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# Bonding and Structural Variations of Commercial Electroplatings $2-55 \times 10^{-6}$ Inch Thick

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#### INTRODUCTION

**`**HE deposition of metal platings which afford satisfactory protection against corrosion of a wide variety of fabricated metal products is a problem of great practical importance, accentuated by present war demands. There is a fundamental and theoretical significance to the problem of producing a satisfactory plating which involves a knowledge of the bonding between a coating, particularly the very first layers of atoms, and the underlying substrate metal. In this bond there resides the ability of the plated film to adhere even to a dissimilar metal under disruptive conditions. A number of studies<sup>1</sup> have been made by x-ray and electron diffraction of the structure of the whole film of metal produced by electrodeposition and then peeled off. In a few cases beams have been reflected from surfaces to produce diffraction patterns which integrate the structure through a considerable thickness and thus fail to show the true *interfacial* structure. The present study was undertaken for the purpose of (1) developing a convenient x-ray diffraction technique for evaluation of commercial platings directly on the base metals and over a series of thicknesses from the first invisible thinnest layer  $(2 \times 10^{-6})$ stepwise to films about 30 times this thickness; (2) correlating these results especially for the thinnest interfacial layers with electron diffraction patterns which hitherto have been considered the only possible source of information on these very thin films; (3) and also correlating with measurements of optical reflectances on the Hardy recording spectrophotometer. Such a study would be expected to show not only the true interfacial or interpenetrating crystalline structure and texture, but also variations as the film increases in thickness so that the last atoms

deposited are farther and farther removed from the atomic forces of the base metal.

#### EXPERIMENTAL

#### (a) Preparation of Samples

Samples used in this study were prepared using commercial plating methods and equipment. The substrate metals chosen for the experiments were 1.5 inches wide, 8 inches long, and 0.010 inch thick. After cleaning the surface of the substrate material electrolytically in an alkaline bath, the sheet was submerged in the plating bath containing the proper solution. After electrical contact was made, the sheet was plated for a specified period. Then the sheet was raised one inch out of the solution and plating continued on the submerged portion for another increment of time. The current was adjusted at each step to maintain a constant current density on the area being plated. Each time the plate was lifted from the solution the exposed portion was sprayed with water in order to remove the electrolyte which would redissolve the plating. The process of stepwise plating was repeated until a graded series of eight platings of varying thicknesses was obtained on each sample sheet. The time of plating for each step for all the samples was constant and of course determined the thickness. For example, most of the samples had a final plating thickness, as determined by microscopic measurement at a magnification of  $800 \times$  checked by weights, for step 8 of  $55 \times 10^{-6}$  (0.000055) inch. Thicknesses of lower steps are also constant and approximately proportional to the plating time as follows:

Step	1	2	3	4	5	6	7	8
Time (sec.)	10	20	35	55	80	120	180	260
ness (in.)	2.1	4.2	7.4	11.55	16.9	25.3	38.0	55.0×10 <sup>-6</sup>

In Table I are given descriptions of the substrate materials and platings for all samples investigated.

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<sup>&</sup>lt;sup>1</sup> For the most recent summary, see Barrett, *Structure of Metals* (McGraw-Hill Book Company, New York, 1943), p. 437.

After the samples were plated, they were first sheared around the edges to remove the plated portion excessively thickened due to the sharp edge effect which allowed the plating to build up more rapidly. Finally the sheet was sheared into strips approximately one inch by eight inches. These were individually wrapped in several thicknesses of heavy paper and finally sealed in Cellophane to protect the surface from air oxidation until needed for the experiments. When it was found necessary to store the samples for any length of time, they were placed in vacuum.

When a sample was ready to be investigated, the sheared edges of the sample sheet were honed to remove the cold work produced by the shearing process. Each plated step was then cut off giving samples of about one inch square—a convenient size for the equipment used.

### (b) X-Ray Diffraction Method

In order to be sure that the patterns from each series of graded stepwise samples gave patterns which did not vary in sample-film distance and angular tilt, it was desirable to construct a sample holder and collimating system suitable for this work. After several experimental arrangements were tried, the combination sample holder and collimating system indicated in Fig. 1 was finally considered most satisfactory for the experiments. The entire apparatus was made of brass with the exception of the sample hold-down clip which is spring bronze. The sample platen could be tilted

Carita a	Base	Cleaning	Flash	Plating	Deposited	
Series	metal	procedure	coat	solution	metal	Interface structure
A	Steel	$A^{1}$	Cu	Copper cyanide	Cu	Base metal: Fe pattern; random orientation Cu flash: Cu pattern; random orientation Platings 1-8: Cu pattern; random orientation
В	Steel	$C^2$	None	Copper cyanide	Cu	Base metal: Fe pattern; random orientation Platings 1-8: Cu pattern; random orientation
С	Zinc	A	Cu	Copper cyanide	Cu	Base metal: Zn pattern; random orientation Cu flash: Cu pattern; random orientation Platings 1–8: Cu pattern; random orientation
D 1	Tinplate	A	Cu	Copper	Cu	Base metal: Sn, Fe patterns; random orien-
		- · ·		cyanide		tation Cu flash: Cu pattern; line shift indicating solid solution; random orien-
						Platings 1–8: Cu pattern; random orientation
Ε	Copper- plated	С	None	Nickel sulfate	Ni	Base metal: Cu, Fe pattern; random orien- tation
	steel					Platings 1–8: Ni pattern; random orientation
F	Copper	С	None	Nickel sulfate	Ni	Base metal: Cu pattern; random orientation Platings 1-8: Ni pattern; random orientation
G	Brass soft	A	Cu	Nickel sulfate	Ni	Base metal: α-brass pattern; random orien- tation
	temper					Cu flash: Cu pattern, random orientation Platings 1-8: Ni pattern; random orientation
H E	Brass half-hard	A	Cu	Nickel sulfate	Ni	Base metal: <i>a</i> -brass pattern; nearly random orientation
	temper					Cu flash: Cu pattern; random orientation Plating 1: No Ni—same as Cu flash Platings 2–8: Ni pattern; random orientation
Ι	Tinplate	A	Cu	Nickel sulfate	Ni	Base metal: Sn, Fe pattern; random orien-
						Cu flash: Cu pattern; line shift indicating solid solution; random orien-
						tation Platings 1-8: Ni pattern; random orientation

TABLE I.

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TABLE I.-Continued.

Series	Base metal	Cleaning procedure	Flash coat	Plating solution	Deposited metal	Interface structure
J	Zinc	A	Cu	Nickel sulfate	Ni	Base metal: Zn pattern; random orientation Cu flash: Cu pattern; random orientation Platings 1-8; Ni pattern; random orientation
Q	Cold-rolled steel	С	None	Zinc cyanide	Zn	Base metal: Fe, oriented [111] direction Plating 1: No Zn; same as substrate steel Plating 2: Zn oriented [111] or [110] di- rection
						Platings 3–8: Zn, random orientation
R	Cold-rolled copper	С	None	Zinc cyanide	Zn	Base metal: Cu, oriented [110] Platings 1–2: No Zn, same as substrate Plating 3: Zn, oriented [110] Platings 4–8: Zn, random orientation
S	Cold-rolled brass	С	None	Zinc sulfate	Zn	Base metal: α-brass, oriented [110] Plating 1: Zn, oriented [110] Platings 2–8: Zn, random orientation
V	Cold-rolled steel	С	None	Copper cyanide	Cu	Base metal: Fe, oriented [111] Plating 1: Cu, oriented Cu [111] or [110] Platings 2–8: Cu, random orientation
W	Cold-rolled brass	С	None	Copper cyanide	Cu	Base metal: <i>a</i> -brass, oriented [110] Plating 1: No Cu; same as substrate Plating 2: Cu, oriented [110] Platings 3–8: Cu, random orientation
X	Cold-rolled copper	С	None	Nickel sulfate	Ni	Base metal: Cu, oriented [110] Plating 1: No Ni; same as substrate Plating 2: Ni, oriented [110] or [111] Platings 3–8: Ni, random orientation
Y	Cold-rolled brass	С	None	Nickel sulfate	Ni	Base metal: <i>a</i> -brass, oriented [110] Plating 1: Ni, oriented [110] or [111] Platings 2–8: Ni, random orientation

<sup>1</sup> Cleaning procedure A consisted of cathodic cleaning in combination with a commercial cleaner and a copper strike solution (copper cyanide). This was followed by rinsing in water before stepwise plating. <sup>2</sup> Cleaning procedure C was similar to that of A with the exception that the copper strike solution was omitted.

and then permanently fixed into position. The defining front pinhole was 0.025-inch diameter and the back pinhole 0.040-inch diameter.

For the experiments carried out, the reflection method was employed as shown schematically in Fig. 1. The angle of tilt ( $\beta$ -angle) finally decided upon was 50°. Each sample was set in the apparatus so that most of the x-ray beam struck its surface with only a small portion grazing over the honed edge. After the first sample of a series was adjusted upon the sample platen and the sample film-distance adjusted to 1.50 cm, the entire setup (flat film cassette holder and apparatus) was firmly clamped to the top of the x-ray table. With the aid of a vernier micrometer the height of the upper honed edge of the sample was measured. Then each succeeding sample of the series was set to this height on the platen. As a consequence one diffraction pattern may be compared directly with any other of the series since the experimental conditions are constant for any particular series.

All patterns were obtained using radiation from a Machlett cobalt target x-ray tube from which the  $\beta$ -radiation was filtered out using a ferric oxide filter. The tube was operated at 38 kv, 10 ma with an exposure time of one hour for each pattern.

#### (c) Electron Diffraction Method

Purely for confirmatory observation of the first 1 or 2, or thinnest, films, the samples used in the x-ray method were subjected to electron diffraction analysis at grazing incidence. The apparatus used was described fully elsewhere by Clark and Wolthuis.<sup>2</sup> For each sample an exposure  $^{2}$ G. L. Clark and E. Wolthuis, J. App. Phys. 8, 630 (1937).

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FIG. 1. Combination sample holder for oblique angle of incidence and collimation system for x-ray beam.

of a few seconds at 35 kv and 10 ma was required. The sample holder for the electron diffraction apparatus was fixed for the first specimen of each series only. Then the succeeding members of the same series were obtained by slipping each sample into the holder after removing the preceding one.

#### (d) Optical Reflection Measurements

Because of the high reflecting power of many of the electrodeposited film samples, it was decided to measure quantitatively the reflectances both as functions of wave-length of visible light and of plating time on substrates. No record of such measurements on samples of this type could be found in the literature. Conceivably these measurements could throw additional light on the nature of any interface. The apparatus employed for this purpose was the Hardy-General Electric Recording Spectrophotometer. To study the character of the surfaces critically the equipment was adjusted so that the sensitivity of the instrument was accurate to 0.4 percent. Standard magnesium oxide with a reflectance of 98 percent was used throughout this work.

#### DISCUSSION

It is obvious that the structure of the very first layer deposited on a base metal is of greatest significance in disclosing the type of bond between coating and substrate. It was clearly demonstrated that a layer deposited in 10 seconds with a thickness of about  $2.1 \times 10^{-6}$  in.  $(5.36 \times 10^{-6})$ 

cm, or something over a hundred unit cells of crystalline face-centered cubic copper or nickel) is quite adequate for detection not only by electron diffraction but also by the x-ray diffraction technique described in this paper. Thus, when the deposited metal of this minimum thickness produces its own characteristic diffraction interferences on the pattern, in addition to the base metal interferences which appear since the x-ray beam penetrates through to it, this can mean only that the film atoms neither enter the substrate lattice to form a solid solution or intermetallic compound, nor in their own layer simulate exactly the lattice type and spacing of the substrate metal (so-called pseudobasal isomorphism); but that the first deposited atoms assume at once the characteristic lattice structure of the metal in massive form. The bonding, may, therefore, be termed mechanical by clinging to the faults and irregularities which have been demonstrated for even the most highly polished and plane surfaces of metal sheets. On the other hand, if the interferences for this film do not appear, then it is logical to conclude that either solid solution has occurred by penetration of deposited atoms into the substrate lattice, in which case some shift in lines indicative of lattice parameter change would be expected and could be measured; or the deposited atoms have built a layer in which the underlying base metal structure is exactly copied, even though the lattice type and spacing may be entirely foreign to the

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normal positions taken by these atoms on crystallization. This would indicate the powerful forces exerted at this interface which could force atoms under a condition of high strain into an abnormal configuration. It could not be expected that this pseudobasal isomorphism would persist through more than a very few layers, for with increasing thickness the normal lattice forces would prevail over the substrate surface forces. So it is of interest to discover at what step in the plating process the normal characteristic structure of the metal being electrodeposited will first come into evidence.

An examination of Table I shows that even the copper flash coating and all 8 plating steps give evidence of copper superposed with apparently

purely mechanical bonding on steel and zinc (A, B, C) but there is evidence of some solid solution of copper in the tin layer of tinplate base (D); nickel appears from the beginning in copper-plated steel, copper, brass, tinplate, and zinc (E, F, G, I, J), but simulates in the first layer the structure of the copper flash on brass (H); zinc takes the structure of the base steel in plating 1 (Q), and of cold-rolled copper through two platings (R), the only such case, but appears in the first layer on brass (in which copper is already alloyed with zinc); copper appears in the first layer on cold-rolled steel (V), but only in the second plating on cold-rolled brass (W), thus duplicating the interplanar spacing of the brass in the absence of zinc; nickel simulates cold-



FIG. 2. Typical x-ray diffraction patterns of plated layers on base metals with random orientation: C4, zinc base metal; C3, with copper flash coat; C18, with copper plating. D4, tinplate base; D3, with copper flash coat; D18, with copper plating. F3, copper base; F18, with nickel plating.

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FIG. 3. Typical x-ray diffraction patterns of base metals with preferred orientation (0) and deposit thereon (8): R, cold-rolled copper base, zinc plated; X, cold-rolled copper base, nickel plated; Y, cold-rolled brass base, nickel plated.

rolled copper in the first layer (X), but appears for plating 1 on cold-rolled brass (Y). In all cases of non-appearance of characteristic structure in the first layer except for films on a tinplate base, precision measurements have disclosed no evidence of solid solution in the base metal from line shifts. That a discrete film exists is evident from visual inspection and especially from the optical reflectance measurements as described in a later section. Thus pseudobasal isomorphism is indicated both by x-ray and electron diffraction analysis.

In addition to the variations in actual crystalline structure as affected or not by the substrate lattice, another variable, namely, texture, as affected or not by whether the base metal sheet has a random orientation of grains (as produced by recrystallization or annealing), or a preferred orientation or fiber structure such as introduced by cold rolling, can be followed by the diffraction patterns of the stepped samples.

The first samples to be studied were platings upon annealed substrate metals without preferred orientation from cold rolling, or nearly so. Some of the samples were given a very light copper flash before plating. This was done to see if this coating would change the effect of the base metals upon the deposited coatings. Examples of both cases are shown in Table I (series A-J). The typical illustrations in Fig. 2 show the results on x-ray patterns of the base metals (zinc C4, tinplate D4, copper F3), the copper flash coating on the base metal (zinc C3, tinplate D3), and the deposit (copper on zinc C18, copper on tinplate D18, nickel on copper F18).

Results from the x-ray patterns indicated only random orientation of the plating in the first step on the base metal. In the following stepwise deposits only the intensities of the interferences became stronger. The copper flash coatings in the other samples were without preferred orientation also, and the stepwise deposits behaved in exactly the same manner. Thus plating crystals grow out in random fashion on a random array of substrate crystals under the usual commercial conditions of deposition employed.

After repeating the work with highly oriented substrate metals (Table I, series R-Y), different results were observed. The x-ray patterns in Fig. 3 show patterns of the samples before plating (0) and after a deposit was applied (8). When the plating first appeared, it was found always to be oriented. In general the direction of orientation is identical with that of the base metal, and thus simulates the texture. In some samples two possible directions of orientation are indicated in Table I since the data on positions of interference maxima were insufficient to fix the orientation with certainty. The coating following the oriented layer was found to be without orientation again and remained as such to the final deposited coating. So, just as in the case of the lattice structure and spacings, the influence of the base metal in orientation is lost after a critical thickness of the coating is exceeded.

The oriented samples with a flash coating were found to be without orientation in this coating, and therefore no further work was carried out

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since the subsequent platings behave in the same manner as the samples on randomly oriented base metals.

The results obtained by electron diffraction were found to be in exact agreement with those obtained by x-rays.

Traces of percent reflectance  $(\rho)$  versus wavelength were taken of many of the stepwise plated series using the Hardy-General Electric Recording Spectrophotometer. A typical trace of this kind for a complete series (S) is illustrated in Fig. 4. The zero curve corresponds to the unplated base metal of brass and curves  $1, 2, 3, \cdots$ correspond to zinc deposits  $1, 2, 3, \cdots$ .

Each family of the above curves may be plotted as reciprocal percent reflectance  $(1/\rho)$ versus plating time in seconds for the complete series at some definite wave-length. A family of curves of this kind for series S is shown in Fig. 5A. Curves 1, 2, 3, and 4 were plotted for 7000A, 6000A, 5000A, and 4000A, respectively. In this series of zinc deposits upon cold-rolled brass it may be observed that the substrate metal exerts a profound influence upon the plating especially in the initial stages of the deposition process while in the heavier deposits this effect is not very great. As the deposit on the sample increases in thickness, the quality of the surface changes also. In some specimens the heavier deposits became brighter and smoother than the initial deposited layers as in the case of deposited nickel or copper. The opposite also occurs depending upon the nature of the base metal and conditions of plating solution. Various



FIG. 4. Reflectance values (p) as they vary with wavelength for cold-rolled brass with zinc plating.



FIG. 5. A. Reciprocal reflectance plotted against time of plating for zinc on cold-rolled brass: 1, at 7000A; 2, at 6000A; 3, at 5000A; 4, at 4000A. B. Reciprocal reflectance at 7000A plotted against time of plating for zinc deposits on (1) brass, (2) copper, (3) steel.

other samples plotted in the above manner showed the same behavior.

In order to see what effect similar platings had upon different materials, various graphs were plotted using the same coordinates as above. In Fig. 5B are shown the results of zinc deposits upon brass, copper, and steel for 7000A and are represented by curves 1, 2, and 3, respectively (sample series Q, R, and S of Table I). Here again the deposit is strongly affected by the base metal during the first stages of the deposition process and less in the heavier deposits. These curves indicate remarkably well the same phenomena of structure and texture as interpreted from the x-ray and electron diffraction patterns.

#### SUMMARY AND CONCLUSIONS

1. A method of studying the interfacial structure and bonding of electrodeposited metals exactly as produced commercially by the use of a stepwise plating process and without stripping platings from the base metals was devised. By

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this method it was possible to show not only the true interfacial structure but also variations as the film increases in thickness and becomes farther and farther removed from the effects of the base metal.

2. In order to make it possible to obtain x-ray patterns which would not vary in sample-film distance and the angle at which the sample is tilted for the surface reflection studies, a special collimating system containing an adjustable sample holder was constructed. Using this apparatus the angle of tilt could be permanently fixed at any desired position. The sample-film distance was measured once and then the entire assembly clamped into position. With this arrangement patterns obtained could be compared accurately for any series of electroplated substances.

3. X-ray and electron diffraction patterns (the latter purely for confirmatory purposes) were obtained of various substrate materials (with both random and preferred orientation) upon which were stepwise deposited platings of different metals. In some systems the characteristic structure of the deposited metal is observed in the first plating only 0.000002 in. thick; in others the deposited metal simulates the lattice and interplanar spacings of the base metal through steps 1 and sometimes 2, before subsequently assuming normal structure. It was found that under the conditions of deposition employed, deposited platings upon base material with random orientation follow the random structure throughout the entire thickness. On the other hand, coatings deposited on fibered base metals were also fibered in the initial plating. Subsequent to the initial plating additional steps no longer show the orientation.

4. An attempt was made to correlate results obtained by x-ray diffraction with those of optical reflectance measurements. Various traces were made of the samples using a recording spectrophotometer. These were replotted into simpler form and show that the substrate metal affects the deposited metal very markedly in the initial stages of the deposition process. This effect then diminishes in characteristic fashion as the thickness of the film increased.

5. Three types of bonding of electroplates on substrate metals have been demonstrated in the various combinations studied:

a. Mechanical, in which the deposited metal forms its own characteristic lattice from the beginning and clings to the faults and irregularities of the base metal surface which may appear at only high microscopic magnifications or in electron micrographs; the first atoms undoubtedly come within range of strong fields of force of the base metal atoms in these minute faults which increase the effective total surface of the interface.

b. Solid solutions, in which the first deposited atoms enter the lattice of the substrate metal, the resulting solid solution forming a transition layer between normal base metal and normal electroplated metal, which appears as a separate phase beyond a limiting thickness.

c. Pseudobasal isomorphism, in which through a few transitional atomic layers the deposited metal forms a crystalline arrangement which similates and extends the type and dimensions of the base metal, though this may be entirely foreign to the depositing metal, until in thickening films it reverts to its normal structure.

Under best conditions bonds of great strength of all three types are possible and commonly observed in commercial practice.

Further work is now in progress on films deposited in steps of (1) 1-second interval up to 10 seconds plating time (this being the minimum in the work here reported); (2) electron microscope examinations of interfaces and transition zones by a new technique; (3) study of structures after samples are subjected to repeated stresses and fatigue in order to evaluate bonding strengths by degree of resistance to rupture or change.

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