Some Possible Roles of Cathodic Films In Electrodeposition of Alloys, Part I

By Thomas C. Franklin and Venita Totten

A series of experiments was run on electrodeposition of alloys from aqueous pastes of insoluble compounds in a sandwich cell, to test the hypothesis that the 1:1 atomic ratio of the nickel-tin alloy could be formed by electrodeposition from a film of an insoluble compound containing the metals in a 1:1 ratio precipitate on the cathode. It was shown that the reduction of pastes of several insoluble compounds containing two reducible metal ions produced binary alloys in which the atomic ratios of the two metals were the ratios of simple whole numbers, in agreement with the prediction. The ratio of the metals varied with the substrate, however, and the ratios in the deposit were not the same as the ratios in the insoluble compounds. From this, it was concluded that the insoluble compounds used were converted to another insoluble compound before they were reduced to the metal.

A recent review of the research[1] for AESF Project 80 listed several ways in which some observed unusual behavior in the deposition of alloys could be accounted for by processes in which electrodeposition of the metal occurs by reduction of cathodic films of insoluble compounds, rather than by reduction of compounds in solution.

Anomalous Codeposition of Alloys

In anomalous codeposition of alloys, the electrodeposited alloy is richer in the metal that is normally more difficult to deposit.[2] Until the recent paper by Hessami and Tobias,[3] the most accepted model for this phenomenon envisioned precipitation of the more difficult-to-deposit metal as an insoluble compound on the electrode surface, interfering with reduction of the second metal. Electrodeposition of the more difficult-to-plate metal then occurred by reduction of the insoluble film, rather than by reduction of ions in solution.[3-9]

Fixed Ratio Alloys

An extreme example of anomalous codeposition is the nickel-tin alloy that deposits in a 1:1 atomic ratio over a wide range of experimental conditions.[10] There appears to be no metallurgical reason for this particular ratio, and attempts to find a soluble complex in the plating bath having a nickel-to-tin ratio of 1:1 have failed. An explanation could be that an insoluble, reducible 1:1 compound precipitated on the cathode, and that reduction of this compound produced the 1:1 alloy.

Induced Codeposition

In this type of system, one of the metals in an alloy being deposited is a metal not normally platable from that solution. This is merely a special example of anomalous codeposition and a mechanism similar to the regular anomalous codeposition mechanism can be visualized.

The initial phase of the study of the role of electrode filming was a study duplicating some of the effects of anomalous codeposition, by the formation of insoluble films during the deposition of copper and copper alloys.[11] The intent was to use these mechanisms in Project 80 to determine whether these were models that could explain the various phenomena. This is a report on a study that preceded Project 80 to determine whether it was possible to deposit, from insoluble salts, binary alloys with atomic ratios that were simple whole numbers, similar to the 1:1 atomic ratio observed with the nickel-tin alloy. This was investigated by reducing aqueous pastes of insoluble compounds.[12]

Experimental Procedure

Literature and experimental studies were made to find insoluble compounds that contained two reducible metals. The chemical experiments for the preparation of these insoluble compounds consisted of mixing a variety of cations containing a reducible metal ion with a variety of anions containing another reducible metal, and to determine whether a precipitate formed. If a precipitate formed, it was filtered, washed, dried, and analyzed by X-ray fluorescence to determine the ratio of the two metals in the compound and thus to determine a reasonable formula for the precipitate. X-ray diffraction patterns were also obtained and compared with the pattern of known compounds expected to be present. Table 1 shows the compounds that were formed and used in the study.

Once an insoluble compound was formed containing the two metals, experiments were performed to determine whether electrodeposition would occur from an aqueous paste of the insoluble compound. In these experiments, a sandwich cell (see figure) was used.[13] The sandwich cell consisted of two electrodes separated by a piece of filter paper. The anode

Table 1
Insoluble Compounds Used to Deposit Alloys Of Fixed Ratio Composition

Compound	Origin
•Titanium(III) ferricyanide	aqueous $TiCl_3$ + $K_3Fe(CN)_6$
*Titanium(III) hexacyanochromate	aqueous $TiCl_3$ + $K_3Cr(CN)_6$
•Zinc(II) ferricyanide	aqueous $ZnCl_2$ + $K_3Fe(CN)_6$
•Zinc(II) ferricyanide	aqueous $ZnCl_2$ + $K_4Fe(CN)_6$
•Zinc(II)hexacyanochromate	aqueous $ZnCl_2$ + $K_3Cr(CN)_6$
•Iron(III) hexacyanochromate	aqueous $FeCl_3$ + $K_3Cr(CN)_6$
•Cobalt(II) ferricyanide	aqueous $CoCl_2$ + $K_3Fe(CN)_6$
Cobalt(III) ferricyanide	aqueous $CoCl_3$ + $K_3Fe(CN)_6$
Iron(III) hexacyanocobaltate	aqueous $FeCl_3$ + $K_3Co(CN)_6$

•These compounds were confirmed by X-ray diffraction.
*This compound was precipitated from ethyl alcohol rather than water.

Table 2
Ratios of Metals Deposited in the Sandwich Cell On Nickel Cathodes

Insoluble Compound	Experimental Atomic Ratio	Precision	Expected Atomic Ratio
$Zn_3[Cr(CN)_6]_2$	Zn:Cr 4.0:1	±0.1	Zn:Cr 3:2
$Zn_3[Fe(CN)_6]_2$	Zn:Fe 4.0:1	±0.0	Zn:Fe 3:2
$Zn_2Fe(CN)_6$	Zn:Fe 4.0:1	±0.0	Zn:Fe 2:1
$CoFe(CN)_6$	Co:Fe 1:3.0	±0.0	Co:Fe 1:1
$Co_3[Fe(CN)_6]_2$	Co:Fe 1:1.1	±0.1	Co:Fe 3:2
$FeCo(CN)_6$	Fe:Co 1:3.0	±0.0	Fe:Co 1:1
$FeCr(CN)_6$	Fe:Cr 2.0:1	±0.1	Fe:Cr 1:1

Table 3
Ratios of Metals Deposited in the Sandwich Cell On Copper Cathodes

Insoluble Compound	Experimental Atomic Ratio	Precision	Expected Atomic Ratio
$Zn_3[Cr(CN)_6]_2$	Zn:Cr 2.0:1	±0.1	Zn:Cr 3:2
$Zn_3[Fe(CN)_6]_2$	Zn:Fe 8.0:1	±0.0	Zn:Fe 3:2
$Zn_2Fe(CN)_6$	Zn:Fe 7.0:1	±0.2	Zn:Fe 2:1
$CoFe(CN)_6$	Co:Fe 1.0:0	±0.0	Co:Fe 1:1
$Co_3[Fe(CN)_6]_2$	Co:Fe 5.0:1	±0.0	Co:Fe 3:2
$FeCo(CN)_6$	Fe:Co 2.5:1	±0.1	Fe:Co 1:1
$FeCr(CN)_6$	Fe:Cr 1.0:1	±0.1	Fe:Cr 1:1

was a large silver/silver chloride electrode. The cathode was copper, platinum or nickel. The two electrodes were separated with a piece of filter paper, and a paste of the insoluble compound mixed with the aqueous supporting electrolyte was placed adjacent to the cathode. The supporting electrolyte was 0.1 N potassium chloride. The cell was held together by placing a weight on the cell. Voltammetric experiments were run to determine whether the solid compound was reducible. Controlled current reductions were then performed on the reducible pastes; the deposits adhering to the cathode were analyzed by X-ray fluorescence and X-ray diffraction.

The working electrodes were 1 cm^2 in area. The anode/reference electrode was a silver/silver chloride foil. The supporting electrolyte was 0.10 M in potassium chloride. Unless otherwise stated, electrolysis was performed at a constant current of 50 mA for 1 hr.

The primary problem in the sandwich cell was the slow rate of reduction. Although increasing the temperature increased the rate at first, it also caused evaporation of the solvent, which led to decreases in the rate. For this reason, all of the experiments reported were run at room temperature. Because solvent evaporation was a problem, the length of the filter paper was increased; one end was dipped into a reservoir of the supporting electrolyte, so that it acted as a wick drawing more liquid into the cell as the water was destroyed by electrolysis.

Experimental Results

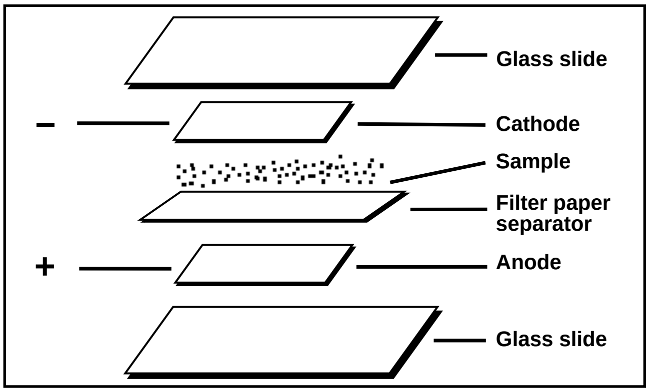
A survey was made of the reduction of aqueous pastes of a series of insoluble double cyanide complexes in the sandwich cell. These experiments were made to determine whether (1) electroreduction to the metal could occur using insoluble compounds; (2) the deposits were constant in composition; (3) the composition of the deposited binary alloys had atomic ratios of small whole numbers; and (4) the deposit ratios were the same as the ratio in the insoluble compound. Tables 2, 3 and 4 summarize the results obtained for a series of insoluble compounds containing cyanide complexes.

It can be seen that in all of the experiments on nickel and copper cathodes, deposition occurred, and the deposits, similar to the nickel-tin deposit, were alloys with the two metals having a composition in which the atomic ratios were small whole numbers. The ratios were not the same as the ratios in the insoluble compounds, however. Accordingly, in Table 2, from the model that had been developed, it was thought that reducing $Zn_3[Cr(CN)_6]_2$ or $Zn_3[Fe(CN)_6]_2$ would produce an alloy with a Zn/Cr or Zn/Fe atomic ratio of 3:2, the ratio in the insoluble compound, but it can be seen that in both cases the ratio was 4:1. In fact, though starting with a totally different compound, such as $Zn_2Fe(CN)_6$, in which the expected Zn/Fe ratio was 2:1, the ratio was still 4:1. The only experiment in Tables 2 and 3 that gave the expected 1:1 ratio was the reduction of $FeCr(CN)_6$ on copper.

It can also be seen that a shift from a nickel to a copper substrate produces a shift in the composition of the alloy; for example, electroreduction of $Zn_3[Cr(CN)_6]_2$, $Zn_3[Fe(CN)_6]_2$, and $Zn_2Fe(CN)_6$ all yielded an experimental zinc/$metal_2$ ratio of 4:1 on nickel, but on copper the zinc/ $metal_2$ ratios were 2:1, 8:1, and 7:1, respectively.

The most obvious shift with the composition of the base metal is seen in Table 4 for the electroreduction of titanium(III) ferricyanide [$TiFe(CN)_6$]. It can be seen that the deposit composition on platinum or copper was a whole number, independent of the thickness of the deposit or the time of deposition, but the ratio of Ti:Fe was 1:10 on platinum and 1:1 on copper. On nickel, the composition varied with the thickness of the deposit, going from 1:1.5 (2:3) to 1:30. Apparently, with the longer times, the plating is almost pure iron. As electrolysis proceeds from plating on pure nickel to an alloy coating, the deposit becomes richer in iron.

From these results, it is obvious that the composition of the deposit was not controlled by the simple mechanism proposed at the start. The deposits were, except in the case of the titanium(III) ferricyanide, independent of the time of deposition, the amount of paste on the electrode, or the thickness



Sandwich cell.

Table 4
Ratio of Metals in Alloys Deposited From Titanium(III) ferricyanide On Copper, Nickel, and Platinum

Substrate Metal	Time of Deposition (hr)	Experimental Atomic Ratio of Ti:Fe	
Platinum 3 runs with a range of 4.5–10 mg	2–4	1:10.0	±0.2
Copper 3 runs with a range of 4–12.5 mg	1–3	1:1.0	±0.0
Nickel			
0.5 mg deposit	1	1:1.5	±0.0
5 mg deposit	2	1:8.0	±0.0
10 mg deposit	8	1:27.0	
12.5 mg deposit	12	1:30.0	

Table 5
X-ray Diffraction Data of Deposits from Reduction Of Insoluble Compounds on Nickel and Copper

Insoluble Compound	Substrate	X-ray Data
$Zn_3[Fe(CN)_6]_2$	Ni	4 Zn lines, Ni and Fe principal lines overlap
	Cu	X-ray amorphous
$Zn_2Fe(CN)$	Ni	4 Zn lines, Ni and Fe principal lines overlap, 2 Fe_3Zn_{10} lines, 1 $FeZn_7$ line
	Cu	X-ray amorphous
$CoFe(CN)_6$	Ni	X-ray amorphous
	Cu	X-ray amorphous
$Co_3[Fe(CN)_6]_2$	Ni	X-ray amorphous
	Cu	X-ray amorphous
$FeCo(CN)_6$	Ni	X-ray amorphous
	Cu	X-ray amorphous
$FeCr(CN)_6$	Ni	X-ray amorphous
	Cu	X-ray amorphous
$Zn_3[Cr(CN)_6]_2$	Ni	4 Zn lines, 1 Cr line
	Cu	X-ray amorphous

Table 6
Summary of X-ray Diffraction Data From Reduction of $TiFe(CN)_6$

Substrate	Appearance of Deposit	X-ray Data
Pt Pt_3Fe	Black, adherent, coherent	3 Ti lines, 2 Fe lines, 1 line, 1 Pt_3Ti line
Ni	Black, crumbly, adherent	X-ray amorphous
Cu	Black, crumbly, adherent, coherent	2 Ti lines

Current density of 50 mA/cm^2

of the deposit. These binary deposits obtained from pastes of insoluble compounds had small whole numbers as atomic ratios of the metals. These facts are in agreement with what is observed in deposition of the 1:1 atomic ratio nickel-tin alloy, indicating that deposition from an insoluble compound could be a reasonable mechanism for the deposition of this type of alloy. The fact that the alloys do not generally have the same composition as the insoluble compound in the paste indicates that there are other reactions occurring before reduction to produce the deposit.

There is the question whether the deposits are alloys or some reduced compound. Tables 5 and 6 show the results of X-ray diffraction measurements of the deposits. It can be seen that in many cases the deposits were amorphous. In the experiments in which they were not amorphous, however, the deposits were metallic.

During electrolysis, there are several things that happen in the sandwich cell, adjacent to the cathode, that might lead to changes in the formula of the insoluble compound being reduced. Water in the system is electrolyzed. In addition, normal power losses in the system cause heating that evaporates water. This loss of water leads to readily observable drying of the filter paper. At the cathode, there is not only loss of water, but electrolysis produces hydrogen atoms and hydroxyl ions at the cathode surface. Transition metal ions readily undergo polymerization. Accordingly, chromium is readily changed from chromate to dichromate to chromic oxide by loss of water. It has also been shown that plumbite ions in the sandwich cell were readily converted to $Pb_6O_5(NO_3)_2$.[11] It is suspected that in these experiments, the dehydration and the generated hydroxyl ions caused the formation of new solid-phase compounds, and that electrodeposition is occurring from these new insoluble compounds. The variability of the formula of the alloy with the base metal may be related to the fact that the hydrogen overvoltage is different on different substrates; thus the rate of dehydration is variable on the different base metals.

Conclusions

The fact that it was possible to reduce aqueous pastes of a number of insoluble compounds and deposit binary alloys with small, whole-number atomic ratios indicates that a reasonable mechanism for the deposition of the 1:1 atomic ratio nickel-tin alloy would be deposition of an insoluble film that precipitates on the cathode during reduction, then the subsequent reduction of this film. It should be emphasized, however, that these results indicate only that this is a reasonable mechanism. The question of the probability of this mechanism is further complicated by the fact that although the alloy deposits have simple atomic ratios, these ratios are not the same as those found in the insoluble compounds originally introduced to be reduced.

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