surface being about 0.002 sq.cm; the anode was an iron or tungsten wire. A saturated calomel half-element was used as comparison electrode. The change in the potential of the electrode was recorded by means of the reflected light beam from the galvanometer on photographic film carried by a drum rotating at 1.5 mm per second.

Fig. 1 shows one of the records so obtained; it is a record of the change in the cathodic polarization of an iron electrode with time, the ordinates being potentials in millivolts and the abscissas time in seconds. The plot of the potential on the film was made as follows. A plot was first made of the zero position of the galvanometer, which corresponded to the potential of the calomel half-element to which all values of potential were referred. This line was plotted in a series of separate portions along the whole length of the film (lower, broken line). When the polarization current was switched on, the displacement of the reflection from the galvanometer from the zero line was a measure of the potential φ_1 for the separation of metal. For the determination of the stationary potential φ_0 of the electrode, the polarizing current was switched off after electrolysis had proceeded for a short time, and the position of the reflection from the mirror galvanometer after 15 seconds (sufficient time for the establishment of the potential) could be taken as a measure of φ_0. The deflection of the galvanometer when the current was switched on for a second time corresponded to the potential for the separation on a freshly deposited one-component cathode surface. The overvoltage for the separation of metal is therefore expressed by the difference –

$$\eta = \varphi_1 - \varphi_0 .$$

Experimental Results

In our study of the mechanism of the deposition of alloy, we first studied the cathodic polarization in citric acid solutions containing only iron ions or only tungsten ions, and then studied the simultaneous discharge of these ions. Following Holt, we used solutions containing, per liter, 66 g of citric acid, 50 g of Na_2WO_4, 2 g of Fe^{++} and Fe^{+++}, and NH_4OH to pH 8-8.5.

Cathodic Polarization in the Electrolysis of Solutions Containing Iron Ions. In the investigation of the polarization of iron in citric acid solutions, its dependence on current density, temperature, and the charge of the iron ions was examined. Fig. 2 represents the variation in polarization with time in the electrodeposition of iron from citric acid solution at 25° and at a current density of 5 amp per sq.dm. It will be seen from Fig. 2 that the potential for the separation of iron under these conditions is 1093 mv (section on the left), the stationary potential for iron is 727 mv (middle section), and the overvoltage is 366 mv.

Effect of Temperature. Study of the polarization of an iron electrode has shown that the temperature of electrolysis has a great effect on the polarization and overvoltage during the separation of iron. The results of the investigation are given in Table 1; each experiment was done in duplicate. As will be seen from Table 1, the error in measurement is about 20-30 mv, for the necessity of finding place on 70-80 mm photographic film for a polarization of about 1000 mv makes it impossible to increase the sensitivity of the

TABLE 1

Temperature (°C)	Separation potential (mv)	Stationary potential of iron (mv)	Overvoltage at $i = 5$ amp/sq.dm, in mv
16	1067; 1095	690; 727	379; 366
70	948; 930	690; 690	253; 241

measurement to more than 15-20 mv per 1-mm deflection of the galvanometer. It will be seen from Table 1 that raising of the temperature facilitates discharge of iron ions to the extent of 80-100 mv.

Effect of Current Density. The effect of current density on the polarization of iron was studied by the rapid method of recording polarization curves. Fig. 3 shows the polarization curve for the iron electrode, and it will be seen that the polarization does not vary linearly with current density. The form of the curve is analogous to the polarization curve for nickel obtained in sulfuric acid solutions [6]. According to the curve, the overvoltage at a current density of i = 5 amp per sq.dm is 374 mv. When the polarization curve is obtained at a different speed, the value of the polarization does not change, thus indicating the absence of concentrational polarization. The broken line in Fig. 3 is the stationary potential of iron at pH 8, which has the value 715 mv. As will be seen from the curve, after a short time the stationary potential is sharply displaced in the positive direction to a value corresponding to the potential of copper, which is the result of the autodissolution of iron in these solutions.

Cathodic Polarization in the Electrolysis of Solutions Containing Tungsten Ions. In the electrolysis of solutions containing only tungsten ions, i.e., in absence of a codepositing metal, no separation of tungsten could be detected, neither by analytical methods, nor by electrochemical methods, such as stationary potential measurements.

Cathodic Polarization in the Electrolysis of Solutions Containing Iron and Tungsten Ions. Study of the polarization in the simultaneous electrodeposition of iron and tungsten has shown that the separation potential for the alloy in citric acid solution at pH 8.1, at room temperature, and at a current density of i = 5 amp/sq.dm is 978 mv, the stationary potential of the alloy is 682 mv, and the overvoltage is 300 mv. The potential for the separation of the iron-tungsten alloy is, therefore, less than that for iron alone by about 120 mv.

It is impossible to compare the potential for the separation of the iron-tungsten alloy with that of pure tungsten, since we have not succeeded in causing the latter to separate from aqueous solutions, but in comparison with the standard potential of tungsten the separation potential for the iron-tungsten alloy (according to thermodynamical calculations) is depressed by 300 mv.

The effect of the electrolysis temperature on the polarization during electrodeposition of the alloy is shown in Table 2, from which it will be seen that raising of the temperature to 70° facilitates the separation of the iron-tungsten alloy to the extent of 100 mv.

TABLE 2

Temperature (°C)	Separation potential at i = 5 amp/sq.dm (mv)	Stationary potential at i = 5 amp/sq.dm (mv)
18	978	632
	978	672
70	879	628
	897	646

TABLE 3

Temperature (°C)	Depression of separation potential of alloy (mv) in comparison with —		$\frac{\Delta\varphi W}{\Delta\varphi Fe}$
	Standard potential of tungsten, $\Delta\varphi W$	Separation potential of iron	
20	320	109	2.9
70	430	208	2.1

It will be seen from these results that the separation potential of iron at a current density of i = 5 amp/sq.dm, and at room temperature, is 1087 mv; at 70° it is 930 mv. The separation potential for the alloy, however, is 978 mv at 20° and 879 mv at 70°. The position is made clearer in Table 3, in which the lowering of the separation potential of the alloy with the respect to those of iron and tungsten is shown. It will be seen that the more positive the separation potential of the alloy, the less becomes the relative difference between the separation potentials of iron and tungsten. Rise in temperature, therefore, leads to a positive displacement in the separation potential of the alloy, and so increases the concentration of tungsten in the deposit.

Discussion of Results

In order to obtain an iron-tungsten alloy the separation potentials of the two components must be made to approach one another so that simultaneous deposition is possible. This can be attained in two ways: 1) raise the potential for the separation of the more positive metal (Fe) to that of the tungsten, for example, by complex formation; and 2) lower the separation potential of the more negative metal, for example, by formation of a chemical compound or solid solution.

Fig. 1. Change of cathodic polarization with time, before and after switching off the current.

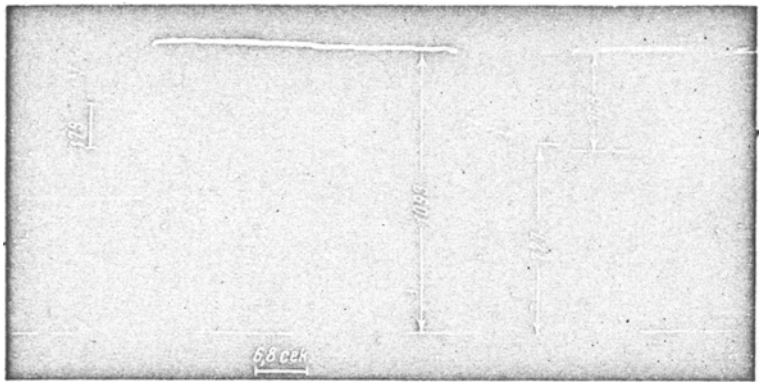

Fig. 2. Change of cathodic polarization with time in the electrodeposition of iron from citric acid solution at 25°C and at a current density of 5 amp/sq. dm.

Fig. 3. Variation of polarization with current density in the electrodeposition of iron (broken line: change in the potential of the electrode with time after switching off the current.)

The first way would not be satisfactory, for at a more negative potential of the electrode in aqueous solutions vigorous separation of hydrogen would occur. The second way is the more expedient, but it must be remembered that the work of formation of the chemical compound must be sufficiently large, in order to make the separation of tungsten possible.

We have already pointed out that, according to Holt and his students, the first stage in the electrodeposition of alloy is the separation of an iron-group metal on the electrode, after which separation of a layer of tungsten occurs on the surface of the catalyst. Holt, unfortunately, does not discuss the mechanism of the catalyzing action of the iron-group metal. In confirmation of his theory, he refers to the photomicrographs of sections taken by Brenner. From the photomicrographs, however, it may be seen that the thickness of individual layers is about 1 μ.

If alternate deposition of tungsten and iron does occur on the cathode, then a periodic variation in the potential should occur, for the potential of the electrode should have a higher value during the separation of an iron-group metal, and then fall by about 100 mv during the separation of the alloy. The period with which the potential would vary would be appreciable, for the deposition of a layer visible on the photomicrographs (X 250) to which Holt refers would require several seconds.

However, as our experiments on the variation of polarization with time have shown, no such variation of potential during electrodeposition of alloy occurs. It is impossible, therefore, to treat the layered structure of the electrolytic deposit that is visible on microsections as the result of the periodic deposition of two metals, all the more since a similar layered structure can be observed in the electrodeposition of a single metal.

It appears more likely that we are concerned here with the same mechanism of deposition as that found in the separation of sodium at a mercury cathode, where as a result of the formation of a chemical compound the potential required for the discharge of a sodium ion is greatly reduced. In the deposition of tungsten alloys, we probably again have the formation of a chemical compound (of the type Fe_2W), and the discharge of tungsten ions is, therefore, greatly facilitated, and the potential required for its separation becomes even less than the standard tungsten potential. The difference lies in the fact that in the electrolytic deposition of tungsten alloys, simultaneous separation of iron and tungsten occurs with formation of an alloy and periodic variation in potential therefore does not occur.

SUMMARY

1. An investigation of the simultaneous deposition of iron and tungsten has shown that the separation potential for the alloy is 100 mv less than the separation potential for iron and 300 mv less than the standard potential of tungsten.

2. It has been shown that the possibility of discharging tungsten ions depends on the depolarizing action of the simultaneous discharge of iron and tungsten ions.

3. It has been shown also that there is no periodic variation in the potential during the electrodeposition of tungsten and iron; which is in conflict with Holt's ideas on the layered deposition of iron and tungsten.

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