

The Journal of the American Chemical Society

VOL. 54

JULY, 1932

No. 7

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS
AND WASHINGTON UNIVERSITY]

THE CRYSTAL STRUCTURES OF ELECTRODEPOSITED ALLOYS. AN X-RAY DIFFRACTION STUDY OF SILVER-CADMIUM DEPOSITS¹

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RECEIVED NOVEMBER 20, 1931

PUBLISHED JULY 6, 1932

The electrodeposition of alloys is a comparatively recent development. The number of binary alloys which may be successfully electroplated has increased greatly during the last few years due to a realization of their many practical applications. Very little is known of the structure of these alloys, however, since in all phase rule studies of binary alloys the system is usually in equilibrium when the several phases are identified. These results cannot be applied to electrodeposited alloys, since the latter are probably not in equilibrium. An x-ray diffraction study of electrolytic brass made some years ago² proved that under specified conditions a true α -phase is deposited, a solid solution rather than a mixture of the metals. Recently several rather superficial papers have been published³ giving diffraction data for the electrodeposited alloys: Cd-Ag, Cu-Zn, Cd-Sn, Cd-Ni. The only definite conclusion drawn is that the plate is not a mixture of the two metals, but contains compounds or solid solutions. The compounds are not identified, nor has any one of the binary alloys been systematically studied.

There are several variables which might influence the structure of an electrodeposited alloy. Among these are: (1) the composition of the plate, (2) the current density, (3) the temperature of deposition, (4) the rate of stirring and (5) the nature of the base metal. The aim of the present investigation of electrodeposited silver-cadmium alloys has been to study systematically by means of x-ray diffraction data the relation between the composition and the crystal structure of the plates. All deposits

¹ This paper was presented at the Buffalo meeting of the American Chemical Society, September, 1931.

² Nakamura, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **2**, 287 (1925).

³ Roux and Cournot, *Ind. élect.*, **37**, 455 (1928); *Compt. rend.*, **186**, 1733 (1928); *Rev. mét.*, **26**, 655 (1929).

have been prepared at constant temperature and constant current density without stirring, and the effect of these other variables will be studied later.

Experimental

Some of the deposits investigated were prepared and analyzed by Stout at Washington University. Chemical analyses and the x-ray diffraction studies of all the plates were made at the University of Illinois. The baths from which the alloys were deposited were made as described by Stout and Thummel.⁴ The alloy was deposited on sheet copper, 10 × 2 cm. and 0.1 cm. in thickness. Two duriron anodes were used, the cathode being adjusted between them and equidistant from each. The deposits were made at room temperature (27°) using a current density of one ampere per square decimeter. Three plates were prepared for each composition studied. In each case the first and third were analyzed and the second was used to determine the diffraction data. The equilibrium diagram for the silver-cadmium system has been studied by x-ray diffraction methods by several investigators⁵ and the compositions of the alloys which were electroplated were chosen after a consideration of these equilibrium data.

The composition of the plates was determined by precipitating silver as silver chloride, removing the copper electrolytically from an acid solution and precipitating cadmium electrolytically from a basic cyanide solution.⁶ The composition of the edge of a plate is different from that of the center. The center area was the portion analyzed in each case since the x-ray diffraction pattern was obtained from this area.

The relation between the composition of the bath and the composition of the deposit is shown in Table I.

TABLE I⁷

Silver in bath, %	9.1	12.0	23.1	25.9	41.2
Silver in deposit, %	18.5	23.4	47.4	52.0	69.0

The x-ray diffraction data were obtained by the powder method, using the General Electric multiple apparatus and a Coolidge tube with a

⁴ Stout and Thummel, *Trans. Electrochem. Soc.*, 59, 337 (1931).

⁵ (a) Astrand and Westgren, *Z. anorg. allgem. Chem.*, 175, 90 (1928); (b) Natta and Freri, *Atti. accad. Lincei*, [6] 6, 422, 505 (1927); 7, 406 (1928); *J. Inst. Metals*, 39, 537 (1928); 40, 573 (1928).

⁶ Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, 1929, pp. 197, 205.

⁷ These values do not agree with those of Stout and Thummel.⁴ The values in Table I have been checked independently by the present authors. The errors in the earlier values will be corrected in a publication by Stout soon to appear.

The relations between the crystal structures and compositions of the deposits, set forth in a previous note [Stillwell, *THIS JOURNAL*, 53, 2416 (1931)] are invalidated by this revision of the chemical analyses of the deposits. The conclusions drawn in the note were based on the earlier data of Stout and Thummel.

molybdenum target. A firmly adhering electrodeposited layer may be very conveniently handled by this method. The copper strip on which the alloy was deposited was cut to a convenient size and bent through an angle of 180° , the radius of curvature of the outer plated surface being about 2.0 mm. Mounted properly at the center of curvature of the quadrant cassette, this affords a sharply curved surface from which the x-rays are reflected. The specimen is thick enough to prevent transmission of the x-ray beam, so that the lines of the resulting diffraction pattern are clearly defined and as narrow as it is possible to get them. The length of exposure is cut to a minimum under these conditions. Good patterns of a homogeneous deposit were obtained in fifteen to twenty hours with 20 m. a. It is convenient to reflect the radiation from a curved surface for another reason. When metals are electrodeposited, the crystals often assume a preferred orientation in respect to the base metal. If the orientation is sufficiently regular many of the planes of the crystal would not be in the proper position to diffract the x-rays and the pattern would be incomplete and more difficult to identify. In using a curved specimen, although the crystals may be oriented with respect to the base metal, there is sufficient variation in their orientation with respect to the x-ray beam to permit reflection from many more planes.

The alloy deposit was thin enough in every case to permit diffraction of the x-rays by the copper base, and the diffraction pattern for copper which was present in every film was used as a reference in measuring the patterns of the alloy phases, affording much greater accuracy than would otherwise be possible.

Analysis of Data

The diffraction data for the ten different alloys examined have been recorded and analyzed. The general procedure is illustrated in Table II for alloy 82.0% cadmium. The others were analyzed in the same way. The composition of the alloy is expressed in atomic per cent. of cadmium. The interplanar spacings, in Ångström units, are in the first column. The intensity of the lines was estimated as very strong (vs), strong (s), medium (m), weak (w) or very weak (vw). The lines of the copper pattern used as a calibration are designated "Cu." All of the alloys proved to be heterogeneous and the identifications of the several different crystalline phases are included in the table.

The accuracy with which the size of the unit cell may be determined from films obtained by this method is limited. The maximum probable error for the determination of the values of a_0 in the several phases has been estimated in the following way. As different values of the constant are tried in the $\sin^2 \theta$ equation, the difference between constants may be reduced to the point where the calculated values for two successive constants

TABLE II
 INTERPLANAR SPACINGS FOR ALLOY NO. 14—82.0 PER CENT. Cd. IDENTIFICATION OF
 THE ϵ , β' , γ AND η PHASES IN THE ALLOY

d_{hkl}	Inten- sity	The ϵ -phase			The β' -phase			The γ -phase			The η -phase		
		$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl	$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl	$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl	$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl
2.67	s	0.0177	0.0177	100				0.0177	0.0178	321			
2.57	m										0.0191	0.0188	100
2.40	w	.0219	.0218	002	0.0219	0.0218	002						
2.33	vs	.0232	.0231	101				.0232	.0229	411	.0232	.0230	101
2.28	w				.0242	.0241	101						
2.08	s(Cu)												
2.03	vw							.0306	.0307	422			
1.885	w										.0355	.0356	102
1.802	m(Cu)												
1.785	s	.0396	.0395	102									
1.575	vw							.0507	.0507	620			
1.540	vs	.0532	.0531	110				.0532	.0533	541			
1.501	w				.0559	.0559	110	.0559	.0560	622	.0559	.0564	110
1.490	m										.0567	.0564	103
1.462	vw							.0589	.0585	631			
1.433	vw				.0613	.0613	111	.0613	.0611	444			
1.407	vw							.0637	.0637	543 550 710			
1.375	m	.0666	.0667	103									
1.335	w	.0708	.0708	200				.0708	.0711	642			
1.306	w				.0739	.0744	200	.0739	.0738	730	.0739	.0732	112
1.295	vs	.0750	.0749	112									
1.272	m(Cu)				.0778	.0777	112						
1.254	m				.0800	.0798	201				.0800	.0790	201
1.225	vw							.0840	.0838	554 741 811			
1.201	vw	.0873	.0872	004	.0873	.0872	004						
1.167	m	.0926	.0926	202							.0926	.0920	202
1.093	vw	.1052	.1049	104									
1.087	m(Cu)				.1062	.1058	104						
1.055	w										.1130	.1130	203
1.042	w(Cu)												
1.025	m	.1200	.1198	203									
1.010	w	.1238	.1239	210	.1238	.1234	203				.1238	.1236	114
0.988	s	.1291	.1293	211									
.958	w												
.947	m	.1405	.1403	114									
.932	mm	.1452	.1457	212									
.920	w										.1485	.1485	212
.892	w	.1588	.1584	204									
.862	w										.1696	.1694	213
.855	s				.1728	.1726	301				.1728	.1734	301
.837	m				.1799	.1792	213						
.828	m(Cu)												
.817	vw	.1892	.1893	115									
.807	m(Cu)												
.802	vw	.1960	.1960	006									
.781	w	.2067	.2070	205							.2070	.2070	303
.773	m				.2103	.2106	205						
.737	m(Cu)										.2320	.2317	215
.716	w				.2453	.2450	222				.2453	.2445	310
.712	w										.2486	.2487	311
.697	m	.2594	.2604	215									
.694	m(Cu)	.2617	.2614	223							.2617	.2613	312
.673	w	.2783	.2791	313									
.662	vw										.2880	.2878	108

TABLE II (Concluded)

d_{hkl}	Inten- sity	The ϵ -phase			The β' -phase			The γ -phase			The η -phase		
		$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl	$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl	$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl	$\text{Sin}^2 \theta$ Obs.	Calcd.	hkl
0.650	w	0.2983	0.2996	224	0.2983	0.2975	400						
.638	w(Cu)												
.632	vw	.3165	.3173	314							0.3165	0.3170	402
.617	w												
.609	m	.3398	.3382	320									
.601	w	.3489	.3486	225	.3489	.3490	314						
.587	w	.3657	.3663	315									
ϵ -phase $\text{sin}^2 \theta = 0.0177 (h^2 + k^2 + hk) + 0.00545 (l)^2$ $a = 3.081 \pm 0.004$ $c = 4.81$													
β' -phase $\text{sin}^2 \theta = 0.0186 (h^2 + k^2 + hk) + 0.00545 (l)^2$ $a = 3.006 \pm 0.004$ $c = 4.81$													
γ -phase $\text{sin}^2 \theta = 0.001275 (h^2 + k^2 + l^2)$ $a = 9.936 \pm 0.025$													
η -phase $\text{sin}^2 \theta = 0.0187 (h^2 + k^2 + hk) + 0.0042 (l)^2$ $a = 2.998 \pm 0.004$ $c = 5.49$													

satisfy the experimental values equally well, but constants greater or smaller than these two are unsatisfactory. At this point the values for a_0 have been calculated from each of these constants, the mean value of the constants has been used in the equation, and the error of the determination is indicated as plus or minus half the difference between the values of a_0 originally computed. For example, the experimental values for the β' -phase in alloy 82.0 (Table II) are satisfied equally well by values calculated from the constants 0.01855 and 0.01865, but are not satisfied by values from constants 0.01850 or 0.01870. The values of a_0 calculated from the accepted constants are 3.010 Å. and 3.002 Å., respectively. The constant used in the final equation is 0.0186, the value of $a_0 = 3.006 \pm 0.004$ Å. It is believed that this method of expressing the error gives a true picture of the degree of accuracy of the results. Since the purpose of this study is merely to identify the several phases present, great accuracy is not demanded in most cases. In connection with the discussion below, however, it is desirable to know as nearly as possible the values of a_0 for the β' -phase, and the limit of error on this phase has been carefully estimated.

The analyses of the specimens should be considered in the light of the following factors.

1. The multiplicity of phases and reflecting planes recorded in each pattern leads to the possible superposition of important lines of one phase on those of another. Thus in some cases it may be said that a certain phase may be present, but is not necessarily so, if the positions which would be taken by all of its important diffraction lines are already occupied by lines identified with other patterns. A weak pattern for the β -phase in particular may be obscured by the γ -phase pattern.

2. A consideration of relative intensities cannot be used in establishing

the presence or absence of the pattern of a phase, since some, and possibly all, of the crystalline phases are deposited in a preferred orientation with respect to the base metal. Although this difficulty has been minimized by curving the specimens, the intensities are still abnormal, as may be seen by a casual examination of the intensities of the reflections from the more important planes of the ϵ -phase in the several specimens. A direct comparison of the films brings out these abnormal intensities most strikingly.

3. It should also be noted that some evidence points to an apparently non-uniform distribution of the phases over the surface of the electrode.

Of several specimens chosen from the same plate (82.0% cadmium) some give only the pattern of the ϵ -phase even after long exposure, while others show in addition the patterns of the other phases.

4. There is a minimum concentration for each phase, below which it cannot be detected by this method. This concentration will depend to a considerable extent on the thickness of the deposit. In general, the weight of alloy deposited on the plates used for this investigation was about 0.3 g. If thicker deposits were made, smaller concentrations of the several phases could be detected.

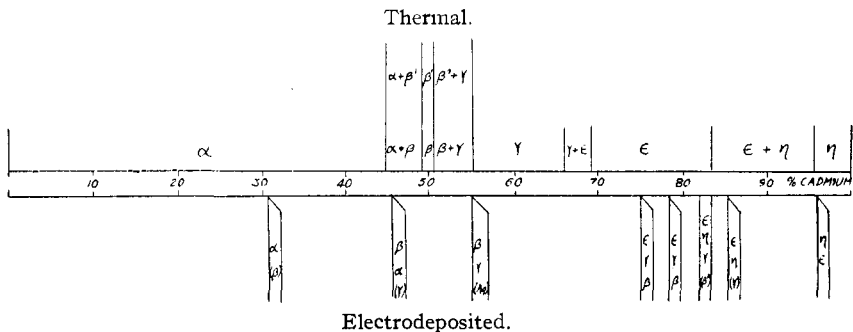


Fig. 1.—A comparison of the composition ranges of the several phases of the thermal silver-cadmium alloys with those of the same phases in the electrodeposited alloys.

The conclusions drawn from the several analyses are assembled in Table III and Fig. 1. For convenience the phases identified in the electrodeposited alloy are compared with those found by Astrand and Westgren^{5a} in the thermal alloys of corresponding composition. The η -phase has the close-packed hexagonal structure—a solid solution of silver in cadmium. The ϵ -phase (AgCd_3) is also close-packed hexagonal, but of a different axial ratio. The γ -phase ($4\text{Ag}_5\text{Cd}_3$) is body-centered cubic, containing fifty-two atoms in the unit cell. The β -phase (AgCd) is of the cesium chloride type; while the α -phase is face-centered cubic, a solid solution of cadmium in silver. The β' -phase is metastable at room temperature for the compositions indicated. It is more fully discussed below. In each case the phase which predominates in the electrodeposited alloy is placed nearest

TABLE III
THE STRUCTURE OF SILVER-CADMIUM ALLOYS

Diffraction lines on film	Electrodeposited				Atomic per cent of cadmium		Thermal ^{12a}
20			ϵ	$a = 3.090$ $c = 4.81$	$a = 2.988$ $c = 5.49$	96.0	η $a = 2.986$ $c = 5.49$ (ϵ)
				10(8)	11(9)		
27		(γ)	$a = 9.93$ 5(2)	$a = 2.998$ $c = 5.49$	$a = 3.081$ $c = 4.81$	85.0	ϵ $a = 3.091$ $c = 4.81$ (η)
				9(4)	15(11)		
56	$a = 3.006$ (β') $c = 4.81$	γ	$a = 9.93$ 12(4)	$a = 2.998$ $c = 5.49$	$a = 3.081$ $c = 4.81$	83.0	ϵ $a = 3.086$ $c = 4.81$
				17(6)	26(16)		
56	$a = 3.006$ (β') $c = 4.81$	γ	$a = 9.93$ 12(5)	$a = 2.998$ $c = 5.49$	$a = 3.081$ $c = 4.81$	82.0	ϵ $a = 3.084$ $c = 4.81$
				20(7)	27(16)		
		β	$a = 3.325$ 4(2)	$a = 9.93$ 7(5)	$a = 3.047$ $c = 4.81$	78.0	ϵ $a = 3.070$ $c = 4.81$
					16(16)		
35		β	$a = 3.325$ 7(3)	$a = 9.93$ 12(7)	$a = 3.047$ $c = 4.81$	75.0	ϵ $a = 3.060$ $c = 4.81$
					19(18)		
29	$a = 2.99$ (β') $c = 4.81$ 7(0)	$a = 3.006$ (β') $c = 4.81$ 8(0)	(Ag) $a = 4.068$ 9(2)	$a = 9.93$ 19(11)	β $a = 3.325$ 11(6)	55.0	γ $a = 9.935$ β $a = 3.327$ β' $a = 2.989$ $c = 4.81$
37	$a = 3.006$ (β') $c = 4.81$ 7(0)	$a = 3.047$ (ϵ) $c = 4.81$ 7(2)	γ $a = 9.93$ 10(2)	α $a = 4.16$ - 4.17 12(1) ^a	β $a = 3.325$ 12(4)	46.0	α $a = 4.175$ β $a = 3.323$ β' $a = 2.973$ $c = 4.81$
					α $a = 4.12$ - 4.16		
21			(β) $a = 3.32$ 2(1)	$a = 3.32$ 15(11)	31.0	α $a = 4.145$	

^a The intensity of most of these twelve lines shows conclusively that the α -phase is present.

the center of the dividing line between thermal and electrodeposited alloys. This order is observed in both table and figure. After the most predominant phase has been recorded, the order of the other phases listed is usually arbitrary, since their relative concentrations cannot be accurately estimated. Column 1 lists the total number of lines measured on each film. The figure beneath each phase designates the number of lines on a particular 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. The presence of most of the phases listed is definitely indicated by the diffraction patterns. The phases which may or may not be present, when considered in the light of diffraction data, are listed in parentheses.

Discussion

The β' -Phase.—Astrand and Westgren^{5a} have obtained the β' -phase by heating the β -phase for five to ten hours just below 460°. The β' -phase is recorded in Table III in such a way as to indicate that it is a phase, stable at higher temperatures over the range of composition occupied by the β -phase at room temperature. The β' -phase has the close-packed hexagonal structure and the same axial ratio as the ϵ -phase, differing from the latter only in the size of the unit cell. Moreover, the magnitude of this difference in the size of the unit cell suggests that the β' -phase is a continuation of the ϵ -phase; that the ϵ -phase at the higher temperature extends over the range of composition occupied by the β - and γ -phases at room temperature. This is the interpretation suggested by Astrand and Westgren. If it be the correct one it should be possible to heat and quench the γ -phase and prepare a metastable close-packed hexagonal phase in which the value of a_0 lies between 2.989 Å. (the upper limit for the metastable $\beta'(\epsilon)$) and 3.040 Å. (the lower limit for the stable ϵ -phase). Astrand and Westgren were unable to do this. Natta and Freri^{5b} claim to have prepared a $\beta'(\epsilon)$ phase in which $a_0 = 3.01$ Å., leaving a gap only from $a_0 = 3.01$ Å. to $a_0 = 3.04$ Å. Since electrodeposition seems to be a good method for the preparation of metastable metals, it was hoped that this gap between $a_0 = 3.04$ for the ϵ -phase and $a_0 = 3.01$ Å. for the $\beta'(\epsilon)$ phase might be closed. As may be seen from the data, however, no close-packed hexagonal lattice with a value of a_0 between these two has been identified in any of the specimens.

It is questionable whether the $\beta'(\epsilon)$ phase is deposited at all under the conditions of the experiment. There is no positive evidence of a $\beta'(\epsilon)$ lattice on the patterns for plates of 55 and 49% cadmium where it should naturally occur. The possibility of its presence in these plates is indicated in Table III. The most evidence in its favor exists in the pattern analyzed in Table II. Even here there are only three unique lines. Furthermore,

it is difficult to account for the occurrence of the metastable phase in this composition range. It means that there are two phases of close-packed hexagonal structure and identical axial ratios coexistent in the same deposit. If the interpretation of the nature of the β' -phase is correct, they may be thought of as two disconnected "sections" of a supposedly continuous phase. They differ only in the size of the unit cell, by which size one of them (ϵ) is identified as a stable phase at ordinary temperatures and the other (β') as metastable. Needless to say, this relation is not apt to exist.

General Discussion.—The unexpected complexity of the results obtained makes it difficult to draw a complete comparison between the electrodeposited and thermal alloys. The data bring out several interesting points, however, some of which may have a practical bearing.

The heterogeneous nature of the deposits is noteworthy. A consideration of Fig. 1 shows that the predominant phase in any alloy is the one predicted from the thermal equilibrium diagram. The minor phases are present in considerable amounts, however, and their presence cannot be predicted from the equilibrium diagram. There is a general overlapping of phases evident, particularly for the γ - and β -phases. The former, stable in the range 55–67% cadmium, may be found in electrodeposited alloys in the composition range 46–83% cadmium. The latter, stable in a narrow range at 50% cadmium, may be electrodeposited in alloys containing 46–78% cadmium. The η - and ϵ -phases and the α -phase seem to remain within their expected bounds.

Fink and Gerapostolou⁸ have studied silver–cadmium deposits microscopically and have reported that pure silver is deposited first. It should be noted that the results of the x-ray diffraction analysis do not contradict this. For most of the deposits analyzed, the positions of the lines of the diffraction pattern for pure silver (if $a_0 = 4.068$ is used for calculating d_{hkl}) are already occupied by lines belonging to the patterns of other phases known to be present. Small amounts of silver, therefore, may or may not be present in the deposits. If an appreciable amount were present, the diffraction lines for the smaller spacings should be found.

It is not difficult to offer a reasonable explanation for the heterogeneous nature of the deposits. The composition of the plate deposited at any instant depends upon the relative concentration of silver and cadmium ions in the solution, particularly in the stationary film of electrolyte around the cathode. Generally this ratio will be such as to cause the deposition of the phase to be expected from the chemical analysis of the plate. Occasionally the ratio of silver to cadmium ions in the stationary film will

⁸ Fink and Gerapostolou, *Metal Ind. (New York)*, **28**, 519, 562 (1930). The results of these authors do not bring out the complexity of the deposits. They distinguish only two phases—pure silver and a phase which appears brown and is a cadmium-rich alloy.

vary, due to momentary convection currents and other local conditions, and for short periods, then, the composition of the deposit will vary from the average composition, and the phase deposited will vary accordingly. The composition of some of the plates is such that, judging from the thermal equilibrium diagram, a mixture of two phases is to be expected even under uniform conditions of deposition.

A homogeneous deposit may have advantages which would make it preferable to a heterogeneous deposit for practical purposes. Certainly vigorous stirring during deposition should produce a more homogeneous deposit if the above explanation of the heterogeneity is correct. The effects of stirring, current density and temperature on the nature of the deposit are being investigated at the present time.

Summary

The crystal structures of electrodeposited silver-cadmium alloys ranging in composition from 96.0% cadmium to 31.0% cadmium have been obtained from x-ray diffraction data. All known factors, other than the composition of the plate, which might affect the structure of the alloys have been held constant.

The results are summarized in Table III and Fig. 1.

The most significant points brought out by the study are:

1. Every deposit consists of solid solutions or compounds. In no case is the deposit merely a mixture of cadmium and silver.
2. The phase stable in a given range of composition of the thermal alloys is the predominant phase in an electrodeposited alloy in that same composition range. Therefore the predominant phase in the electrodeposit may be predicted from its chemical composition.
3. In general the deposits are heterogeneous, containing appreciable amounts of phases which do not exist in an annealed alloy of the composition in question. The complete composition of the electrodeposit, therefore, cannot be predicted from its chemical composition.
4. There is little evidence indicating the formation of a metastable (β' -phase) deposit under the conditions of the experiment.

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