5. It has been shown that the action of diethylamine and piperidine as bases in dilute solution is not specific when determining the strength of a given acid.

6. Neutral Red behaves anomalously as an indicator in benzene.

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The Structure of Electrodeposited Alloys. II. The Effect of Current Density and Temperature of Deposition on the Structure of Silver–Cadmium Deposits[1]

BY CHARLES W. STILLWELL AND HENRY I. FEINBERG

In a recent paper[2] the relation between the composition and crystal structure of electrodeposited silver–cadmium alloys was reported. It was found that the two metals are deposited either as solid solutions or compounds, corresponding in general to the solid solutions or compounds existing in thermal alloys of the same composition. A mixture of the two metals is never deposited.

The present investigation was undertaken to determine the effect of current density and temperature of deposition on the structure of the deposits. It is at least possible that under extreme conditions of deposition the two metals might be plated independently rather than as solid solutions or compounds.

Experimental

The baths from which the alloys were plated were made as described by Stout and Thummel.[3] Cadmium oxide was dissolved in sodium cyanide with specified quantities of sodium sulfate, nickel sulfate, sodium tartrate and turkey red oil. The solution contained 39 g. of cadmium per liter. The composition of the bath was varied by adding to this the desired quantities of a sodium argenticyanide solution containing 58 g. of silver per liter. The alloys were deposited on sheet copper, 10 × 2 cm. and 0.1 cm. in thickness. Two duriron anodes were used, the cathode being adjusted between them, 5.0 cm. from each. Three plates were prepared for each set of conditions. In each case the first and third were analyzed and the second was used to determine the diffraction data. The composition of the plates was determined by precipitating silver as silver chloride, removing the copper electrolytically from an acid solution and precipitating the cadmium electrolytically from a basic cyanide solution.[4]

The effect of current density upon the composition of the deposits is shown in Table I. All the specimens were deposited at room temperature (27°), and from a bath containing 11.6 g. of silver and 31.5 g. of cadmium per liter.

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[1] This paper was presented at the Denver meeting of the American Chemical Society.

[2] Stillwell and Stout, THIS JOURNAL, **54**, 2583 (1932).

[3] Stout and Thummel, *Trans. Electrochem. Soc.*, **59**, 337 (1931).

[4] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, pp. 197, 205.

TABLE I

Percentage of silver in plate	98.0	61.0	51.0	44.0	25.0	20.0
Current density (amp./sq. dm.)	0.113	0.56	1.10	4.00	40.00	1000.00

These results confirm the trend reported by Stout and Thummel,[3] and Fink and Gerapostolou.[5] It is to be expected that the higher composition would favor the deposition of cadmium, which is the more difficult to plate out. The conclusion of these authors that an increase in temperature favors the deposition of silver has also been confirmed.

It should be pointed out that the alloys deposited at extreme current densities or high temperatures are non-adherent deposits. If the deposit is buffed, however, a good adherent deposit is exposed. Both the non-adherent powder and the metallic deposits have been studied. The x-ray diffraction data were obtained by the method described in the preceding paper[2] and the same principles observed therein have been applied to the analysis of the data. Data for a typical analysis are shown in Table II. The values designated "Cu" are the spacings for copper. These serve as a calibration on all films. This illustrates particularly the complications and uncertainties introduced by the large number of lines and the superposition of lines of two or more phases. Thus, there may be fourteen lines of the pattern for pure cadmium present, but eleven of these are in positions already occupied by lines of phases known to be present. It may be said, therefore, that a very small amount of pure cadmium may be present, but there is little evidence to prove its presence.

TABLE II

INTERPLANAR SPACINGS FOR ALLOY NO. 10

IDENTIFICATION OF $Cd(OH)_2$ AND THE γ AND β' PHASES

		$Cd(OH)_2$			The γ-phase			The β'-phase			Cadmium		
d_{hkl}	Intensity	$\sin^2 \Theta$ Obs.	Calcd.	*hkl*	$\sin^2 \Theta$ Obs.	Calcd.	*hkl*	$\sin^2 \Theta$ Obs.	Calcd.	*hkl*	$\sin^2 \Theta$ Obs.	Calcd.	*hkl*
4.63	s	0.0059	0.0059	001									
2.98	m	.0142	.0140	100									
2.85	w				0.0155	0.0153	222				0.0155	0.0160	002
2.62	w							0.0184	0.0186	100			
2.53	vs	.0199	.0199	101									
2.40	m							.0219	.0218	002			
2.34[a]	vs				.0231	.0230	330 411				.0231	.0229	101
2.29	m	.0240	.0236	002				.0240	.0240	101			
2.12	m				.0281	.0281	332						
2.08	Cu												
2.03[a]	m				.0306	.0306	422						
1.945	w				.0333	.0332	510						
1.844	s	.0370	.0376	102									
1.801	Cu				.0388	.0383	521						
1.770	w				.0403	.0408	440	.0403	.0404	102			
1.732	s	.0420	.0420	110									
1.710	vw				.0437	.0434	530						
1.657	m				.0459	.0459	600						
1.626	m	.0477	.0479	111									

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(5) Fink and Gerapostolou, *Metal Ind.* (*N. Y.*), **28**, 519 (1930).

TABLE II (*Concluded*)

		$Cd(OH)_2$			The γ-phase			The β'-phase			Cadmium		
d_{hkl}	Intensity	$\sin^2\Theta$ Obs.	Calcd.	*hkl*	$\sin^2\Theta$ Obs.	Calcd.	*hkl*	$\sin^2\Theta$ Obs.	Calcd.	*hkl*	$\sin^2\Theta$ Obs.	Calcd.	*hkl*
1.517	blur w										0.0548	0.0549	103
1.505		0.0557	0.0560	200	0.0557	0.0561	622	0.0557	0.0558	110			
1.463	w				.0588	.0587	631						
1.432^a	s	.0614	.0618	201	.0614	.0612	444	.0614	.0612	111	.0610	.0607	111
1.400	w				.0644	.0638	710				.0644	.0640	004
1.382	w	.0660	.0656	112	.0660	.0663	640						
1.365	w	.0675	.0671	103				.0675	.0676	103			
1.348	s				.0695	.0689	721						
1.276	blur w							.0774	.0776	112			
1.263		.0790	.0792	202	.0790	.0790	651	.0790	.0798	201	.0790	.0796	201
1.223^a	m				.0845	.0842	811						
1.172^a	w				.0917	.0918	822				.0917	.0916	202
							660						
1.162	w	.0935	.0942	004									
1.137	w	.0975	.0980	210	.0975	.0970	662						
1.105	m	.1033	.1039	211	.1033	.1020	840						
1.087	Cu				.1065	.1070	842	.1065	.1058	104			
1.050	vw				.1145	.1147	930						
1.042	Cu												
1.027	w				.1200	11.98	932						
1.007^a	w				.1240	12.47	870	.1240	.1234	203			
0.965	vw							.1355	.1356	211	.1355	.1363	211
.940^a	vw							.1428	.1430	114			
.917	vw	.1500	.1503	204				.1500	.1513	212	.1500	.1483	212
.901	Cu							.1550	.1549	105			
.883	vw	.1620	.1616	105				.1620	.1616	204	.1620	.1629	106
.869	vw							.1673	.1673	300			
.855	w							.1727	.1728	301			
.847	w										.1758	.1756	205
.837	vw	.1802	.1791	303				.1802	.1792	213			
.827^a	Cu												
.806	Cu												
.788	vw	.2030	.2036	205									
.777^a	vw												
.763	vw							.2170	.2173	214			
.736	Cu										.2320	.2323	215
.724^a	vw							.2410	.2418	310			
.711	vw										.2495	.2498	311
.693	Cu	.2630	.2623	224				.2630	.2636	312			
.683^a	vw	.2710	.2719	321				.2710	.2707	206	.2710	.2716	207
.663	vw							.2868	.2858	107			
.651	vw	.2980	.2971	403				.2980	.2980	400			
.638	Cu												

$Cd(OH)_2$ $\sin^2\Theta = 0.0140\,(h^2 + k^2 + hk) + 0.0059\,l^2$

$a = 3.46 \quad c = 4.62$

γ-phase $\sin^2\Theta = 0.01275\,(h^2 + k^2 + l^2)$

$a = 9.94 \pm 0.025$

β'-phase $\sin^2\Theta = 0.0186\,(h^2 + k^2 + hk) + 0.00545\,l^2$

$a = 3.007 \pm 0.004 \quad c = 4.81$

Cadmium $\sin^2\Theta = 0.0189\,(h^2 + k^2 + hk) + 0.0040\,l^2$

$a = 2.975 \quad c = 5.61$

[a] These lines belong to the pattern for pure silver.

The complete results are summarized in Table III. The phases found in the electrodeposited alloys are compared with those found by Astrand and Westgren[6] in thermal alloys of corresponding composition. The η-phase has the close-packed hexagonal structure, a solid solution of silver in

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(6) Astrand and Westgren, *Z. anorg. allgem. Chem.*, **175**, 90 (1928).

TABLE III

RELATION BETWEEN CURRENT DENSITY AND TEMPERATURE OF DEPOSITION AND THE CRYSTAL STRUCTURE OF SILVER-CADMIUM DEPOSITS

Number	1	2	3	5	6	7
Current density (temp.)	0.11 (27°)	0.56 (27°)	0.56 (27°)	0.56 (27°)	4.0 (27°)	32.0 (27°)
Plating bath—Cadmium, g./l.	31.5	31.5	32.4	35.7	27.4	31.5
Silver, g./l.	11.6	11.6	9.7	4.9	16.5	11.6
Per cent. silver in plate	98.0	61.0	52.0	30.0	44.0	30.0
Appearance	Adherent	Adherent	Adherent	Adherent	Adherent	Adherent
Crystal phases in thermal alloys	α	α	$\alpha + \beta$	ϵ	γ	ϵ
Total lines on pattern	10	21	24	35	38	44
Crystal phases in electrodeposit predominant phase listed first	α	α-10(10) γ-4(4)	β-8(7) α-9(7) γ-3(2) Cd(OH)$_2$2(1)	ϵ-27(27) γ-4(4)	β-11(4) γ-19(12) Cd-7(0) Ag-9(2)	ϵ-20(15) γ-19(11) Cd(OH)$_2$-8(1) Cd-6(0) Ag-7(0)

Number	8	9	10	11	12	13
Current density (temp.)	32.0 (27°)	1000 (27°)	1000 (27°)	1.0 (90°)	20.0 (90°)	20.0 (90°)
Plating bath—Cadmium, g./l.	31.5	31.5	31.5	36.8	36.8	36.8
Silver, g./l.	11.6	11.6	11.6	3.7	3.7	3.7
Per cent. silver in plate	30.0	20.0	20.0	43.0	11.0	11.0
Appearance	Burnt	Adherent	Burnt	Burnt	Burnt	Adherent
Crystal phases in thermal alloys	ϵ	ϵ	ϵ	γ	$\eta + \epsilon$	$\eta + \epsilon$
Total lines on pattern	45	28	49	38	48	38
Crystal phases in electrodeposit predominant phase listed first	ϵ-20(15) γ-19(11) Cd(OH)$_2$-8(1) β-3(3) Cd-5(0) Ag-7(0)	ϵ-16(12) γ-11(8) Cd-8(0) Ag-6(0)	γ-24(12) Cd(OH)$_2$-22(8) β'-25(8) Cd-14(3) Ag-11(1)	γ-24(13) β'-14(5) Cd-10(0) Ag-5(0)	η-13(7) ϵ-17(7) Cd(OH)$_2$-12(8) γ-15(7) β-3(2)	η-14(11) ϵ-17(13) γ-4(3) Cd-6(0) Ag-7(0)

cadmium. The ϵ-phase ($AgCd_3$) is also close-packed hexagonal, but of a different axial ratio. The γ-phase ($4Ag_5Cd_8$) is body-centered cubic, The β-phase (AgCd) is of the cesium chloride type. The α-phase is face-centered cubic, a solid solution of cadmium in silver. Data have been selected to show the results for deposits, the compositions of which vary between the widest possible limits. In some cases (7 and 8, 9 and 10, 12 and 13) two analyses are presented for the same deposit, one for the burnt, non-adherent powder and the other for the bright adherent alloy next to the base metal. The figures in the sixth line represent the total number of lines on each diffraction pattern. Two sets of figures accompany the notation of each phase in the electrodeposit. The first designates the number of lines on the film which may indicate the presence of this phase. The figure in parentheses is the number of lines which indicate only this phase and can belong to no other phase.

Discussion

In identifying the phases present in the deposits, as summarized in Table III, three primary objectives were kept in mind. 1. To compare the phases present in the electrodeposited alloys with those in thermal alloys of the same composition. 2. To determine whether or not silver and cadmium are ever deposited independently as a mixture. 3. To determine whether or not the metastable β'-phase is deposited under the conditions of the experiment.

It may be seen from Table III that in general the predominant phase in the electrodeposited alloys is the same as that in a thermal alloy of the same composition. The deposits are heterogeneous, however, and there is a tendency for the phases to be present which are richer in silver than the alloy as a whole. Thus, in alloys Nos. 7 and 9 there are considerable amounts of the γ-phase present, a phase stable in the thermal alloys between 31–49% silver. In alloy No. 6 the β-phase predominates, although its composition places it in the range of the γ-phase of the thermal alloys. The structures of deposits containing 50% or more of silver correspond closely with those of thermal alloys of the same composition. The relations pointed out agree with those reported in the previous paper.[2] It is apparent that the phases deposited depend principally on the composition and are not directly affected by the current density or temperature.

The possibility of pure silver or pure cadmium existing in the deposits is indicated for most of the alloys. Whereas lines may usually be found to make a fairly complete pattern for each metal, these lines always belong to another phase known to be present. In every case, then, small amounts of silver and cadmium may be present; but since there is no conclusive evidence indicating their presence it may be assumed that their deposition is not favored by the conditions.

There are no data to indicate the presence of a β'-phase in any of the adherent deposits. Its formation is most strongly evidenced in the non-adherent alloy analyzed in Table II, particularly when the intensities of some of its lines are noted. A recent exhaustive study[7] has defined the exact nature of this phase. It is stable between the temperatures 211 and 430°. It is adjacent to the α-phase at 58% silver; exists in equilibrium with the α-phase to 50% silver; exists as a single phase from 50–46% silver; and is in equilibrium with the γ-phase from 46–43% silver. The structure is that of the ϵ-phase with the same axial ratio but a smaller unit cell.

As reported in the first paper,[2] no positive evidence of a β'-phase was found in the analysis of alloys deposited at 27° at current densities of one ampere/sq. dm. The present work indicates that its formation may be favored by deposition at high current density and high temperature (see Alloys 10 and 11, Table III). The point is of interest because other cases have been reported[8] in which metastable forms of metals are electrodeposited under special conditions. In the case of antimony and chromium the deposition of the metastable form is favored by low temperatures, which seems more reasonable.

Homogeneity and Orientation of Deposits.—A comparison of alloys 5 and 7, both of the same composition, suggests that a more homogeneous alloy is deposited at low current densities, since only a minute quantity of the γ-phase is present in 5. This is to be expected, if one attributes heterogeneity to momentary variations in the relative concentrations of silver and cadmium ions in the solution next to the cathode, due to unequal rates of the deposition of ions from the stationary layer of electrolyte and the diffusion of ions into this layer.

Preliminary results indicate also that when deposited at low current densities the crystals of the ϵ-phase, at least, assume a preferred orientation with the (100) planes of the crystals parallel to the cathode. This is very marked in Alloy No. 5.

These results are interesting in the light of Hunt's recent discussion of electrodeposition, in which it is stated that the variable factors (current density, temperature, agitation) do not influence the structure (grain size, orientation, etc.) of an alloy deposit but merely alter its composition.[9] It is suggested that the co-deposition of two cations "will cause distortion and breaking up of the lattice with consequent changes in orientation." This will be particularly true of heterogeneous deposits. The preliminary results reported seem to confirm Hunt's proposed explanation of why the variable factors do not ordinarily influence structure since Alloy 5, in which orientation is strong, is also the most homogeneous. They also

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(7) Fraenkel and Wolf, *Z. anorg. allgem. Chem.*, **189**, 145 (1930).

(8) Antimony—Cohen and Coffin, *Z. physik. Chem.*, [A] **149**, 417 (1930); Stillwell and Audrieth, THIS JOURNAL, **54**, 472 (1932); cobalt—Kersten, *Physics*, **2**, 204 (1932); chromium—Sasaki and Sekito, *Trans. Electrochem. Soc.*, **59**, 437 (1931).

(9) Hunt, *J. Phys. Chem.*, **36**, 2269 (1932).

demonstrate, of course, that current density may influence the orientation of an alloy deposit.

The Burnt Deposits.—All non-adherent deposits are referred to as "burnt." They are so designated in Table III. They are usually not considered as metallic deposits in the true sense of the word, since they contain hydroxides and other impurities. It is therefore of interest to note in Table III that in spite of their marked difference in physical appearance, the metals exist in the burnt deposits as compounds and solid solutions and there is no positive evidence of the deposition of pure cadmium and pure silver.

Summary

An x-ray diffraction study of the structure of alloys deposited at current densities ranging from 0.1 to 1000 amp./sq. dm. and at 27 and 90° has brought out the following results, most of which are illustrated in Table III.

1. The metals are always deposited as solid solutions or compounds. Under no conditions is the deposit a mixture of silver and cadmium crystals. This holds true for both metallic and non-adherent deposits.
2. The phase stable in a given range of composition of the thermal alloy is usually the predominant phase in an electrodeposited alloy in that same composition range. Exceptions have been noted.
3. The deposits are heterogeneous, containing small amounts of phases which do not exist in annealed alloys of the same composition.
4. Preliminary results indicate that an alloy deposited at low current density is more homogeneous than one of the same composition deposited at high current density; and in a homogeneous alloy deposited at low current density the crystals are oriented with respect to the cathode.
5. There is some indication that the metastable β'-phase is deposited at high current densities and high temperatures.
6. Crystalline cadmium hydroxide is present in all burnt deposits.

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